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# Estimation of the Thermochemical Radii and Ionic Volumes of Complex Ions

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ABSTRACT The estimation of the thermochemical radius is very important because most of the properties of the electrolyte solutions are, to some extent, linked to this property. Also, these thermochemical radii can be used to estimate lattice energies, which can be a very important parameter to be evaluated when assessing the possibility of synthesizing new inorganic materials. This study presents a formulation for estimating the thermochemical radii of complex ions. More specifically, these thermochemical radii are estimated using a weighted sum based on the radii of the contributing cations and anions. Also, the influence of the ionic charge on these thermochemical radii is assessed and discussed. Finally, the parameters obtained from the estimation of the thermochemical radii of complex cations are used to estimate cation volumes, and this estimation is then validated through comparison with literature values. As a result, the equations developed for thermochemical radii of complex ions produce predictions that are accurate to within 15% in general, whereas the equation developed to estimate cation volumes produces predictions that are accurate to within 20% considering cation volumes greater than  $70 \text{ \AA}^3$ .

KEYWORDS Thermochemical Radius, New Correlations, Complex Anions.

## INTRODUCTION

The thermochemical radius plays a very important role in electrolyte solutions since most of the interactions between the ions in the solution are, to some extent, distance-dependent. For instance, the thermodynamic, transport, kinetics and solvation are highly dependent on the size of the ions<sup>1,2</sup>. In addition to this, the thermochemical radii can be used to calculate the lattice energy of the crystals, for example, either via the Kapustinskii equation<sup>3</sup>, which has been more recently generalized by Glasser<sup>4</sup>, or through the volume based equations developed by Jenkins et al.<sup>5</sup>, and these lattice energies can be important parameter to be evaluated when assessing the feasibility of synthesizing new inorganic materials<sup>5</sup>. In terms of the equations that can be used to calculate the lattice energies, it is important to note that the volume based equations<sup>5</sup> have emerged largely to replace the Kapustinskii's equation<sup>3</sup>, and the advantage of these volume based equations is that they can gain their data from either the density or the set of lattice constants, and a structural determination is not required, as a recent article produced by Glasser and Jenkins<sup>6</sup> demonstrates.

In terms of modeling, the only attempt found in the literature to estimate the thermochemical radii based on its monatomic ions was performed by Solís-Correa et al.<sup>7</sup>. In their study, the thermochemical radii of polyatomic ions with a general formula  $\text{MX}_n^{z-}$  are calculated taking into account the ionic and the covalent character of the M-X bond, with the covalent character being obtained through the Pauling electronegativity values. Although in some cases the results were in a good agreement with the literature values, their method of calculation in general was only effective in describing ions that have a nearly spherical symmetry.

In contrast to Solís-Correa et al.<sup>7</sup>, this study aims to estimate the thermochemical radii for any polyatomic anion regardless of the geometry and chemical formula. To achieve this, a new

expression containing fitting parameters is suggested, and these fitting parameters are obtained using the data of the thermochemical radii obtained from the literature<sup>8,9</sup>.

## GENERAL EQUATIONS

### **Predominance of Ionic or Covalent Bonds**

The complex anions were treated in this study as fundamentally ionic bonded because these complex anions are formed predominantly by metal/non-metal bonds, whereas complex cations were treated as fundamentally covalently bonded, because they are predominantly formed by non-metal/non-metal bonds. It is important to note that we are not assuming that the bond is purely ionic or purely covalent. Rather, these bonds are treated as either predominantly covalent or predominantly ionic. For instance, for complex anions, the difference of electronegativity between the forming cations and the forming anions was higher than 1 in over 82% of the cases analyzed, whereas for complex cations this difference of electronegativity was higher than 1 in only about 23% of the cases. This suggests that the most electronegative atoms forming a complex anion will tend to accumulate electron density, and hence the shape of these atoms will tend to be more spherical. In contrast, the complex cations, which are formed predominantly by covalent bonds, will tend to have a more homogeneous electron density between the atoms involved in the bond, and thus they will tend to have a non-spherical shape.

### **Complex Anions**

Complex anions are predominantly formed by ionic bonds, but the covalent contribution in some of the cases analyzed can be significant. Therefore, ideally the thermochemical radii of the complex anions should be modeled taking into account the covalent character of the bond, and in this case quantum mechanics is the most suitable theory to describe the geometry of the single monatomic ions that form the complex anion, since this theory accounts for orbital shapes,

orbital overlapping, electron densities, etc. However, before introducing excessive complexities to the model, it is reasonable first to test if these complex anions can be described through a more classical view, in which the cations and the anions are represented as hard spheres that do not overlap<sup>10</sup>. In this context, if the thermochemical radii obtained through this simplified model agrees well with the tabulated thermochemical radii from the literature<sup>8,9</sup>, then this simplification can be regarded as satisfactory, otherwise it should be disregarded and replaced by more sophisticated methods, such as the ones involving quantum mechanics theory.

In terms of equations, it is assumed that the thermochemical radius of a complex anion with a chemical formula  $(M_1M_2 \dots M_j, X_1X_2 \dots X_k)^{z-}$  may be correlated with its forming single ions as follows:

$$r_{MX_i} = |z_{MX_i}|^{\varepsilon_1} \left( \sum_j \nu_j r_{M_j}^3 + \sum_k \nu_k r_{X_k}^3 \right)^{1/3} \quad (1)$$

In other words, the thermochemical radius of a complex anion is summation of spherical ion volumes, converted to a radius by cube root. Also, this equation accounts for the contribution of repulsion between incoming electrons. This volume dependence becomes more evident if the term  $4\pi/3$  is multiplied in both sides of eq 1. Further, in eq 1  $\nu_j$  and  $\nu_k$  are the number of cationic and anionic species, respectively. In addition, there is one unknown parameter, the power term  $\varepsilon_1$ , which can be obtained by fitting eq 1 to the reference values obtained from the literature<sup>8,9</sup> of the thermochemical radii. Finally, the term  $|z_{MX_i}|$  accounts for the increase in the volume of the complex anions due to the extra repulsion produced by the incoming electrons. For example, this term explains the different thermochemical radii<sup>8</sup> of the  $CeF_6^{2-}$  and the  $CeF_6^{3-}$ , which are 2.49 Å and 2.78 Å, respectively.

## Complex Cations

In contrast to complex anions, complex cations are predominantly formed by covalent bonds, and thus the simplification suggested for the complex anions, which is based on the assumption of hard spheres that do not overlap, will clearly not be directly applicable for this case. However, in a similar manner to the complex anions, it is worth evaluating if a simpler model can be employed to describe these complex cations. In this context, after several evaluations have been performed, it has been found that by changing the power terms of the monatomic ions radii in eq 1 into fitting parameters would be the best way to account for the more irregular shapes of these monatomic ions. In this case, a constant  $\kappa_1$  is required in order to make this new equation dimensionally consistent. Therefore, the equation assumed to investigate the thermochemical radii of complex cations with a chemical formula  $(M_1M_2 \dots M_j, X_1X_2 \dots X_k)^{z+}$  is as follows:

$$r_{MX_l} = z_{MX_l} \varepsilon_2 \kappa_1 \left( \sum_j v_j r'_{M_j} \varepsilon_3 + \sum_k v_k r'_{X_k} \varepsilon_3 \right)^{1/3} \quad (2)$$

where  $\varepsilon_2$ ,  $\varepsilon_3$  and  $\kappa_1$  are fitting parameters, and  $z_{MX_l}$  is the ionic charge of the complex cation, which in this case accounts for contraction of the radius due to the deficit of electrons. In contrast to the complex anions, the  $r'_{M_j}$  and  $r'_{X_k}$  are the covalent radii<sup>11</sup>, since as mentioned above the bonds between ions forming the complex cations are predominantly covalent. As for complex anions, the agreement between the calculated thermochemical radii and the literature values will support the assumption that eq 2 is suitable to describe the thermochemical radii of the complex cations.

## METHOD OF FITTING AND DATA USED

The power term  $\varepsilon_1$  in eq 1 was estimated using linear regression. Regarding the terms in eq 2, namely the constant  $\kappa_1$  and the power terms  $\varepsilon_2$  and  $\varepsilon_3$ , they were estimated using a nonlinear least squares method, which is based on the minimizing of the following objective function:

$$S(r_{MX_l}) = \sum_{l=1}^n (r_{MX_l}^{\text{ref}} - r_{MX_l}^{\text{calc}})^2 \quad (3)$$

In terms of the data used, the data tabulated by Roobottom et al.<sup>8</sup> were selected as the main reference, and this is because these data represent a large self-consistent set of thermochemical radii. In particular, these radii were estimated via the Kapustinskii equation<sup>3,9</sup>, as well as using a correlation between the lattice potential energy and the inverse cube root of the volume per molecule<sup>8</sup>. It is important to note that Kapustinskii equation<sup>3,9</sup> contains a constant 0.0345, and this assumption of constancy is a vital part of the thermochemical radii as developed by Roobottom et al.<sup>8</sup>.

## RESULTS

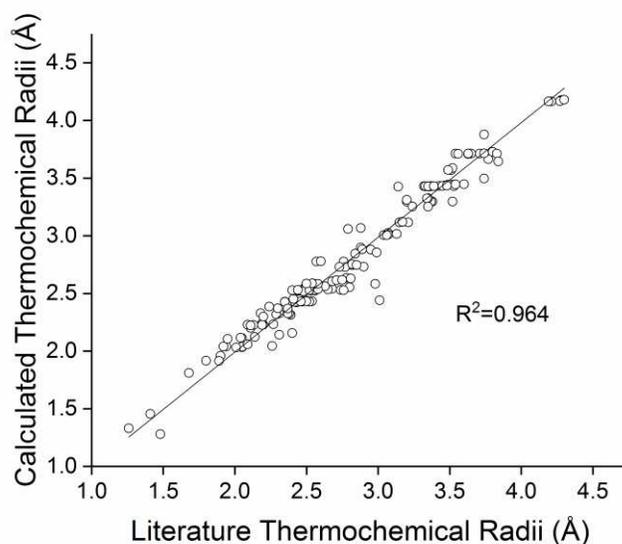
### **Value of the terms $\kappa_1$ , $\varepsilon_1$ , $\varepsilon_2$ and $\varepsilon_3$**

The value of the term  $\varepsilon_1$  in eq 1 obtained through linear regression is (0.057±0.005). Regarding the terms in eq 2, namely the constant  $\kappa_1$  and the power terms  $\varepsilon_2$  and  $\varepsilon_3$ , which were obtained through the minimization of the objective function represented by eq 3, the values obtained were (1.249±0.013) Å<sup>2</sup>, (-0.264±0.025) and (1.50±0.11), respectively. It is important to note that the constant  $\kappa_1$ , which has Å<sup>2</sup> units, makes eq 2 dimensionally consistent. Also, it is important to mention that the value of 1.50 was rounded from 1.496.

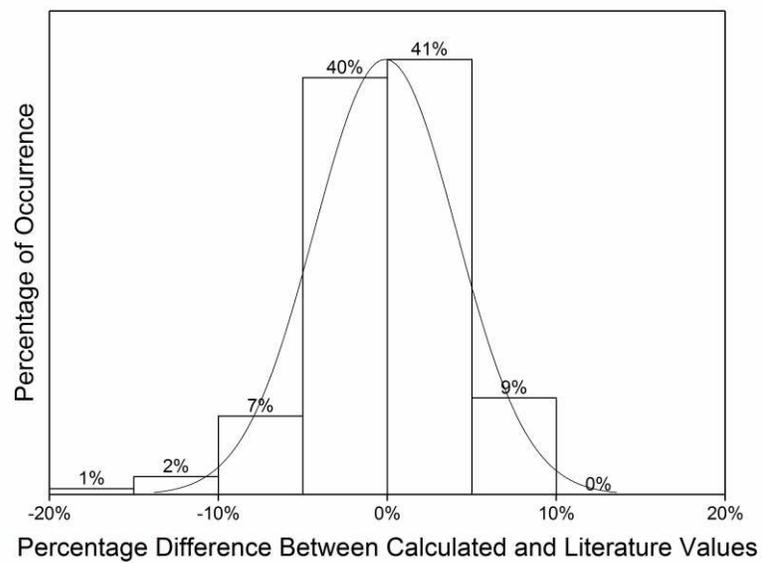
## Thermochemical Radii of Complex Anions

The complex anions tabulated in the literature<sup>8,9</sup> were divided in two sets of data: (i) containing only metal - non-metal bonds, and (ii) containing other combinations. The term  $\varepsilon_1$  in eq 1 was estimated using dataset (i), whereas dataset (ii) was used to test the predictability capacities of this equation. Dataset (i) was selected to estimate the term  $\varepsilon_1$  in eq 1 because this equation was derived assuming predominance of ionic bonds over covalent bonds, and this predominance is normally more pronounced in metal- non-metal bonds. A comparison between the calculated values of  $r_{MX_i}$  using eq 1 and the literature values<sup>8,9</sup> of  $r_{MX_i}$  from dataset (i) is presented in figure 1. As can be seen in this figure, the agreement between the thermochemical radii calculated through eq 1 and the literature values<sup>8,9</sup> is remarkably good. In addition, figure 2 shows the percentage deviation between the calculated and the literature values<sup>8,9</sup>, and as can be seen in this figure, a deviation less than 10% was achieved in over 97% of the cases analyzed. Finally, more detailed information is shown in Table S1 in the Supporting Information, which contains the values of  $r_M$ ,  $r_X$ ,  $r_{MX}^{calc}$ ,  $r_{MX}^{ref}$ . The values of  $r_M$  and  $r_X$  were taken from the Shannon tabulation<sup>12</sup>, except for  $N^{3-}$  and  $H^-$ , which were taken from Roobottom et al.<sup>8</sup> and Sato et al.<sup>13</sup>, respectively. In particular, the value of Sato et al.<sup>13</sup> was selected because their reported radius explains better the bond distance obtained by electron diffraction<sup>14</sup> for the  $BH_4^-$  anion, which is about 1.20 Å, as well as the bond distance reported for the  $ReH_9^-$  ion<sup>15</sup>, which is about 1.70 Å. This becomes evident when the contribution of the  $B^{3+}$  and  $Re^{7+}$  ions for the bond distance, which are 0.27 Å and 0.53 Å<sup>12</sup>, respectively, is removed. In this case, the  $H^-$  anion becomes 0.93 Å and 1.17 Å, respectively, which is closer to the value of 1.28 Å reported by Sato et al.<sup>13</sup>.

Additionally, the values of  $r_{MX}^{\text{ref}}$  were taken from Roobottom et al.,<sup>8</sup> which also include most of the values of the thermochemical radii tabulated by Jenkins et al.<sup>9</sup>. It is important to note that the selection of the values of  $r_M$  and  $r_X$  has to take into account not only the ionic charge, but also the coordination number. This is because the ionic radii depend on these two quantities to be accurately defined. However, it has been found that selecting the ionic radii at a coordination number of 6 do not cause any significant impact on the results. Indeed, this simplification is very convenient because most of the information on the ionic radii is tabulated for this coordination number. Therefore, the values in Table S1 are mainly based on a coordination number of 6.



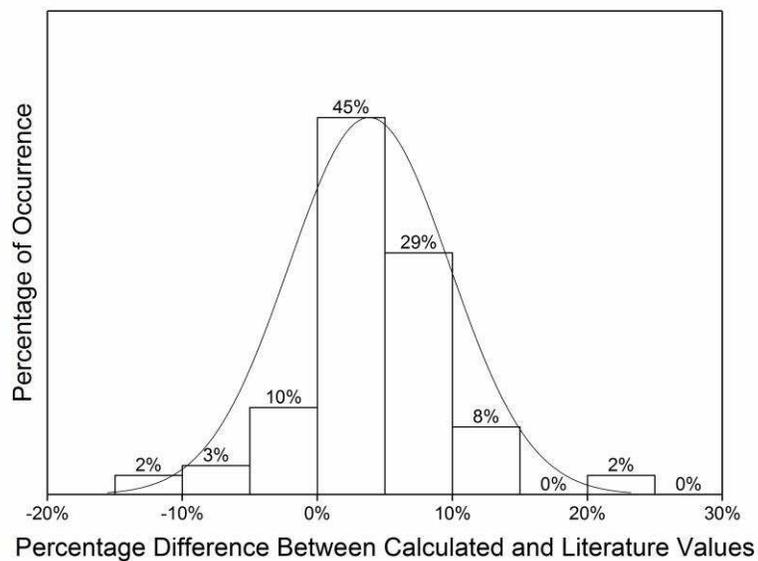
**Figure 1.** Parity plots comparing the reference values of thermochemical radii<sup>8,9</sup> in Table S1 in the supporting information with those calculated using eq 1 (solid line:  $y=x$  line,  $\circ$ : thermochemical radii).



**Figure 2.** Percentage difference between the calculated and the reference values<sup>8,9</sup> of the thermochemical radii using dataset (i).

Table S2 in the Supporting Information shows the dataset (ii), which contains complex anions with a higher covalent character. This dataset is important for two reasons: first because it demonstrates the capability of eq 1 to predict the thermochemical radii of complex anions that were not included in the fitting shown in figure 1, and second because it demonstrates that even in cases in which the covalent contribution is significant, a good estimation can still be obtained by applying eq 1. Furthermore, Table S2 contains the values of  $r_M$ ,  $r_X$ ,  $r_{MX}^{calc}$ ,  $r_{MX}^{ref}$  using the same references for  $r_M$ ,  $r_X$ ,  $r_{MX}^{ref}$  as Table S1<sup>8,9,13</sup>, apart from the covalent radii of carbon ions, which were taken from Cordero et al.<sup>11</sup>. Likewise in Table S1, the values of  $r_M$  and  $r_X$  in Table S2 were selected at a coordination number of 6, whenever possible. In contrast to Table S1, Table S2 contains a comment column, and in this column it has been shown that even in cases in which the values of  $r_M$  are unknown, these values can be estimated based on reasonable approximations. Conversely, these approximations were not applicable to  $r_X$ , since in this case this radius is only tabulated for a specific ionic charge. For instance, the nitrogen anion is tabulated<sup>8</sup> only for the charge -3, and then no other ionic charge is available to generate a curve that would allow the estimation of, for example, the Nitrogen with a charge of -1. In addition to this, the comment column shows some data that were excluded due to unclear or insufficient information. For example, it was not possible to find the structure of the  $SNCl_5(CH_3CN)^-$  anion in the literature.

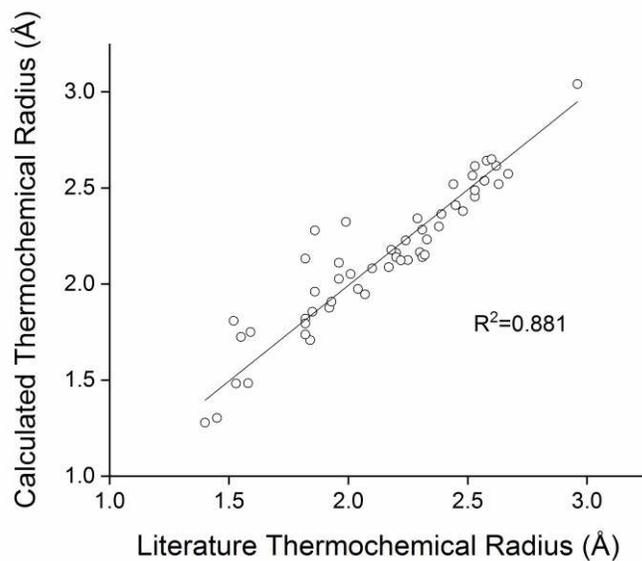
Figure 3 shows the agreement between dataset (ii)<sup>8,9</sup> and the calculated values using eq 1. As can be seen in this figure, eq 1 was able to predict the values of the thermochemical radii for complex anions that were not included in the fitting shown in figure 1. In addition, over 97% of the cases analyzed were accurate to within 15%, whereas over 87% were accurate to within 10%.



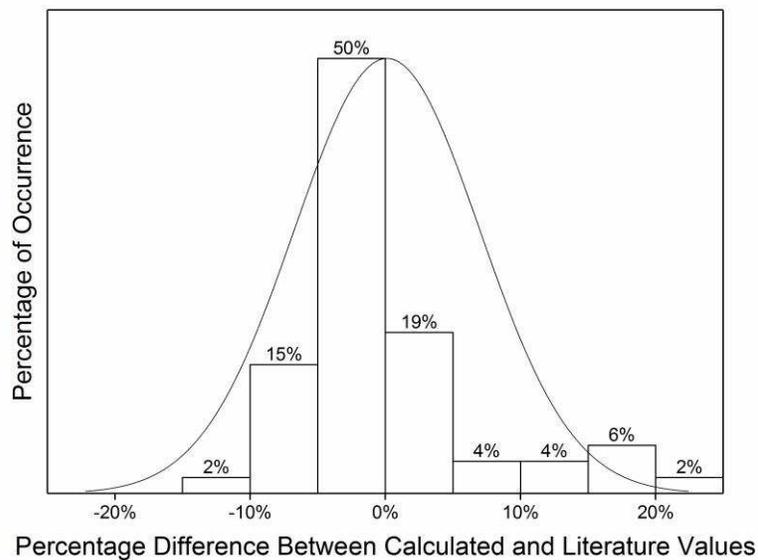
**Figure 3.** Percentage difference between the calculated and the reference values<sup>8,9</sup> of the thermochemical radii using dataset (ii).

## Thermochemical Radii of Complex Cations

The complex cations tabulated in the literature<sup>8,9</sup> were divided in two datasets: (i) containing complex cations with a electronegativity difference between constituent cation and anionic ligands less than 0.5, and (ii) containing higher differences of electronegativity. The constant  $\kappa_1$  and the power terms  $\varepsilon_2$  and  $\varepsilon_3$  in eq 2 were estimated using dataset (i), whereas dataset (ii) was used to test the capability of eq 2 to predict the thermochemical radii of complex cations that were not used to estimate these fitting parameters. In particular, dataset (i) was selected to estimate the parameters  $\kappa_1$ ,  $\varepsilon_2$  and  $\varepsilon_3$  because eq 2 was derived assuming predominance of covalent bonds, and thus it is important to choose the set of data with lower influence of the ionic character of the bond. A comparison between the calculated values of  $r_{MX_l}$  using eq 2 and the dataset (i)<sup>8,9</sup> is presented in Figure 4. As can be seen in this figure, the agreement between the thermochemical radii calculated through eq 2 and the literature values<sup>8,9</sup> is good. In addition to this, Figure 5 shows the percentage deviation between the calculated and the dataset (ii)<sup>8,9</sup>, and as can be seen in this figure, a deviation less than 10% was achieved in over 88% of the cases analyzed. Finally, more detailed information is shown in Table S3 in the Supporting Information, which contains the values of  $r'_M$ ,  $r'_X$ ,  $r_{MX}^{calc}$ ,  $r_{MX}^{ref}$ ,  $V_{MX}^{calc}$  and  $V_{MX}^{ref}$ . The values of  $r'_M$  and  $r'_X$  were taken from Cordero et al.<sup>11</sup>. Additionally, the values of  $r_{MX}^{ref}$  were taken from Roobottom et al.<sup>8</sup> and Jenkins et al.<sup>9</sup>. Finally, the values of  $V_{MX}^{ref}$  were taken from Jenkins et al.<sup>5</sup>. It is important to note that the  $r'_M$  and  $r'_X$  are the covalent radii, rather than the ionic radii. Since these values are independent on the ionic charge and the coordination number, then the oxidation states are not shown in this table.



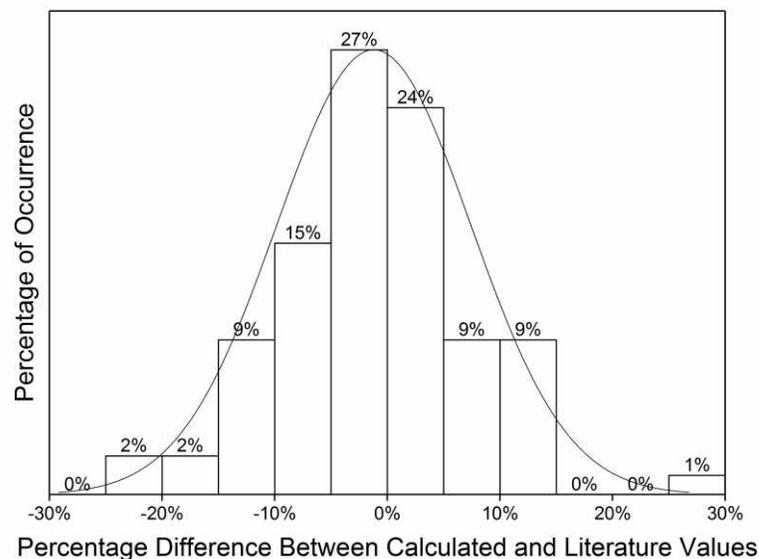
**Figure 4.** Parity plots comparing the reference values of thermochemical radii<sup>8,9</sup> in Table S3 in the Supporting Information with those calculated using eq 2 (solid line:  $y=x$  line,  $\circ$ : thermochemical radii).



**Figure 5.** Percentage difference between the calculated and the reference values<sup>8,9</sup> of the thermochemical radii using the dataset (i).

Table S4 in the Supporting Information shows the dataset (ii), which contains complex cations with differences of electronegativity higher than 0.5, i.e. polar covalent bond. This dataset shows the effectiveness of eq 2 to predict the values of the thermochemical radii for complex cations that were not involved in the estimation of  $\kappa_1$ ,  $\epsilon_2$  and  $\epsilon_3$ . The values of  $r'_M$ ,  $r'_X$ ,  $r_{MX}^{\text{ref}}$  and  $V_{MX}^{\text{ref}}$  were taken from the same references as Table S3<sup>5,8,9,11</sup>. In contrast to Table S3, Table S4 contains a comment column, and the purpose of this column is mainly to show the data that were not considered in the analysis due to apparent inconsistencies in the values of the thermochemical radii. For instance, the thermochemical radii of  $\text{Se}_{17}^{2+}$  should lie between  $\text{Se}_{19}^{2+}$  and  $\text{Se}_{10}^{2+}$ , but the reported value<sup>8</sup> of 2.36 Å is even lower than the value reported for  $\text{Se}_{10}^{2+}$ , which is 2.53 Å. Also, if the consistency cannot be assessed, then the data are not used. For example, the complex cations with charges +3 and +4, namely  $\text{I}_{15}^{3+}$  and  $\text{Te}_2(\text{su})_6^{4+}$ , were not included in the analysis because there are no other complex cations with similar ionic charges that could be compared with them.

Figure 6 illustrates the agreement between dataset (ii)<sup>8,9</sup> and the calculated values using eq 2. As can be seen in this figure, eq 2 was able to predict with a good accuracy the values of the thermochemical radii for complex anions that were not included in the fitting shown in figure 4. More specifically, over 93% of the cases analyzed were accurate to within 15%, whereas over 75% were accurate to within 10%.



**Figure 6.** Percentage difference between the calculated and the reference values<sup>8,9</sup> of the thermochemical radii involving the dataset (ii).

### Volume Correlations for the Complex Cations

The volume based equations developed by Jenkins et al.<sup>5</sup> have emerged largely to replace Kapustinskii's equation<sup>3</sup>, although it was evolved from it. These equations correlate the lattice energies with the molecular volume of the salt, and the advantage of these equations is that they can gain their data from either the density or the set of lattice constants, and a structural determination is not required. In their approach, the free space in the crystal structure is assigned to the anion volumes, and then these anion volumes are then further employed to generate cation volumes. It is important to note that this procedure has been improved by Glasser and Jenkins<sup>16</sup>, but this improvement was applied for only 43 cations and anions. Therefore, we have maintained the paper from Jenkins et al.<sup>5</sup> as the main reference for the ionic volumes, since this paper includes a much larger database. In this context, it is interesting to evaluate if these cation

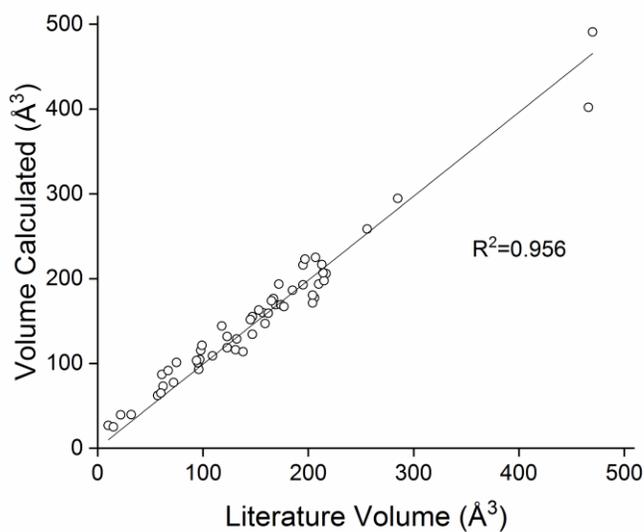
volumes correlate with the ionic radii of the single ions forming the complex cations. To achieve this, the following correlation was assumed:

$$V_{MX_l} = z_{MX_l} \varepsilon_2 \kappa_2 \left( \sum_j \nu_j \Gamma'_{M_j} \varepsilon_3 + \sum_k \nu_k \Gamma'_{X_k} \varepsilon_3 \right) \quad (4)$$

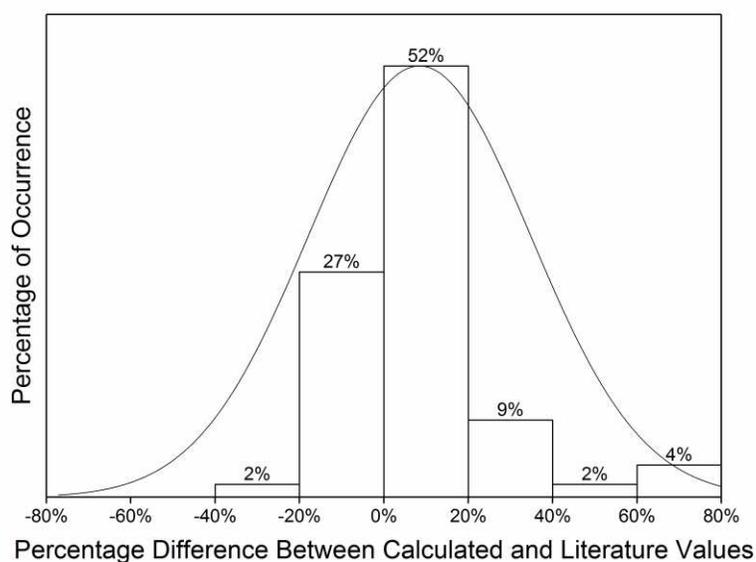
This equation is similar to eq 2, and includes the same power terms  $\varepsilon_2$  and  $\varepsilon_3$ . This is because in theory these parameters should be nearly the same since they are both related to the volume of the cation. In contrast, a new constant  $\kappa_2$  is required to be added, and this constant is different from  $\kappa_1$  since the left hand side of eq 2 is  $r_{MX_l}$  rather than  $V_{MX_l}$ . Also, this constant accounts for any free space not assigned to the anion volume. As in eq 2, the constant  $\kappa_2$  was estimated using dataset (i) in Table S3, whereas dataset (ii) in Table S4 was used to test the predictability capacities of eq 4. The linear regression was the method used to estimate the constant  $\kappa_2$ , and the value obtained was  $(23.61 \pm 0.32) \text{ \AA}^2$ .

A comparison between the calculated values of  $V_{MX_l}$  and the dataset (i)<sup>5</sup> is presented in Figure 7. As can be seen in this figure, the agreement between the calculated and the reference values is very good. In addition to this, Figure 8 illustrates the percentage difference between datasets (i) and (ii)<sup>5</sup> and the calculated values using eq 4. As can be seen in this figure, over 79% of the cases analyzed were accurate to within 20%, but in some cases the disagreements were more pronounced. In fact, these disagreements were higher for volumes less than  $70 \text{ \AA}^3$ , as illustrated in Figure 9, which shows that over 90% of the cases analyzed were accurate to within 20% for volumes higher than  $70 \text{ \AA}^3$ . Thus, eq 4 can be in general recommended to estimate cation volumes that exceed  $70 \text{ \AA}^3$ , which paradoxically are the cations structurally more complex. Nevertheless, it is remarkable how well the parameters  $\varepsilon_2$  and  $\varepsilon_3$ , which were estimated via the thermochemical radii, could describe the volume of the complex cations, which were obtained

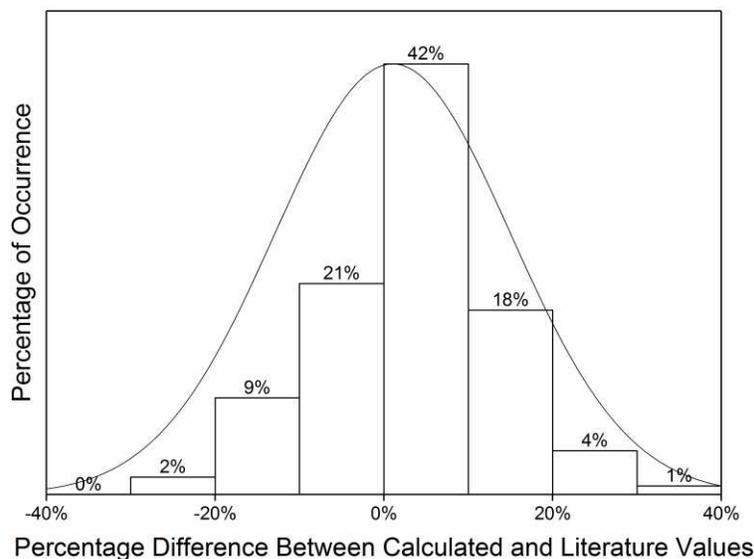
from a completely different database. This clearly illustrates the consistency of the methodology utilized in this study.



**Figure 7.** Parity plots comparing the reference values of the cation volume<sup>5</sup> with those calculated using eq 4 (solid line:  $y=x$  line,  $\circ$ : cation volume).



**Figure 8.** Percentage difference between the calculated and the reference values<sup>8,9</sup> of the cation volume considering all the complex cations analyzed.



**Figure 9.** Percentage difference between the calculated and the reference values<sup>8,9</sup> of the cation volume considering only volumes higher than  $70 \text{ \AA}^3$ .

## DISCUSSION

### Complex Anions

On developing eq 1, three assumptions were made as follows: (i) the complex anions are predominantly formed by ionic bonds, and thus these single ions could be modeled as cotangent spheres that do not overlap; (ii) the thermochemical radius of complex anions is dependent on the volume of their single ion components, and (iii) an expansion term represented by  $|z_{MX_i}|^{\epsilon_1}$  is required, since incoming electrons may increase repulsion, and consequently may increase the ionic radii.

Regarding the assumption (i), it is important to note that the precision of eq 1 to predict the complex anions with higher ionic character was higher than the accuracy of this equation to represent complex anions with higher influence of covalent bonds. This becomes evident when Figure 2 is compared to Figure 3, since in the Figure 2 over 97% of the anions were accurate to

within 10%, whereas in Figure 3 over 97% were accurate to within 15%, which represents 5% deterioration in accuracy. Nevertheless, 15% is still a very high accuracy considering the simplicity of eq 1 in contrast to the complexity of the anions analyzed. For instance, although the sulfate ion contains only covalent bonds, i.e. the electrons are not completely transferred from the sulfur atom to the oxygen atom, the agreement between the calculated value, 2.31 Å, and the literature value<sup>8</sup>, 2.18 Å, was very good, to within 5%, and this shows that eq 1 is effective at predicting the values of the thermochemical radii of complex anions even for cases in which the bonds are not entirely ionic. Also, it is important to note that improvements can be made in eq 1 to improve its accuracy, at the expense of sacrificing its simplicity. For instance, this model can be refined by incorporating into it important effects such as polarizability, orbital overlapping, electron density, etc.

With regards to the assumption (ii), the volumes of the individual ions have proven to be very strongly correlated to the thermochemical radii of complex anions, since eq 1 is very accurate at describing the thermochemical radii of these complexes.

Finally, the assumption that income electrons increase repulsion, i.e. assumption (iii), has also been proven correct, since the power term  $\epsilon_1$  obtained by linear regression was positive. This term increases the radii of the complex anions by about 4% for an ionic charge of -2, and about 7% for an ionic charge of -3. However, if the extra electron is added to a higher energy level, then this increase in radius can be even stronger, as in the case of the  $O^{3-}$ , which is twice as large as the  $O^{2-}$  ion.

#### *Extending Predictions beyond the Roobottom et al. Database for Complex Anions*

In order to demonstrate that the predictability capacities of eq 1 extend beyond the Roobottom et al. database<sup>8</sup>, this eq 1 was used to estimate the  $GeO_4^{4-}$  thermochemical radius, which is not

included in their database. The thermochemical radius of this ion can be calculated via Kapustinskii's equation<sup>3</sup>, using Born - Fajans - Haber cycle lattice energies available in the literature<sup>17</sup> for  $\text{Ca}_2\text{GeO}_4$  and  $\text{Ba}_2\text{GeO}_4$ , which are 7306 kJ/mol and 6643 kJ/mol, respectively. Considering the Goldschmidt radius<sup>18</sup> for  $\text{Ca}^{2+}$  and  $\text{Ba}^{2+}$  ions, the resultant thermochemical radius is 2.55 Å for  $\text{Ca}_2\text{GeO}_4$  and 2.58 Å for  $\text{Ba}_2\text{GeO}_4$ , and this represents a thermochemical radius of  $(2.56 \pm 0.02)$  Å, not including the errors associated to the lattice energies estimations. If this same thermochemical radius is calculated via eq 1, using the ionic radii of 0.53 Å and 1.40 Å for the  $\text{Ge}^{+4}$  and  $\text{O}^{2-}$  ions<sup>12</sup>, respectively, the resultant thermochemical radius is 2.38 Å. This represents a difference of only 7.1 %.

### **Complex Cations**

Complex cations are far more complex than complex anions, since their geometry is more irregular and their forming single ions are not spherical, since the bonds between them are predominantly covalent. Also, the literature values reported for complex cations are in general less accurate than are the values for the complex anions. Therefore, it is not unexpected that the agreement between experimental and calculated data for complex cations is not as good as the agreement achieved for complex anions. Nevertheless, this agreement was better than 15% in the vast majority of the cases analyzed, see Figures 5 and 6.

Three assumptions were made for the complex cations on deriving eq 2: (i) bonds are predominantly covalent, (ii) the thermochemical radius of complex cations is dependent on the radii of their single ion components and (iii) a contraction term represented by  $z_{\text{MX}_l} \epsilon^2$  is required, since the deficit of electrons increases the attraction towards the positively charge nucleus.

Regarding the assumption (i), it is important to note that the precision of eq 2 to predict the complex anions with higher covalent character was higher than the accuracy of this equation to

represent complex cations with higher influence of ionic bonds. This becomes evident when Figure 5 is compared to Figure 6, since in Figure 5 over 97% of the cations were accurate to within 15%, whereas in the Figure 6 a lower percentage of 93% was accurate to within 15%. Nevertheless, likewise stated to the complex anions, this precision can possibly be improved if refinements are incorporated to the model, such as the effects of polarizability, orbital overlapping, electron density, etc.

With regards to the assumption (ii), the covalent radii of the individual ions have proven to be very strongly correlated to the thermochemical radii of complex cations, since the agreement between calculated and literature values<sup>8,9</sup> was good in general.

Finally, the assumption that the deficit of electrons causes contraction of the thermochemical radius of complex cations, i.e. assumption (iii), has also been proven correct, since the power term  $\varepsilon_2$  is negative. For instance, this term reduces the radii of complex cations about 17% for an ionic charge of +2.

#### *Extending Predictions beyond the Roobottom et al. Database for Complex Cations*

In order to demonstrate that the predictability capacities of eq 2 extend beyond the Roobottom et al. database<sup>8</sup>, this equation can be used to estimate for example the  $\text{PH}_4^+$  thermochemical radius, which is not included in their database. The thermochemical radius of this ion can be calculated via Kapustinskii's equation<sup>3</sup>, using lattice energies available in the literature<sup>19</sup> for  $\text{PH}_4\text{Br}$  and  $\text{PH}_4\text{I}$ , which are 616.3 kJ/mol and 590.8 kJ/mol, respectively. Using these values, the resultant thermochemical radius is 1.60 Å for  $\text{PH}_4\text{Br}$  and 1.52 Å for  $\text{PH}_4\text{I}$ , and this represents a thermochemical radius of  $(1.56 \pm 0.04)$  Å, not including the experimental errors to obtain the lattice energy. If this same thermochemical radius is calculated via eq 2, using the covalent radii

from the literature<sup>11</sup>, the resultant thermochemical radius is 1.52 Å, and this represents a difference of only 3 %.

### **Volume Correlations for the Complex Cations**

The parameters obtained for eq 2, namely the power terms  $\varepsilon_2$  and  $\varepsilon_3$  were used to estimate the volume of the cations, and then these estimations were compared with the values available in the literature<sup>5</sup>. This comparison, illustrated in figure 7, presented a very high coefficient of determination ( $R^2=0.956$ ), which is remarkable considering that the ion volumes are estimated using a completely different methodology from the one used to estimate the thermochemical radii. Therefore, these agreements indicate good consistency of the methodology used to estimate both the thermochemical radii and the ion volumes for complex cations.

In order to show the applicability of these equations, the case of the tetrasulfur dication  $S_4^{2+}$  can be analyzed. Jenkins et al.<sup>5</sup> estimated the volume of this cation based on extrapolation of the known ion volumes of  $Se_4^{2+}$  and  $Te_4^{2+}$ , and the value obtained was 84 Å<sup>3</sup>. Applying eq 4 to estimate this cation volume, the value of 77 Å<sup>3</sup> is obtained, which differs only 9% from the value presented by Jenkins et al.<sup>5</sup>. However, in cases in which either extrapolations or interpolations are difficult to be performed, eq 4 becomes a very important alternative for the estimation of the cation volumes, and consequently for the estimation of the lattice energies.

As mentioned in the results section, eq 4 is more accurate for volumes higher than 70 Å<sup>3</sup>. However, it is important to note that the literature data at volumes less than 70 Å<sup>3</sup> are not in general very accurate either. For instance, the  $NH_4^+$  is tabulated as  $(21 \pm 15)$  Å<sup>3</sup>, i.e. an error as large as 71%. Nevertheless, volumes higher than 70 Å<sup>3</sup> can be in general associated to cations that are more structurally complex, and for these cations volume estimations are in general more

difficult to be performed. Therefore, eq 4 can be a very useful in estimating the volume of these structurally complex cations within a reasonable accuracy.

### **Electrolyte Solutions**

Marcus<sup>1</sup> compared the Pauling crystal ionic radii for a coordination number of 6 with the ionic radii in solution, which can be obtained for example via X-ray diffraction. As a result, both the Pauling crystal radii and the solution ionic radii were very similar in size, and this indicates that the radii obtained in crystals gives a good indication of the radii that the ions have in aqueous solutions. Therefore, it is interesting to compare the results obtained in this study for the complex ions with those reported by Marcus<sup>1,20,21</sup>, and this is done in Table S5 in the Supporting Information. As can be seen in this table, the thermochemical radii of complex ions are in good agreement with the ionic radii obtained in aqueous solutions. Also, it is interesting to observe that the calculated values of the thermochemical radii using eqs 1 and 2 are in many instances closer to the values reported by Marcus<sup>1,20,21</sup> than are the literature values<sup>8,9</sup>. This is another good indication of the consistency of eqs 1 and 2. Finally, the  $\text{UO}_2^{2+}$  ion, which is not included in Roobottom et al. database<sup>8</sup>, is another example that illustrates the good predictability capacities of eq 2, since the percentage difference between the predicted value and the aqueous ionic radius reported by Marcus<sup>21</sup> was only 7%.

### **CONCLUSIONS**

A new approach to calculate the thermochemical radius of polyatomic ions has been presented. In particular, an expression that correlates the thermochemical radii of the polyatomic ions with their forming single ions was developed and validated using reference values of the thermochemical radii obtained from the literature<sup>8,9</sup>. Likewise, a new approach to estimate the volumes of complex cations is presented and validated using literature values. Moreover, the

results of the thermochemical radii are compared with the ionic radii of these complex ions in aqueous solutions. As a conclusion, the new expressions developed in this study produce results that were in a very good agreement with the literature values. In addition, these equations can be refined to improve their accuracy, and these possible improvements are discussed in the text, and these refinements could be the subject of future investigations.

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## ABBREVIATIONS

### *Latin Symbols*

CN, coordination number

n, number of experimental data points

$r_{M_j}$ , Ionic radii of the cations of a polyatomic ion

$r'_{M_j}$ , Covalent radii of the cations of a polyatomic ion

$r_{MX_i}$ , Ionic radii of the of a anion with the chemical formula  $(M_1M_2 \dots M_j, X_1X_2 \dots X_k)^{z-}$

$r_{MX_i}$ , Ionic radii of a cation with the chemical formula  $(M_1M_2 \dots M_j, X_1X_2 \dots X_k)^{z+}$

$r_{X_k}$ , Ionic radii of the anions of a polyatomic ion

$r'_{X_k}$ , Covalent radii of the anions of a polyatomic ion

$S(r_{MX_i})$ , objective function

$V_{MX_i}$ , Volume of a cation with the chemical formula  $(M_1M_2 \dots M_j, X_1X_2 \dots X_k)^{z+}$

$Z_{MX_i}$ , Ionic radii of the of a anion with the chemical formula  $(M_1M_2 \dots M_j, X_1X_2 \dots X_k)^{z-}$

$Z_{MX_i}$ , Ionic radii of the of a cation with the chemical formula  $(M_1M_2 \dots M_j, X_1X_2 \dots X_k)^{z+}$

### *Greek Symbols*

$\kappa_1$ , constant that correlates the thermochemical radii of a complex cation with the ionic radii of its individual ions.

$\kappa_2$ , constant that correlates the volume of a complex cation with the ionic radii of its individual ions.

$\varepsilon_1$ , power factor that correlates the thermochemical radii of a complex anion with its ionic charge.

$\varepsilon_2$ , power factor that correlates the thermochemical radii of the complex cation with its ionic charge.

$\varepsilon_3$ , power factor that correlates the thermochemical radii of a complex cation with the ionic radii of its individual single ions.

$\nu_j$ , number of single cations of a given specie

$\nu_k$ , number of single anions of a given specie

*Subscripts*

*i*, polyatomic anion i

*j*, number of cations

*k*, number of anions

*l*, polyatomic cation l

M, cation

X, anion

*Superscripts*

aqueous, aqueous solutions

calc, calculated

ref, value obtained from the literature

## SUPPORTING INFORMATION

Supporting Information material includes Tables from S1 to S5. Tables S1 to S4 show detailed information involving the thermochemical radii of complex anions and cations, as well as the ionic volumes of complex cations, whereas Table S5 shows a comparison between the thermochemical radii and the ionic radii in aqueous solutions for complex ions.

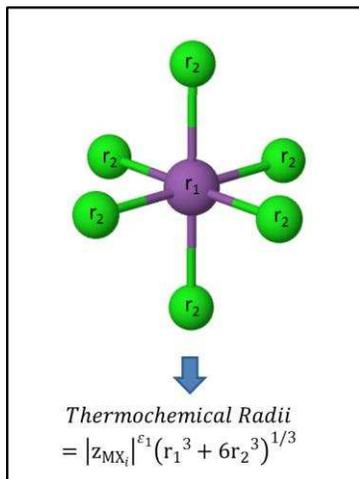
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A new expression that correlates the thermochemical radius of complex ions with the ionic radii of its monatomic ions is presented, and this expression is accurate to within 15% in most of the cases analyzed. Also, a new expression, with similar accuracy, is presented to calculate the volume of complex cations. Finally, these expressions can be used to estimate the lattice energy of the crystals, as well as other properties that are linked to the size of the ions.