Research Article

On the reliability of volume-based thermodynamics for inorganic-organic salts and coordination compounds with uncharged ligands

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Abstract In the present work, the reliability of the volume-based thermodynamics (VBT) methods in the calculation of lattice energies is investigated by applying the "traditional" Kapustinskii equation [8], as well as Glasser-Jenkins [3] and Kaya [5] equations to calculate the lattice energies for Na, K and Rb pyruvates [9-11] as well as for the coordination compound $[Bi(C_7H_5O_3)_3C_{12}H_8N_2]$ [12] (in which $C_{12}H_8N_2$ = 1,10 phenathroline and $C_7H_5O_3^-$ = *o*-hyddroxybenzoic acid anion). As comparison, the lattice energies are also calculated using formation enthalpy values for sodium pyruvate and $[Bi(C_7H_5O_3)_3C_{12}H_8N_2]$. For the pyruvates, is verified that none of the considered approach, Kapustinskii, Glasser, Kaya or density, provides values that agrees, in an acceptable % difference, with the lattice energy values calculated from the formation enthalpy values. However, it must be pointed out that Kaya approach (which deals with a chemical hardness approach) is the better one for such kind of inorganic-organic salts. Based on data obtained for $[Bi(C_7H_5O_3)_3C_{12}H_8N_2]$ is concluded that the only one VBT method that provides reliable lattice energies for compounds with bulky uncharged ligands is that one based on density values (derived by Glasser-Jenkins).

Keywords Thermochemistry, Volume-based thermodynamics, lattice energy, pyruvates, coordination compounds

Introduction

As shown to PtF_6 [1], thermochemical data can be of paramount importance to a fully understanding of the properties of inorganic compounds.

The volume-based thermodynamics (VBT) [2] has been successfully employed to the calculation of lattice energies for a series of inorganic salts [3] as well as for complex solids such as silicates and double salts [4].

Volume-based thermodynamics can also be successfully applied using a chemical hardness approach [5] and both, Glasser-Jenkins [3] and Kaya [5] equations have been recently employed in order to provide a thermochemical explanation for the stability of unusual compounds such as $NaCl_3$ and $NaCl_7$[6].

Have also been shown that even for salts with organic cation and anion [7] the VBT approach can provide very good results.

But what about when we are dealing with a inorganic (cation)-organic (anion) salt ?or for coordination compounds with uncharged (specially for bulky)ligands ? This work aims to provide some answers to these questions.

In the present work, the "traditional" Kapustinskii equation [8], as well as Glasser-Jenkins [3] and Kaya [5] equations are applied to calculate the lattice energies for sodium, potassium and rubidium pyruvates [9-11], as well

as for the coordination compound $[Bi(C_7H_5O_3)_3C_{12}H_8N_2]$ [12] (in which $C_{12}H_8N_2$ = 1,10 phenathroline and $C_7H_5O_3^-$ = *o*-hyddroxybenzoic acid anion).

Methodology

The structural parameters, as well as density values previously obtained [9-11] are employed.

For sodium pyruvate, the lattice energy was also calculated using the formation enthalpy values for the respective cation [13], the pyruvate [10] and the pyruvate anion:

$$Na^+_{(g)} + C_3H_3O_3^-{}_{(g)} \rightarrow NaC_3H_3O_{3(s)}; U_{POT}$$
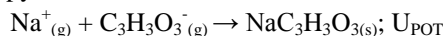
For $M^+_{(g)}$ ($M^=$ Na, K and Rb) the radius and formation enthalpy values (for Na^+) are from literature [13, 14]. The formation enthalpy for gas phase pyruvate anion was obtained by quantum-chemical calculations.

All computations were performed by using Spartan´16 [15], version 1.1.8: SE-PM6. The SE-PM6 approach was chose taking into account its minor computer time consuming and its reliability, as verified for PtF_6 [1].

As "calibration" and reliability test, the gas phase formation enthalpy ($kJmol^{-1}$) for pyruvic acid was calculated by the same approach, and the obtained value compared with those from literature. The (exp./calc.) values are as follows: (-482.64/-496.54). So, the suitability/reliability of the chose quantum chemical approach was proved.

The gas phase formation enthalpy calculated for the pyruvate anion is -683.75 $kJmol^{-1}$. The calculated lattice enthalpy (from formation enthalpy values) for sodium pyruvate was -761.68 $kJmol^{-1}$ which was corrected [16] to the energy value shown in Table 1.

To use the Kapustinskii equation it was necessary to calculate the "radius" of the pyruvate anion. Such radius were obtained as follows: since both equations, for the surface area and volume of the sphere, have a 4π term, the quantum chemical calculated area and volume were used to obtain, after the proper algebraic manipulations, a radius of 232.03 pm. As comparison, the quantum chemical calculated volume is 0.080 nm^3, in very good agreement with the thermochemical value [10, 11] (0.088 nm^3).

When using Kaya equation, the η_M value for NaCl was employed. When using Kaya and Glasser-Jenkins equations, the parameters for a MX salt were employed.

Table 1: Calculated lattice energies ($kJmol^{-1}$) for sodium, potassium and rubidium pyruvates.

Compound/method	$NaC_3H_3O_3$	$KC_3H_3O_3$	$RbC_3H_3O_3$
Kapustinskii	-649.38	-593.02	-573.55
Glasser-Jenkins	-601.87	-567.74	-569.55
By density[a]	-649.44	-603.37	-607.19
Kaya	-692.38	-671.68	-672.78
By ΔH_f values[b]	-764.16	_	_

[a]By using the equation derived by Glasser, in which a ionic-strength like term is present. [b]Using experimental formation enthalpy value for the solid pyruvates and the $Na^+_{(g)}$ cation [10, 13], as well as the SE-PM6 calculated gas phase formation enthalpy value for the pyruvate anion.

Results and Discussion

The obtained lattice energy values are summarized in Table 1.

Using sodium pyruvate as model (the only one for which solid state formation enthalpy is available) [10] it is verified that none of the considered approach, Kapustinskii, Glasser-Jenkins, Kaya or density, provides values that agrees in an acceptable % difference, with the lattice energy value calculated from the formation enthalpies which is, from a thermodynamic point of view, the most reliable one.

Kaya value is the closer one, with a difference to the formation enthalpy value of 10.4%. However, it must be pointed out that Kaya equation, with deals with a chemical hardness approach (and, consequently, with the concept of polarizability and the homo and lumo orbitals energies) is the better one for such kind of inorganic-organic salts.

As can be verified, the lattice energy values calculated by Kapustinskii equation decreases as the cation radius increases. On the other hand, the lattice energy values for $KC_3H_3O_3$ and $RbC_3H_3O_3$ calculated by Glasser-Jenkins, Kaya or density approach are practically insensitive to the cation radius.

This fact can be explained taking into account that Glasser-Jenkins, Kaya and density approach are, properly speaking, VBT approach. For $KC_3H_3O_3$ V_m = V/Z = 0.51709/4= 0.1293, whereas for RbC_3H_3O, V_m= 0.25566/2= 0.12783, that is, both pyruvates have practically the same V_m value. So, as illustrated with this compounds, VBT approach are "dominated" by the $(V_m)^{1/3}$ term, making them insensitive to variations (such as cation radius) that do not affect, directly, the molar volume of the compound.

In agreement with the "sensitivity" of Kapustinskii equation, when the lattice energies values are plotted as a function of the ionic radius, a straight line (r= 0.999) is obtained (Figure 1).
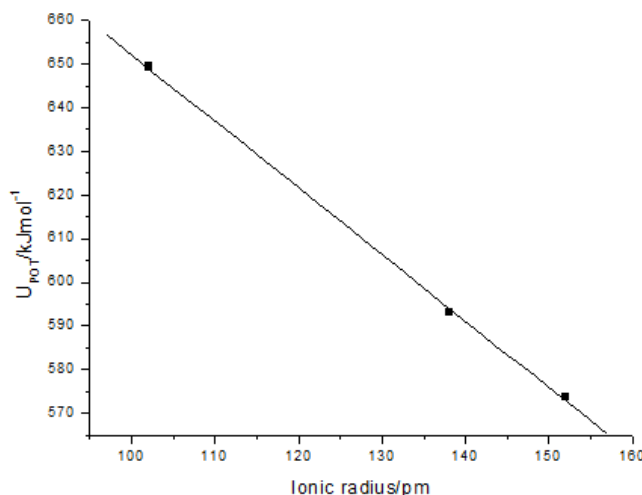

Figure 1: Lattice energies (Kapustinskii equation) as function of the ionic radius for Na, K and Rb pyruvates

On the other hand, it is worth noting that the atoms polarizabilities[13]/10^{-24}cm^3, are Na(24.11), K(43.06) and Rb(47.24), that is, from K to Rb there is a small variation in the polarizability, in agreement with the small variations in the lattice energy values calculated using Glasser-Jenkins, Kaya and density approach.

The reliability of the volume-based thermodynamics was also verified with the coordination compound $[Bi(C_7H_5O_3)_3C_{12}H_8N_2]$ [12] in which $C_{12}H_8N_2$ = 1,10 phenanthroline and $C_7H_5O_3^-$= *o*-hydroxybenzoic acid anion. So, we have here a compound with a bulky uncharged ligand molecule.

Experimental ΔH_f^g and density for such compound were employed [17]. The formation enthalpy for $Bi^{3+}_{(g)}$ was taken from literature [12]. The gas phase formation enthalpy for 1,10phenanthroline (298.10 kJmol^{-1}) was obtained by using the solid state formation enthalpy, as well as the melting and vaporization enthalpies for such compound [17].

The gas phase formation enthalpy for $C_7H_5O_3^-$ (-613.24 kJmol^{-1}) was calculated by SE-PM6 method. The obtained lattice energy values for such compound are summarized in Table 2. The calculated lattice enthalpy (kJmol^{-1}), from formation enthalpy values was -3761.79, which was corrected [15] to the energy value shown in Table 2.

Also here, the lattice energy value calculated by using formation enthalpy values will be considered the more reliable one. The poor results obtained by using the linearized Glasser-Jenkins and Kaya equations can, in a first moment, be explained by the simplifications used: since there are not *a* and *b* values (Kaya) for MX_3 salts, the used values were those obtained by extrapolation, for NaCl$_3$[6]. Furthermore, since there is not (Kaya) a η_M value for MX_3 salts, the η_M value for NaCl was employed.

For Glasser-Jenkins we have the same problem: since there are not α andβ values for MX_3 salts, I have used values obtained by extrapolation for those for MX and MX_2 salts (extrapolated values: α = 151.94; β = 71.46). So, the poor results are not, necessarily, a failure of both equations/approach, but only a question of lacking of suitable

parameters. For Glasser-Jenkins approach, using α and β parameters for a generic M_pX_q salt, the obtained U_{POT} value is lower than that obtained by using the extrapolated α and β values.

Table 2: Calculated lattice energies (kJmol^{-1}) for [Bi(C$_7$H$_5$O$_3$)$_3$C$_{12}$H$_8$N$_2$]

Glasser-Jenkins	-3123.35[b]
	-2408.86[d]
	-2072.39[c]
Kaya	-2978.86
By density[a]	-3753.74
By ΔH_f values	-3765.51

[a]By using the equation derived by Glasser-Jenkins[3]. [b]Using the linearized Glasser-Jenkins equation with α and β extrapolated values. [c]Using the generalized Glasser-Jenkins equation, with a ionic strength like term. [d]Using α and β parameters for a generic M_pX_q salt in the linearized Glasser-Jenkins equation.

However, the generalized (with a ionic strength like term) Glasser-Jenkins equation provides, generally, very good results [3, 4] for compounds with U_{POT} of thousands of kJmol^{-1}. So, it is really a surprise the poor result obtained by using such generalized equation. The only conclusion is that the presence of a very large and uncharged molecule (1,10-phenanthroline) in the coordination compound lattice, is compromising the premises of the employed approach. Can be supposed that for compounds with bulky uncharged ligands, the mass contribution (affecting density, of course) prevails over the charge contribution.

Anyway, such as for the pyruvates, Kaya equation provides better (closer to the U_{POT} obtained from formation enthalpy values) results than Glasser-Jenkins equation. Such fact suggests that an approach base on chemical hardness can be a better way to describe the thermochemical behaviour of coordination compounds.

Most important, as can be verified, the lattice energy calculated by using the density for the compound [Bi(C$_7$H$_5$O$_3$)$_3$C$_{12}$H$_8$N$_2$] agrees very well (-0.3%) with the value calculated by using formation enthalpy values. So, it is verified that despite the fact that a bulky uncharged ligand molecule is present in the lattice, the VBT approach is "sensitive" enough to compute the contribution of such uncharged molecule to the lattice energy. Hence, can be concluded that for compounds with uncharged ligands (specially for bulky ligands), the only one volume based method that provides reliable results is that one based on density values. It is possible to suppose that for such kind of compounds, the (mass/volume) contribution prevails over the charge contribution.

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