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# Ion volumes: a comparison

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Single ion volumes calculated using different procedures are compared and are found to be strongly linearly correlated. Since these correlations demonstrate that the (independent) methods are mutually supportive, it is possible to obtain values for any one method from data generated by the other methods. The validity of this procedure is demonstrated for a small selection of ions.

## Introduction

Although traditionally the measure of ion size is generally taken to be the radius, few ions can truly be regarded as spherical. The volume, $v$, of an ion therefore provides an improved and more precise description of its topological form than does the assignment of a radius. Two recent studies[1,2] by two of us linked structural properties of salts and ions with their thermodynamic ones. In one paper they have authenticated the existence of a rectilinear dependence between volume and absolute entropy $S^0_{298}$ for minerals, smaller ionic solids, hydrates, organic liquids and solids.[1] In a further paper they, together with their co-authors,[2] examined the relationships among ionic lattice energies, formula unit volumes, and thermochemical radii. A set of effective close-packing ion volumes resulted from this study, designated in the following as $v_J$; these are more effective measures of the relative ionic sizes. Because of this increased prominence attributed to ion volume it is of interest to relate these volumes to other estimates of the ionic volumes, in order to be able to judge their validity and gain insight concerning the actual volumes that the ions occupy within crystalline salts.

Natural estimates of ionic volumes arise from their ionic radii, designated in the following as $r_M$, leading to the volumes $v_M = (4\pi/3)r_M^{1/3}$. These radii have been selected by one of us,[3] based mainly on the Shannon and Prewitt radii of monatomic ions in crystals.[4,5] These 'effective' radii were based on the interatomic distances derived from X-ray diffraction, accurate to better than 1 pm, assuming their constancy and additivity and that the radius of the hexa-coordinated $F^-$ ion is 0.133 nm. Radii of other ions were based on geometrical considerations for some polyatomic ions, and on thermochemical radii for others as annotated in ref. 3.

It is of further interest to examine whether other attributes of ions that have the dimensions of volume, such as the volumes derived from the ionic polarizability (obtained from the molar refraction) and from the diamagnetic susceptibility, correlate with the ionic volumes $v_J$ and /or $v_M$.

Consider a binary crystalline salt $M_pX_q$, where $M^{q+}$ is the cation and $X^{p-}$ is the anion. The close-packed volume of the ions in the crystal is usually obtained from the unit cell parameters derived from X-ray diffraction (eqn. 1):

$$V = (abc/Z)[1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma]^{1/2} \quad (1)$$

where $a$, $b$, and $c$ are the unit cell edges, $\alpha$, $\beta$, and $\gamma$ are the unit cell angles, and $Z$ is the number of formula units per unit cell. This close-packing volume is made up from volumes ascribable to the cations, $v(M^{q+})$, and to the anions, $v(X^{p-})$ (eqn. 2):

$$V = pv(M^{q+}) + qv(X^{p-}) \quad (2)$$

Then, if the volume ascribable to one ion is known, those of others can be calculated from the presumed constancy and additivity of the ionic volumes. Since, in general, the volumes of the anions are considerably larger than those of the cations, the latter can be considered to occupy interstices among the former. Any remaining void volume in the crystal is then attributed to the anions. Goldschmidt radii,[6] $r_G$, were ascribed to the alkali metal and alkaline earth metal cations, so that for them $v_J = v(M^{q+}) = (4\pi/3)r_G^{1/3}$. Hence, $v_J = v(X^{p-})$ for the anions was obtained for binary salts involving these cations by difference, using eqn. 2.[2] This can lead to a considerable range of values for $v_J$ of anions. For the example discussed,[2] $AgF_4^-$, $v(AgF_4^-)$ = 0.078, 0.095, 0.100, and 0.112 nm$^3$ resulting from the $Na^+$, $K^+$, $Rb^+$, and $Cs^+$ salts. The average, 0.096 ± 0.014 nm$^3$, was then assigned to $v_J$ for this anion. The values of $v_J$ from ref. 2 are listed in Table 1, alongside the corresponding $v_M$ values, obtained from the 'selected' values from ref. 3.

The molar refraction of ions is generally considered to be insensitive to the environment in which the ion is situated (*i.e.*, vacuum, solution, or crystal) and therefore the values for salts should be additive in terms of the values of the constituting ions.[7,8] The molar refraction $R$ is related to the refractive index $n$ according to the Clausius–Mossotti eqn. 3:

$$R = (M/d)(n^2 - 1)/(n^2 + 2) \quad (3)$$

where $M$ is the molar mass and $d$ is the density. The molar refraction of a salt at the sodium D-line, $R_D$, is taken as a fair representative of the intrinsic value (at infinite frequency) and is equated to that in solution at infinite dilution, $R_D^\infty$, where available.[3] The $R_D$ values are generally known to ±0.1 cm$^3$ mol$^{-1}$ or better. The value assigned by Heydweiller[7] to the sodium ion, $R_D(Na^+)$ = 0.65 cm$^3$ mol$^{-1}$, based on differences among alkali metal cations and the iso-electronic rare gas atoms, was used to obtain the individual ionic values.[3] The ionic polarizability volume[9] is given by eqn. 4:

$$\alpha' = (3/4\pi N_A)R_D = 0.3964 \times 10^{-30}(R_D/\text{cm}^3\ \text{mol}^{-1}) \quad (4)$$

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**Table 1** Individual ionic volumes, refractions, and diamagnetic susceptibilities, in nm$^3$/ion. Values of $R_D/N_A$ and $-\chi_m 10^{-6}/N_A$ from ref. 3 except where otherwise noted

| Cation | $v_M$ | $v_J$ | $R_D/N_A$ | $-\chi_m 10^{-6}/N_A$ | Anion | $v_M$ | $v_J$ | $R_D/N_A$ | $-\chi_m 10^{-6}/N_A$ |
|---|---|---|---|---|---|---|---|---|---|
| $Li^{+}$ | 0.0014 | 0.0020 | 0.0001 | $0.001^{a}$ | $F^{-}$ | 0.0099 | 0.025 | 0.0037 | 0.022 |
| $Na^{+}$ | 0.0044 | 0.0039 | 0.0011 | 0.004 | $Cl^{-}$ | 0.0248 | 0.047 | 0.0143 | 0.047 |
| $K^{+}$ | 0.0110 | 0.0099 | 0.0045 | 0.019 | $Br^{-}$ | 0.0315 | 0.056 | 0.0203 | 0.065 |
| $Rb^{+}$ | 0.0139 | 0.0139 | 0.0068 | 0.033 | $I^{-}$ | 0.0446 | 0.072 | 0.0315 | 0.094 |
| $Cs^{+}$ | 0.0206 | 0.0188 | 0.0114 | 0.057 | $OH^{-}$ | 0.0099 | 0.032 | 0.0077 | 0.020 |
| $Cu^{+}$ | 0.0037 |  | 0.0051 | 0.020 | $HS^{-}$ | 0.0372 | 0.057 | 0.0213 |  |
| $Ag^{+}$ | 0.0064 |  | 0.0085 | 0.040 | $HSe^{-}$ | 0.0361 | 0.070 |  |  |
| $Tl^{+}$ | 0.0141 |  | 0.0191 | 0.057 | $O_2^{-}$ | 0.0165 | 0.046 |  |  |
| $NH_4^{+}$ | 0.0136 | 0.021 | 0.0078 | 0.019 | $CN^{-}$ | 0.0292 | 0.050 | 0.0131 | 0.030 |
| $MeNH_3^{+}$ | 0.0335 | 0.051 |  |  | $NCO^{-}$ | 0.0350 | 0.054 |  | 0.035 |
| $HONH_3^{+}$ | 0.0287 | 0.021 |  |  | $SCN^{-}$ | 0.0405 | 0.071 | 0.0282 | 0.058 |
| $N_2H_5^{+}$ | 0.0287 | 0.028 |  |  | $N_3^{-}$ | 0.0311 | 0.058 | $0.0186^{g}$ |  |
| $Me_4N^{+}$ | 0.0920 | 0.113 | 0.0380 | 0.108 | $I_3^{-}$ | 0.4349 | $0.180^{j}$ |  |  |
| $Et_4N^{+}$ | 0.1603 |  | $0.0714^{f}$ |  | $HF_2^{-}$ | 0.0213 | 0.047 |  |  |
| $Pr_4N^{+}$ | 0.2280 |  | $0.1013^{f}$ |  | $ClO_2^{-}$ | 0.0655 | $0.063^{j}$ |  |  |
| $Bu_4N^{+}$ | 0.2951 |  | $0.1312^{f}$ |  | $NO_2^{-}$ | 0.0296 | 0.055 | 0.0144 | 0.025 |
| $Pe_4N^{+}$ | 0.3642 |  | $0.1594^{f}$ |  | $NO_3^{-}$ | 0.0240 | 0.064 | 0.0173 | 0.038 |
| $Ph_4As^{+}$ | 0.3216 |  | $0.1914^{g}$ | 0.380 | $ClO_3^{-}$ | 0.0335 | 0.073 | 0.0201 | 0.053 |
| $Be^{2+}$ | 0.00027 | 0.0002 |  | −0.010 | $BrO_3^{-}$ | 0.0292 | 0.072 | 0.0252 | 0.066 |
| $Mg^{2+}$ | 0.0016 | 0.0020 | −0.0012 | $0.008^{a}$ | $IO_3^{-}$ | 0.0248 | 0.075 | 0.0313 | 0.083 |
| $Ca^{2+}$ | 0.0042 | 0.0050 | 0.0026 | $0.013^{a}$ | $VO_3^{-}$ | 0.0253 | 0.070 |  |  |
| $Sr^{2+}$ | 0.0060 | 0.0086 | 0.0044 | 0.015 | $AuCl_4^{-}$ | 0.1505 | $0.164^{j}$ |  |  |
| $Ba^{2+}$ | 0.0105 | 0.0123 | 0.0086 | 0.036 | $ClO_4^{-}$ | 0.0579 | 0.082 | 0.0212 | 0.057 |
| $Ra^{2+}$ | 0.0122 | 0.0147 |  |  | $IO_4^{-}$ | 0.0647 | 0.088 |  | $0.090^{a,b}$ |
| $V^{2+}$ | 0.0021 | 0.0016 |  | $0.025^{i}$ | $MnO_4^{-}$ | 0.0579 | 0.088 |  |  |
| $Cr^{2+}$ | 0.0023 | 0.0024 |  | $0.025^{i}$ | $ReO_4^{-}$ | 0.0736 | $0.098^{j}$ |  | $0.100^{a}$ |
| $Mn^{2+}$ | 0.0024 | 0.0032 | 0.0037 | $0.023^{i}$ | $BH_4^{-}$ | 0.0301 | 0.066 |  |  |
| $Fe^{2+}$ | 0.0020 | 0.0022 | 0.0035 | $0.022^{i}$ | $BF_4^{-}$ | 0.0510 | 0.073 |  | 0.065 |
| $Co^{2+}$ | 0.0018 | 0.0022 | 0.0034 | $0.020^{i}$ | $B(OH)_4^{-}$ | 0.1022 | $0.084^{j}$ |  |  |
| $Ni^{2+}$ | 0.0014 | 0.0020 | 0.0027 | $0.020^{i}$ | $Ph_4B^{-}$ | 0.3126 |  | $0.1805^{g}$ | 0.357 |
| $Cu^{2+}$ | 0.0016 |  | 0.0022 | $0.018^{i}$ | $HCO_2^{-}$ | 0.0202 | 0.056 | 0.0157 | $0.035^{c}$ |
| $Zn^{2+}$ | 0.0018 | 0.0024 | 0.0023 | 0.017 | $MeCO_2^{-}$ | 0.0178 |  | 0.0230 | 0.054 |
| $Cd^{2+}$ | 0.0036 | 0.0046 | 0.0053 | 0.037 | $HCO_3^{-}$ | 0.0159 | 0.064 | 0.0181 |  |
| $Eu^{2+}$ | 0.0067 | 0.0080 |  | $0.037^{i}$ | $HSO_4^{-}$ | 0.0287 | $0.087^{j}$ |  | $0.062^{d}$ |
| $Hg^{2+}$ | 0.0045 | 0.0059 | 0.0102 | 0.061 | $H_2PO_4^{-}$ | 0.0335 |  | 0.0242 |  |
| $Pb^{2+}$ | 0.0069 | 0.0096 | 0.0198 | 0.047 | $Au(CN)_2^{-}$ | 0.1373 | $0.109^{j}$ |  |  |
| $Al^{3+}$ | 0.00062 | 0.0008 | −0.0020 | 0.005 | $O^{2-}$ | 0.0115 | 0.043 |  | 0.020 |
| $Sc^{3+}$ | 0.0018 | 0.0024 | 0.0027 | $0.014^{b}$ | $S^{2-}$ | 0.0261 | 0.067 |  | 0.063 |
| $Ti^{3+}$ | 0.0013 | 0.0014 |  | $0.015^{i}$ | $Se^{2-}$ | 0.0325 | 0.072 |  | 0.080 |
| $V^{3+}$ | 0.0011 | 0.0012 |  | $0.017^{i}$ | $Te^{2-}$ | 0.0452 | 0.091 |  | 0.116 |
| $Cr^{3+}$ | 0.0010 | 0.0011 |  | $0.018^{i}$ | $O_2^{2-}$ | 0.0217 | 0.052 |  |  |
| $Mn^{3+}$ | 0.0012 | 0.0014 |  | $0.017^{i}$ | $CO_3^{2-}$ | 0.0236 | 0.061 | 0.0190 | 0.057 |
| $Fe^{3+}$ | 0.0012 | 0.0013 | 0.0053 | $0.017^{i}$ | $SiO_3^{2-}$ | 0.0411 | 0.062 |  | $0.060^{a,b}$ |
| $Co^{3+}$ | 0.0010 | 0.0011 |  | $0.017^{i}$ | $SO_3^{2-}$ | 0.0335 | 0.071 | 0.0214 | 0.063 |
| $Ga^{3+}$ | 0.0010 | 0.0010 | 0.0008 | $0.013^{a,b}$ | $SO_4^{2-}$ | 0.0510 | 0.091 | 0.0229 | 0.066 |
| $Y^{3+}$ | 0.0031 | 0.0050 | 0.0040 | $0.024^{b}$ | $SeO_4^{2-}$ | 0.0601 |  | 0.0272 | 0.085 |
| $Rh^{3+}$ | 0.0013 | 0.0013 | $0.0118^{f}$ | $0.037^{i}$ | $TeO_4^{2-}$ | 0.0686 | 0.110 |  | $0.091^{a}$ |
| $In^{3+}$ | 0.0021 | 0.0033 | 0.0029 | 0.032 | $CrO_4^{2-}$ | 0.0579 | 0.097 |  | 0.085 |
| $Sb^{3+}$ | 0.0019 | 0.0031 | $0.0147^{f}$ |  | $MoO_4^{2-}$ | 0.0686 | 0.088 |  | 0.091 |
| $La^{3+}$ | 0.0048 | 0.0076 | $0.0045^{h}$ | $0.033^{a}$ | $S_2O_3^{2-}$ | 0.0655 | 0.104 | 0.0385 | 0.081 |
| $Ce^{3+}$ | 0.0043 | 0.0069 | $0.0056^{h}$ | $0.033^{i}$ | $S_2O_4^{2-}$ | 0.0655 | 0.113 |  |  |
| $Pr^{3+}$ | 0.0042 | 0.0065 | $0.0055^{h}$ | $0.033^{i}$ | $S_2O_6^{2-}$ | 0.0655 | $0.150^{j}$ |  |  |
| $Nd^{3+}$ | 0.0039 | 0.0064 | $0.0052^{h}$ | $0.033^{i}$ | $S_4O_6^{2-}$ | 0.1248 | 0.209 |  |  |
| $Sm^{3+}$ | 0.0037 | 0.0060 | $0.0048^{h}$ | $0.033^{i}$ | $S_2O_8^{2-}$ | 0.1022 | 0.169 |  | 0.130 |
| $Eu^{3+}$ | 0.0036 | 0.0060 | $0.0045^{h}$ | $0.033^{i}$ | $Cr_2O_7^{2-}$ | 0.1373 | $0.152^{j}$ |  | 0.149 |
| $Gd^{3+}$ | 0.0035 | 0.0057 | $0.0043^{h}$ | $0.033^{i}$ | $SiF_6^{2-}$ | 0.0728 | 0.112 |  |  |
| $Tb^{3+}$ | 0.0033 | 0.0054 | $0.0042^{h}$ | $0.032^{i}$ | $PdCl_6^{2-}$ | 0.1360 | 0.218 |  |  |
| $Dy^{3+}$ | 0.0032 | 0.0051 | $0.0040^{h}$ | $0.032^{i}$ | $SnCl_6^{2-}$ | 0.1781 | $0.231^{j}$ |  |  |
| $Ho^{3+}$ | 0.0031 | 0.0049 | $0.0037^{h}$ | $0.032^{i}$ | $ReCl_6^{2-}$ | 0.1425 | 0.224 |  |  |
| $Er^{3+}$ | 0.0030 | 0.0047 | $0.0035^{h}$ | $0.030^{i}$ | $IrCl_6^{2-}$ | 0.1575 | 0.229 |  |  |
| $Tm^{3+}$ | 0.0029 | 0.0047 | $0.0033^{h}$ | $0.030^{i}$ | $PtCl_6^{2-}$ | 0.1285 | 0.219 |  | $0.259^{c}$ |
| $Yb^{3+}$ | 0.0028 | 0.0042 | $0.0033^{h}$ | $0.030^{i}$ | $PtBr_6^{2-}$ | 0.1676 | 0.258 |  |  |
| $Lu^{3+}$ | 0.0027 | 0.0041 |  | $0.028^{i}$ | $PO_4^{3-}$ | 0.0565 | 0.090 | 0.0251 | 0.083 |
| $Tl^{3+}$ | 0.0029 | 0.0048 | 0.0036 | 0.052 | $AsO_4^{3-}$ | 0.0639 | 0.088 |  | $0.100^{a,b}$ |
| $Bi^{3+}$ | 0.0044 |  | 0.0134 | 0.042 | $SbO_4^{3-}$ | 0.0736 | 0.071 |  |  |
| $Zr^{4+}$ | 0.0016 | 0.0028 | 0.0016 | 0.021 | $Fe(CN)_6^{3-}$ | 0.3568 | $0.284^{j}$ |  |  |
| $Sn^{4+}$ | 0.0014 | 0.0017 | 0.0021 | 0.027 | $Co(CN)_6^{3-}$ | 0.3331 | $0.263^{j}$ |  |  |
| $Ce^{4+}$ | 0.0021 | 0.0045 | 0.0031 | 0.035 |  |  |  |  |  |
| $Hf^{4+}$ | 0.0015 | 0.0025 |  | $0.027^{a}$ |  |  |  |  |  |
| $Th^{4+}$ | 0.0042 | 0.0056 |  | 0.052 |  |  |  |  |  |
| $U^{4+}$ | 0.0038 | 0.0049 |  | $0.058^{i}$ |  |  |  |  |  |

[a] Ref. 15. [b] Ref. 16. [c] Ref. 21. [d] Ref. 22. [e] Ref. 10. [f] Ref. 17. [g] Ref. 12. [h] Ref. 23. [i] The underlying diamagnetism of paramagnetic ions according to ref. 15. [j] Revised values calculated by H. D. B. Jenkins.

where $N_A$ is Avogadro's number, and has the dimension of an ionic volume, *ca.* 0.239 times as large as $R_D/N_A$. The molar refraction is temperature dependent (*ca.* 0.01 $cm^3$ $mol^{-1}$ $K^{-1}$) and the values at 298.15 K are generally used when the molar refractions of various ions are discussed. The relevant values of $R_D/N_A$ are listed in Table 1. In some cases no 'selected' values were available in ref. 3 because an $R_D$ value was reported from only a single source. Such cases include: $Au^+$, $Ga^{3+}$, $Tl^{3+}$, $Zr^{4+}$, $Sn^{4+}$ and $Ce^{4+}$,[10] $Et_4N^+$, $Pr_4N^+$, $Bu_4N^+$ and $Pe_4N^+$,[11] $N_3^-$, $Ph_4As^+$ and $BPh_4^-$,[12] and the trivalent rare earth cations.[13] It may be expected that highly polarizable ions, which could be designated as 'soft' ions, have ionic refractions larger than their ionic volumes, whilst for other ions these quantities should be commensurate.

The molar magnetic susceptibility of salts, $\chi_m$, measured by using a Gouy balance for example, is a further quantity that has the dimension of a volume.[14] If there are no unpaired electrons in the ions, then diamagnetic susceptibility results, which is independent of the field strength and substantially also of the temperature, the phase in which the salt is situated (crystal, solution or gas) and the compound of which the ion is a constituent. Atomic diamagnetic susceptibility constants pertaining to multi-atomic ions are additive.[15] The values for diamagnetic substances are conventionally negative, since they are repelled out of a magnetic field. Ionic values may be obtained when a value is assigned to a single ion. Following Klemm,[16] $-\chi_m(Na^+) = 2.3 \times 10^{-6}$ $cm^3$ $mol^{-1}$ was selected.[3] The values pertaining to individual ions are obtained from the molar values by division by $N_A$. The relevant 'selected' values[3] of $10^6\chi_m$ are generally given to only two significant digits and, divided by $N_A$, are listed in Table 1. Paramagnetic ions have an underlying diamagnetism, and corresponding (calculated) values[15] are also shown in Table 1.

## Results

The values of $v_M$ and $v_J$ of ions common to the data sources in refs. 2 and 3 have been used as the database for the correlations, see Table 1. (Each of these sources has values for certain ions that are not found in the other and, hence, in such cases, cannot be used for a correlation.) For 55 cations, the values of $v_J$ are found to be directly proportional to those of $v_M$, eqn. 5:

$$v_J = (1.258 \pm 0.016)v_M \qquad (5)$$

with a correlation coefficient of $R = 0.995_9$, a standard deviation of $\sigma = 0.0015$ $nm^3$, and $F_{1,54} = 6356$ measuring the goodness of the fit. Six cations in the database gave outlying points that were not included in the correlation, all having too low $v_J$ values. These include the alkali metal cations, $Na^+$, $K^+$, $Rb^+$, and $Cs^+$, as well as $HONH_3^+$ and $N_2H_5^+$.

A linear correlation is found for 51 anions, eqn. 6:

$$v_J = (0.0205 \pm 0.0028) + (1.342 \pm 0.041)v_M \qquad (6)$$

with a correlation coefficient of $R = 0.977_1$, a standard deviation of $\sigma = 0.0125$ $nm^3$, and $F_{2,49} = 1052$ measuring the goodness of the fit. Eleven anions from the database were not included in the correlation, with too low $v_J$ values being noted for $I_3^-$, $ClO_2^-$, $AuCl_4^-$, $Au(CN)_2^-$, $B(OH)_4^-$, $Cr_2O_7^{2-}$, $SbO_4^{3-}$, $Fe(CN)_6^{3-}$ and $Co(CN)_6^{3-}$, and too high values for $HSO_4^-$ and $S_2O_6^{2-}$.

There exists a generally good correlation of the ionic refractions, $R_D/N_A$, with the ionic volumes. For 63 ions, for which molar refractions are known, the correlation is (eqn. 7):

$$(R_D/N_A)/\mathrm{nm}^3 = (0.594 \pm 0.005)(v_M/\mathrm{nm}^3) \qquad (7)$$

with a correlation coefficient of $R = 0.997_1$, a standard deviation of $\sigma = 0.0025$, and $F_{1,62} = 10621$.

Particularly polarizable ions do not conform to this correlation, as expected (but see the discussion below). Further outlying ponts include those of certain ions for which no 'selected' data were available in ref. 3 but for which data comes exclusively from one source. These include values from Salzmann,[17] converted from gas phase polarizabilities $\alpha'$ to molar refractions [by reversal of eqn. 3]: $V^{3+}$, $Rh^{3+}$, $Sb^{3+}$, $Hf^{4+}$, $Th^{4+}$ (exhibiting too high $R_D/N_A$ values according to eqn. 7), and $BF_4^-$ and $HCO_3^-$ (exhibiting too low $R_D/N_A$ values). Nevertheless, many other values given by these authors have been well confirmed by those of others. The $R_D/N_A$ values for the tetraalkylammonium cations are systematically too low (see the discussion below). A few further ions, for which consistent $R_D/N_A$ values have been obtained by several authors do not fit the correlation either: $Cr^{3+}$ and $IO_3^-$ (exhibiting too high $R_D/N_A$ values), $ClO_4^-$ and $SO_4^{2-}$ (exhibiting too low $R_D/N_A$ values).

The volume diamagnetic susceptibility per ion, $-10^6\chi_m/N_A$, is also related linearly to the ionic volumes of anions or polyatomic cations, eqn. 8:

$$-10^6\chi_m/N_A = (0.022 \pm 0.004) + (10.051 \pm 0.054)v_M \qquad (8)$$

albeit with considerable scatter. The correlation coefficient is $0.957_5$, the standard deviation is $\sigma = 0.017$ and the goodness of fit is $F_{2,34} = 375$ for the 36 diamagnetic polyatomic ions (and monatomic anions) for which 'selected' or other reliable data were available.[3] Due to the large scatter, it is not expedient to single out any outliers.

## Discussion

Individual ionic values pertaining to crystals or solutions are not measurable quantities. Hence, their estimation is based on reasonable assumptions, provided that the constancy of the individual ionic values, their independence of their environment, and therefore their additivity is established. These criteria are based on measurable differences of values for series of salts with a common ion. In the case of $v_J$ the assumption is traceable to that made by Goldschmidt[6] and in the case of $v_M$ to that made by Shannon and Prewitt[4] for the radius of the fluoride ion, both assigning to it the same value, 0.133 nm (although the values for alkali metal ions differ, the later values[4] being derived from more accurate inter-atomic distances)). Therefore these two quantities should be commensurate. In the cases of $R_D/N_A$ and of $-10^6\chi_m/N_A$ the individual ionic values are based[7,16] on those of a small ion, $Na^+$, so that even considerable errors in them would not affect the values of larger ions appreciably, noting that the values for $K^+$ and $F^-$ are already more than three times larger than that for $Na^+$.

Close-packed spheres having radius $r$ in fc-cubic or hexagonal arrays occupy a space that is $6/\pi\sqrt{2} = 1.350$ times their intrinsic volumes, $(4\pi/3)r^3$. This number is very close to the slope of $v_J(v_M)$ in eqn. 6, 1.342 ± 0.041. Hence, the volumes $v_J$ assigned in ref. 1 to the anions appear to be realistic, taking into account the void space between the anions unoccupied by the much smaller cations. The intercept of eqn. 6, 0.0205 ± 0.0028, is probably due to the choice of the Goldschmidt radii made for the alkali metal cations, rather than the Pauling/Shannon and Prewitt radii used for obtaining $v_M$. Conversely, the slope of the relation of $v_J(v_M)$ for the cations in eqn. 5, 1.258 ± 0.016, means that the radii assigned in ref. 2 to the cations, except the alkali metal ones, are 8.0% larger than the intrinsic radii. Alternatively, this may be construed to mean that some of the void space has been assigned to the cations too.

The standard deviations of the correlations are commensurate with the uncertainties assigned to the ionic volumes $v_J$, when more than one salt was used for their estimation. The value ±0.014 $nm^3$ quoted above for the example of $AgF_4^-$ is typical, although for some anions smaller values (*e.g.* ±0.005 $nm^3$) or even larger values (*e.g.* ±0.031 $nm^3$) have been reported.

Altogether, it can be concluded that the correlations in eqns. 5 and 6 can be useful for the estimation of the volumes $V$ according to eqn. 2, to be employed in turn in the estimation of lattice potential energies.[2]

The outlying points in eqns. 5 and 6 (except, as noted, the alkali metal cations) are those of non-spherical ions, although a few, such as $B(OH)_4^-$, $SbO_4^{3-}$, $Fe(CN)_6^{3-}$ and $Co(CN)_6^{3-}$ are regular polyhedra approximating sphericity. The radii assigned in ref. 3 to the outlying prolate ions, $HONH_3^+$, $N_2H_5^+$ and $I_3^-$, and the oblate ones, such as $AuCl_4^-$ and $Au(CN)_2^-$, are $r_M = (a^2b)^{1/3}$, where $a$ and $b$ are the half-axis values of the ellipsoids of rotation ($a$ for the minor/major axis for prolate/oblate ellipsoids). Hence the volume $(4\pi/3)r_M^3$ should represent fairly those of the ellipsoids of rotation. Thus, their shape alone cannot explain why these ions do not fit the correlations, since similar prolate or oblate ions do. The packing of these non-spherical anions and of the cations in their interstices may be a cause for the deviation from eqn. 6, and a re-examination of the $v_J$ values assigned to some of these outlying bulky anions is perhaps also warranted.

On the whole, the more electrons an ion has around its nucleus, the larger can be the field-induced displacement of the center of electronic charge and, hence, the ionic polarizability, and so the more voluminous the ion is, due to the mutual repulsion of the electrons. Thus the proportionality in eqn. 7 is to be anticipated. However, the value of the proportionality factor of the ionic refraction to the intrinsic ionic volume of nearly 3/5, does not have any ready explanation, nor does the corresponding value of the polarizability volume, $\alpha'$, that would be $3/4\pi$ times 3/5, *i.e.* near 1/7. Therefore, eqn. 7 should be taken as an empirical correlation of two measures of the extension of ions in space rather than taking $\alpha'$ to represent the actual volume of an ion.

The ionic refractions of the tetraalkylammonium cations are found to be systematically too low, and tetrahedral anions also have low values of $R_D/N_A$, although not outside the limits of three standard deviations predicted by eqn. 7. If the $R_D/N_A$ values for tetrahedral ions are arbitrarily multiplied by 1.38 they conform well to eqn. 7, but the explanation for this factor is obscure. On the other hand, highly polarizable 'soft' ions[18,19] with outlying points can be brought into better conformation when their $R_D/N_A$ values are divided by $(1.75 + 1.31\varsigma)$, where $\varsigma$ is their softness parameter.[3] This pertains to the $Ag^+$, $Tl^+$, $Cu^{2+}$, $Zn^{2+}$, $Cd^{2+}$, $Hg^{2+}$, $Pb^{2+}$, $Fe^{3+}$, $Ga^{3+}$, $Rh^{3+}$, $Sb^{3+}$, $Bi^{3+}$ and $Tl^{3+}$ cations as well as to $S^{2-}$. Since the values of $\varsigma$ are based on the arbitrary assignment of zero to $H^+$ (or $H_3O^+$), the exact form of this correction factor is not important, whereas the principle is. The more polarizable ('soft') an ion is the larger is its apparent volume as derived from the molar refractivity, $R_D/N_A$, with respect to its intrinsic volume, $v_M$.

The diamagnetic susceptibility of ions is expected to depend on the number of (paired) electrons they possess and, to a first approximation, these will be more numerous in the more voluminous ions and hence the susceptibility will increase. This expectation is upheld approximately in the polyatomic ions, eqn. 8. Still, the latter should be taken as an empirical correlation of two measures of the extent of ions in space rather than taking $\chi_m/N_A$ to represent the actual volume of an ion. Furthermore, for monatomic ions, the effect of each orbital electron is proportional to the square of the average radius of its orbit,[15] *i.e.* $v_M^{2/3}$. A very approximate correlation between $-10^6\chi_m/N_A$ and $v_M^{2/3}$ indeed exists for most monatomic cations such that:

$$v_M^{0.58} \le [-10^6\chi/N_A] \le v_M^{0.68} \qquad (9)$$

On the basis of the values of $v_J$ of ions in salts for which unit cell dimensions and occupancy are known,[2] together with eqns. 5 or 6, it is possible to estimate the values of ionic *radii*, $r_M$, for ions that have not been reported in the compilation[3] (see Table 2). The power 1/3 of the volume, which is required, benefits the accuracy of the radii estimated from the reversal of these correlations: $r_M = 0.2211 v_J^{1/3}$ (cations) and $r_M = 0.2164(v_J - 0.0205)^{1/3}$ (anions). These estimates are compared with the thermochemical radii, $r_R$, values presented by Roobottom *et al.*[20] derived from lattice energies; radii of further ions can readily be calculated by those interested.

**Table 2** Some estimated ionic radii

| Ion | $r_J$/nm[a, b] | $r_M$/nm, estimated | $r_R$/nm[c] |
|---|---|---|---|
| $C_2H_5NH_3^+$ | 0.248 ± 0.019 | 0.230 ± 0.009 | 0.193 ± 0.019 |
| $C_3H_7NH_3^+$ | 0.288 ± 0.013 | 0.267 ± 0.009 | 0.225 ± 0.019 |
| $(C_2H_5)_3NH^+$ | 0.348 ± 0.010 | 0.323 ± 0.011 | 0.274 ± 0.019 |
| $AlCl_4^-$ | 0.333 | 0.289 | 0.317 ± 0.019 |
| $AlBr_4^-$ | 0.361 ± 0.007 | 0.316 ± 0.003 | 0.321 ± 0.023 |
| $FeCl_4^-$ | 0.302 | 0.256 | 0.317 ± 0.019 |
| $GaCl_4^-$ | 0.327 | 0.284 | 0.328 ± 0.019 |
| $SbCl_6^-$ | 0.364 ± 0.010 | 0.319 ± 0.011 | 0.320 ± 0.019 |
| $Al_2Cl_7^-$ | 0.403 ± 0.006 | 0.356 ± 0.008 | |
| $SO_3F^-$ | 0.276 ± 0.004 | 0.229 ± 0.003 | 0.214 ± 0.019 |
| $HgI_4^{2-}$ | 0.388 | 0.342 | 0.377 ± 0.019 |
| $PdBr_6^{2-}$ | 0.389 ± 0.007 | 0.343 ± 0.009 | 0.354 ± 0.019 |
| $FeF_6^{3-}$ | 0.326 ± 0.013 | 0.288 ± 0.019 | 0.298 ± 0.042 |

[a] Estimated using $r_J/\text{nm} = [3(v_J/\text{nm}^3)/4\pi]^{1/3}$. [b] Ref. 2. [c] Ref. 20.

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