The extended Zintl–Klemm concept, ionic strength I and assessment of the relative stability of lattices using the stability enhancement ratio S

Harry D. Brooke Jenkins^{a,b,*} and Angel Vegas^c

^aDepartment of Chemistry, University of Warwick, Coventry, CV4 7AL, England, ^b'Fieldgate', 3, White Hill, Olney, Buckinghamshire MK46 5AY, England, and ^cDepartment of Chemistry, Universidad de Burgos, Hospital del Rey s/n, Burgos, 09001, Spain. *Correspondence e-mail: h.d.b.jenkins@warwick.ac.uk

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This article examines the comparison between the classical formulations used to describe silicates and that derived from the application of the extended Zintl–Klemm concept (EZKC). The ionic strength, I , for 25 silicate lattices is calculated taking into account both formulations, and the results show that, in every single one of the examples, the ionic strength of the Zintl polyanion is higher than that of the classical model which assigns a formal charge of 4+ for silicon. Our earlier study, firstly applied to the germanate $(\text{NH}_4)_2\text{Ge}^{[6]}[\text{Ge}^{[4]}_6\text{O}_{15}]$ [Vegas & Jenkins (2017). *Acta Cryst. B* **73**, 94–100] and to the polyanion $[\text{Ge}^{[4]}_6\text{O}_{15}]^{6-}$ equivalent to the pseudo- As_2O_5 derived from it, explained satisfactorily the charge transfer that takes place in the Zintl compounds. The value of $I = \frac{1}{2} \sum n_i z_i^2$ for the Zintl polyanion was greater than for the compound as formulated in the classical way. In that article, a meaningful relationship was found between the electron transfers as defined by the EZKC and the ionic strength I of the anion $[\text{Ge}^{[4]}_6\text{O}_{15}]^{6-} \equiv \Psi\text{-As}_2\text{O}_5$. Because the ionic strength, I , of a lattice is directly proportional to the lattice potential energy, U_{POT} , the higher the I the greater the U_{POT} ; thus it is harder to break up the lattice into its constituent ions and hence the lattice itself is more stable, giving support to the idea that the application of the EZKC and the resulting electron shifts yields structures which are inherently thermodynamically more stable than the starting configuration.

1. Introduction

In a previous article (Vegas & Jenkins, 2017) we reported a new interpretation of the structure of $(\text{NH}_4)_2\text{Ge}_7\text{O}_{15}$ (Cascales *et al.*, 1998) in terms of the extended Zintl–Klemm concept (EZKC). This germanate is peculiar in having Ge atoms with both tetrahedral and octahedral coordination and so could be formulated as $(\text{NH}_4)_2\text{Ge}^{[6]}[\text{Ge}^{[4]}_6\text{O}_{15}]$. The co-existence of both types of polyhedra is found also among aluminates and silicates and their respective skeletons were interpreted by Santamaría-Pérez & Vegas (2003) and by Santamaría-Pérez *et al.* (2005) as being due to the charge transfer from the $X^{[6]}$ cations ($X = \text{Al}, \text{Si}, \text{Ge}$) towards the $T^{[4]}$ atoms that behave as Zintl polyanions. In $(\text{NH}_4)_2\text{Ge}^{[6]}[\text{Ge}^{[4]}_6\text{O}_{15}]$ the transfer of six electrons from the NH_4^+ and the hexa-coordinated Ge^{4+} cations to the $[\text{Ge}_6\text{O}_{15}]$ moiety converts the latter into the tetrahedral skeleton $[\text{Ge}^{[4]}_6\text{O}_{15}]^{6-}$ that contains the $[\text{Ge}_6]^{6-}$ Zintl polyanion. It is equivalent to a $\Psi\text{-As}_2\text{O}_5$ skeleton in which the $\Psi\text{-As}$ atoms are three-connected according to the $(8 - N)$ rule.

Thus, the application of the EZKC leads to the discovery of interesting new outcomes that arise due to the different roles

played by atoms of the same species (in this case Ge) as a function of their donor/acceptor character. Vegas & Jenkins (2017) found a meaningful relationship between the electron transfer, as defined by the EZKC, and the ionic strength I of the pseudo-anion $[\text{Ge}^{[4]}_6\text{O}_{15}]^{6-} \equiv \Psi\text{-As}_2\text{O}_5$. A similar situation is reported here, in this case for a large variety of silicate lattices.

It should be remembered that the ionic strength, I , of a lattice is directly proportional to the lattice potential energy, U_{POT} (Jenkins & Glasser, 2000), and hence to the lattice stability. The higher the I the greater the U_{POT} , and thus the harder it is to break up the lattice into its constituent ions and hence the more stable is the lattice. For those compounds whose lattice energy U_{POT} is greater than 5000 kJ mol^{-1} this relationship is represented by the equation

$$U_{\text{POT}} = AI(2I/V_m)^{1/3}, \quad (1)$$

where A is a constant and V_m is the formula unit volume. Equation (1) has been thoroughly tested (Jenkins & Glasser, 2000) for a large range of silicate minerals. Experimentally based lattice potential energies (obtained using a Born–Fajans–Haber cycle) have been compared with the calculated values obtained from equation (1). The calculated and experimental results for U_{POT} agree to within $\pm 7\%$ and in many cases are significantly closer than this. This agreement means that the energetics linked to the ionic strength factor have a direct relevance to experimental results and can be relied on to connect to reality. Accordingly then, if, *via* the EZKC, we discuss an electron shift which transforms one lattice into another one having a higher value of $I^{4/3}$, then this will indicate a true increased stability. This calculation could be simplified to monitoring just the value of I itself.

This, in turn, shows that there is a thermodynamic justification and a stabilization following from the EZKC-driven shift in electrons. There is no change in the formula unit volume, V_m [the other parameter involved in equation (1), which can influence U_{POT}] because we are merely proposing a rearrangement of the charge within the *same* lattice framework. From this charge rearrangement we create a more stable pseudo-lattice when compared with the case where we calculate I on the basis of tetravalent Ge cations.

Thus, consideration of $(\text{NH}_4)_2\text{Ge}_7\text{O}_{15}$ as a pseudo-polyanion $\Psi\text{-As}_2\text{O}_5$ (in terms of the Zintl–Klemm concept) implies the existence of a more stable skeleton compared with the originating lattice (as Ge_2O_5). In other words, calculations of I considering Ge as $\Psi\text{-As}$ should predict a higher estimated potential energy than when we calculate I on the basis of tetravalent Ge in the germanate. The ionic strength, I , of a lattice is simply calculated using the formula

$$I = \frac{1}{2} \sum n_i z_i^2 \quad (2)$$

where the summation is performed over the entire lattice and n_i is the number of ions in the formula unit having charge z_i . Thus I for $(\text{NH}_4)_2\text{Ge}_7\text{O}_{15}$ is equal to: $\frac{1}{2}[2 \times (+1)^2 + 7 \times (+4)^2 + 15 \times (-2)^2] = 87$ treating the NH_4^+ as a charge of +1, leading to a predicted value of I for $3 \times \Psi\text{-As}_2\text{O}_5 = \frac{1}{2}[3 \times [2 \times (5)^2 + 5$

$\times (-2)^2] = 105$. Thus I increases from 87 to 105 by virtue of the above rearrangement.

As proof that this new approach, involving as it does a change in I , causes increased thermodynamic stability in the resulting lattice, we have applied the idea to a range of 25 silicates of diverse types. These are listed in Table 1 where the proposed electron shifts caused by invoking the EZKC onto the original structure produce the ‘pseudo-lattice’ always possessing enhanced stability. A measure of the stability enhancement ratio, S , brought about once EZKC has been applied is given by the equation

$$S = (\Psi\text{-}I)/I = I(\text{Pseudo-formula})/I(\text{Classical formula}), \quad (3)$$

where $\Psi\text{-}I$ is the ionic strength computed for the pseudo-formula [= $I(\text{Pseudo-formula})$], whereas I is that obtained for the classical formulation which in the case of Table 1 is $I(\text{Silicate})$. This ratio is an indicator of the stability gained with the charge rearrangement in the Zintl polyanion as explained in *Appendix A*.

2. Discussion

The compounds listed in Table 1 were selected from the different families of silicates as collected in the article by Santamaría-Pérez *et al.* (2005) and are listed together with the calculated values of I from equation (2).

As was the case in the structure of $(\text{NH}_4)_2\text{Ge}_7\text{O}_{15}$ (Vegas & Jenkins, 2017), all silicates listed in Table 1 illustrate the fact that the classical description of inorganic structures in terms of cation-centred anionic polyhedra is now outdated, since it provides poor insight into all the chemical interactions occurring in the crystal (Santamaría-Pérez & Vegas, 2003; Santamaría-Pérez *et al.*, 2005; Vegas & García-Baonza, 2007; Vegas *et al.*, 2009; Vegas, 2011a,b, 2012).

It should be remembered that octahedrally coordinated Al, Si or Ge atoms act as electron donors to the tetrahedrally coordinated X backbones that behave as true Zintl polyanions. This amphoteric character displayed by the atoms also explains satisfactorily the structures of other silicates like SiP_2O_7 (Bissert & Liebau, 1969) and $\text{Ce}_{64}\text{Si}_4[\text{Si}_{56}\text{O}_{24}\text{N}_{128}]$ (Köllisch & Schnick, 1999). Thus a new concept is required and, although slow to gain acceptance (as is often the case when completely new thinking is required), our approach satisfies this need as is demonstrated by the analysis of values of I listed in Table 1.

3. Stability enhancement ratio, S

Comparison of the values of I found in columns 2 and 4 of Table 1 evidence that in all cases the ionic strength for the classical formula (column 2) is always lower than values calculated for the pseudo-formulae listed in column 4. Below the pseudo-formula, we have quoted the values of what we define in equation (3) as the stability enhancement ratio, S , brought about once EZKC has been applied. This ratio is an indicator of the stability gained with the charge rearrangement in the Zintl polyanion. The values range from $S = 1.19$ for the

Table 1

Calculation of the ionic strength for 25 silicates ranging from simple disilicates to the more complex tectosilicates.

The lattice energy, U_{POT} , given by $A(2I/V)^{1/3}$ [equation (1)] is directly proportional to $I^{4/3}/V^{1/3}$. Since the volume, V_m , of the crystal lattice does not vary when the EZKC is applied, we need only study the variation of $I^{4/3}$ or in its simplest form only the variation in I itself. An increase in the ionic strength I implies a higher U_{POT} and hence an increased thermodynamic stability in the pseudo-lattice generated by application of the EZKC.

Compounds	$I(\text{Silicate}) = I(\text{Classical formula})$	$S = I(\text{Pseudo-formula})/I(\text{Classical formula})$	$I(\text{Pseudo-formula})$
Disilicates			
$\text{K}_6[\text{Si}_2\text{O}_7]$	$\frac{1}{2}[6 \times 1^2 + 2 \times 4^2 + 7 \times (-2^2)]$ = 33	$\Psi\text{-Cl}_2\text{O}_7$ $S = 1.91$	$\frac{1}{2}[2 \times 7^2 + 7 \times (-2^2)]$ = 63
$\text{BaBe}_2[\text{Si}_2\text{O}_7]$	$\frac{1}{2}[1 \times 2^2 + 2 \times 2^2 + 2 \times 4^2 + 7 \times (-2^2)] = 36$	$\Psi\text{-Cl}_2\text{O}_7$ $S = 1.75$	$\frac{1}{2}[2 \times 7^2 + 7 \times (-2^2)]$ = 63
$\text{Ca}_2\text{Y}_2[\text{Si}_2\text{O}_7]\text{O}_2$	$\text{Y}_2[\text{Si}_2\text{O}_7] + \{2 \times \text{CaO}\}$ $\frac{1}{2}[2 \times 3^2 + 2 \times 4^2 + 7 \times (-2^2) + \{2 \times 2^2 + 2 \times (-2)^2\}] = 47$	$\Psi\text{-Cl}_2\text{O}_7 + 2 (\text{CaO})$ $S = 1.51$	$\frac{1}{2}[2 \times 7^2 + 7 \times (-2^2) + \{2 \times 2^2 + 2 \times (-2)^2\}] = 71$
Unbranched trisilicates			
$\text{Y}_3[\text{Si}_3\text{O}_{10}]$	$\frac{1}{2}[3 \times 3^2 + 3 \times 4^2 + 10 \times (-2^2)]$ = 57.5	$\Psi\text{-Cl}_3\text{O}_{10}$ $S = 1.51$	$\frac{1}{2}[2 \times 6^2 + 7^2 + 10 \times (-2^2)]$ = 87
Unbranched tetrasilicates			
$\text{Na}_4\text{Sc}_2[\text{Si}_4\text{O}_{13}]$	$\frac{1}{2}[4 \times 1^2 + 2 \times 3^2 + 4 \times 4^2 + 13 \times (-2^2)] = 69$	$\Psi\text{-S}_2\text{Cl}_2\text{O}_{13}$ $S = 1.61$	$\frac{1}{2}[2 \times 6^2 + 2 \times 7^2 + 13 \times (-2^2)]$ = 111
$\text{Rb}_2\text{Si}[\text{P}_4\text{O}_{13}]$	$\frac{1}{2}[2 \times 1^2 + 1 \times 4^2 + 4 \times 5^2 + 13 \times (-2^2)] = 85$	$\Psi\text{-S}_2\text{Cl}_2\text{O}_{13}$ $S = 1.31$	$\frac{1}{2}[2 \times 6^2 + 2 \times 7^2 + 13 \times (-2^2)]$ = 111
Single-ring silicates			
$\text{Ca}_3\text{Y}_2[\text{Si}_3\text{O}_9]_2$	$\frac{1}{2}[3 \times 2^2 + 2 \times 3^2 + 6 \times 4^2 + 18 \times (-2^2)] = 99$	$\Psi\text{-[Si}_3\text{O}_9]_2$ $S = 1.45$	$\frac{1}{2}[6 \times 6^2 + 18 \times (-2^2)] = 144$
$\text{Na}_6\text{Sr}_3[\text{Si}_6\text{O}_{18}]$	$\frac{1}{2}[6 \times 1^2 + 3 \times 2^2 + 6 \times 4^2 + 18 \times (-2^2)] = 93$	$\Psi\text{-S}_6\text{O}_{18}$ $S = 1.55$	$\frac{1}{2}[6 \times 6^2 + 18 \times (-2^2)] = 144$
$\text{Na}_6\text{Si}_3[\text{Si}_9\text{O}_{27}]$	$\frac{1}{2}[6 \times 1^2 + 3 \times 4^2 + 9 \times 4^2 + 27 \times (-2^2)] = 153$	$\Psi\text{-S}_9\text{O}_{27}$ $S = 1.41$	$\frac{1}{2}[9 \times 6^2 + 27 \times (-2^2)] = 216$
Double-ring silicates			
$\text{Na}_3\text{Y}[\text{Si}_6\text{O}_{15}]$	$\frac{1}{2}[3 \times 1^2 + 1 \times 3^2 + 6 \times 4^2 + 15 \times (-2^2)] = 84$	$\Psi\text{-P}_6\text{O}_{15}$ $S = 1.25$	$\frac{1}{2}[6 \times 5^2 + 15 \times (-2^2)] = 105$
Single-chain silicates			
$\text{Ba}_2[\text{Si}_2\text{O}_6]$	$\frac{1}{2}[2 \times 2^2 + 2 \times 4^2 + 6 \times (-2^2)]$ = 32	$\Psi\text{-S}_2\text{O}_6$ $S = 1.5$	$\frac{1}{2}[2 \times 6^2 + 6 \times (-2^2)] = 48$
$\text{Ca}_3[\text{Si}_3\text{O}_9]$	$\frac{1}{2}[3 \times 2^2 + 3 \times 4^2 + 9 \times (-2^2)]$ = 48	$\Psi\text{-S}_3\text{O}_9$ $S = 1.5$	$\frac{1}{2}[3 \times 6^2 + 9 \times (-2^2)] = 72$
Open-branched single-chain silicates			
Astrophyllite $\text{NaK}_2\text{Mg}_2\text{Fe}_5\text{Ti}_2[\text{Si}_4\text{O}_{12}]_2$	$\frac{1}{2}[1 \times 1^2 + 2 \times 1^2 + 2 \times 2^2 + 5 \times 2^2 + 2 \times 4^2 + 8 \times 4^2 + 24 \times (-2^2)]$ = 143.5	$\Psi\text{-(P}_2\text{Cl}_2\text{O}_{12})_2$ $S = 1.37$	$\frac{1}{2}[4 \times 5^2 + 4 \times 7^2 + 24 \times (-2^2)]$ = 196
Loop-branched single-chain silicates			
$\text{Li}_2\text{Mg}_2[\text{Si}_4\text{O}_{11}]$	$\frac{1}{2}[2 \times 1^2 + 2 \times 2^2 + 4 \times 4^2 + 11 \times (-2^2)] = 59$	$\Psi\text{-P}_2\text{S}_2\text{O}_{11}$ $S = 1.41$	$\frac{1}{2}[2 \times 5^2 + 2 \times 6^2 + 11 \times (-2^2)]$ = 83
Liebauite $\text{Ca}_6\text{Cu}_{10}[\text{Si}_{18}\text{O}_{52}]$	$\frac{1}{2}[6 \times 2^2 + 10 \times 2^2 + 18 \times 4^2 + 52 \times (-2^2)] = 280$	$\Psi\text{-P}_4\text{S}_{14}\text{O}_{52}$ $S = 1.45$	$\frac{1}{2}[4 \times 5^2 + 14 \times 6^2 + 52 \times (-2^2)]$ = 406
Unbranched double-chain silicates			
Sillimanite $\text{Al}_2[\text{Al}_2\text{Si}_2\text{O}_{10}]$	$\frac{1}{2}[4 \times 3^2 + 2 \times 4^2 + 10 \times (-2^2)]$ = 54	$\Psi\text{-P}_4\text{O}_{10}$ $S = 1.30$	$\frac{1}{2}[4 \times 5^2 + 10 \times (-2^2)] = 70$
Epididymite $\text{Na}_2\text{Be}_2[\text{Si}_6\text{O}_{15}] \times \text{H}_2\text{O}$	$\frac{1}{2}[2 \times 1^2 + 2 \times 2^2 + 6 \times 4^2 + 15 \times (-2^2)] = 83$	$\Psi\text{-P}_6\text{O}_{15}$ $S = 1.27$	$\frac{1}{2}[6 \times 5^2 + 15 \times (-2^2)] = 105$
Loop-branched double-chain silicates			
Tinaksite $\text{HNaK}_2\text{Ca}_2\text{Ti}[\text{Si}_7\text{O}_{19}]\text{O}$	$\text{K}_2\text{Ca}_2\text{Ti}[\text{Si}_7\text{O}_{19}] + \{\text{HNaO}\}$ $\frac{1}{2}[2 \times 1^2 + 2 \times 2^2 + 1 \times 4^2 + 7 \times 4^2 + 19 \times (-2)^2 + \{1 \times 1^2 + 1 \times 1^2 + 1 \times (-2)^2\}] = 110$	$\Psi\text{-P}_4\text{S}_3\text{O}_{19} + \{\text{HNaO}\}$ $S = 1.32$	$\frac{1}{2}[4 \times 5^2 + 3 \times 6^2 + 19 \times (-2)^2 + \{1 \times 1^2 + 1 \times 1^2 + 1 \times (-2)^2\}]$ = 145
Unbranched quintuple-chain silicates			
$\text{Ba}_6[\text{Si}_{10}\text{O}_{26}]$	$\frac{1}{2}[6 \times 2^2 + 10 \times 4^2 + 26 \times (-2^2)]$ = 72	$\Psi\text{-P}_8\text{S}_2\text{O}_{26}$ $S = 1.31$	$\frac{1}{2}[8 \times 5^2 + 2 \times 6^2 + 26 \times (-2^2)]$ = 188
Layer silicates			
$\text{Ba}[\text{Si}_2\text{O}_5]$	$\frac{1}{2}[1 \times 2^2 + 2 \times 4^2 + 5 \times (-2^2)]$ = 28	$\Psi\text{-P}_2\text{O}_5$ $S = 1.25$	$\frac{1}{2}[2 \times 5^2 + 5 \times (-2^2)] = 35$
Muscovite $\text{KAl}_3[\text{AlSi}_3\text{O}_{10}](\text{OH})_2$	$\text{KMg}_2[\text{AlSi}_3\text{O}_{10}] + \{(\text{OH})_2 + 2\text{e}\}$ $\frac{1}{2}[1 \times 1^2 + 2 \times 2^2 + 1 \times 3^2 + 3 \times 4^2 + 10 \times (-2)^2 + \{2 \times (-1)^2 + 2 \times (-1)^2\}]$ = 56	$\Psi\text{-P}_4\text{O}_{10} + \{(\text{OH})_2 + 2\text{e}\}$ $S = 1.29$	$\frac{1}{2}[4 \times 5^2 + 10 \times (-2)^2 + \{2 \times (-1)^2 + 2 \times (-1)^2\}] = 72$
Kaolinite $\text{Al}_2\text{Mg}_3[\text{Si}_4\text{O}_{10}](\text{OH})_8$	$\text{Na}_2[\text{Si}_2\text{O}_5] + \{\text{Mg}_2 + (\text{OH})_4\}$ $\frac{1}{2}[2 \times 1^2 + 2 \times 4^2 + 5 \times (-2)^2 + \{2 \times 2^2 + 4 \times (-1)^2\}] = 33$	$\Psi\text{-P}_2\text{O}_5 + \{\text{Mg}_2 + (\text{OH})_4\}$ $S = 1.24$	$\frac{1}{2}[2 \times 5^2 + 5 \times (-2)^2 + \{2 \times 2^2 + 4 \times (-1)^2\}] = 41$
Loop-branched double-layer silicates			
$\text{Cs}_3\text{Sc}[\text{Si}_8\text{O}_{19}]$	$\frac{1}{2}[3 \times 1^2 + 1 \times 3^2 + 8 \times 4^2 + 19 \times (-2^2)] = 108$	$\Psi\text{-Si}_2\text{P}_6\text{O}_{19}$ $S = 1.19$	$\frac{1}{2}[2 \times 4^2 + 6 \times 5 + 19 \times (-2^2)]$ = 129

Table 1 (continued)

Compounds	$I(\text{Silicate}) = I(\text{Classical formula})$	$S = I(\text{Pseudo-formula})/I(\text{Classical formula})$	$I(\text{Pseudo-formula})$
Tectosilicates			
Stuffed quartz			
Mg[Al ₂ Si ₃ O ₁₀]	$\frac{1}{2}[1 \times 2^2 + 2 \times 3^2 + 3 \times 4^2 + 10 \times (-2^2)] = 35$	$\Psi\text{-Si}_5\text{O}_{10}$ $S = 1.71$	$\frac{1}{2}[5 \times 4^2 + 10 \times (-2^2)] = 60$
Ce ₆₄ Si ₄ [Si ₅₆ O ₂₄ N ₁₂₈]	$\frac{1}{2}[32 \times 2^2 + 4 \times 4^2 + 56 \times 4^2 + 24 \times (-2^2) + 128 \times (-2^2)] = 848$	$\Psi\text{-P}_{32}\text{S}_{24}\text{O}_{152}$ $S = 1.34$	$\frac{1}{2}[32 \times 5^2 + 24 \times 6^2 + 152 \times (-2^2)] = 1136$

pair Cs₃Sc[Si₈O₁₉]/Ψ-Si₂P₆O₁₉ to $S = 1.91$ for the pair K₆[Si₂O₇]/Ψ-Cl₂O₇. For most compounds in Table 1 S ranges from 1.25 to 1.60. In (NH₄)₂Ge₇O₁₅ the value of S is 1.21.

The last compound in Table 1, the oxonitridosilicate Ce₆₄Si₆₀O₂₄N₁₂₈, needs further explanation. The real formula is quoted as the top entry and the charges are balanced as follows:

$$64 \text{ Ce}^{3+} + 60 \text{ Si}^{4+} = 432 \text{ positive charges.}$$

$$24 \text{ O}^{2-} + 128 \text{ N}^{3-} = 432 \text{ negative charges.}$$

Since all the other compounds in Table 1 are oxides (or oxide hydrates) the compound has been reformulated as an oxide by assuming an internal electron transfer to convert the 128 N atoms per cell into Ψ-O. This can be achieved by transferring 2 e[−] of each Ce atom to the 128 N atoms, the new formula being (Ce⁺)₆₄Si₄[Si₅₆O₂₄Ψ-O₁₂₈]. Since 64 Ce⁺ are equivalent to 32 Ce²⁺ cations the compound could also be reformulated as Ce₃₂Si₄[Si₅₆O₂₄Ψ-O₁₂₈] as is quoted as the bottom entry in Table 1.

The compounds Ca₂Y₂[Si₂O₇]₂ ≡ Y₂[Si₂O₇] + {2CaO}, tinaksite ≡ K₂Ca₂Ti[Si₇O₁₉] + {HNaO}, muscovite ≡ KMg₂[AlSi₃O₁₀] + {(OH)₂ + 2 e} and kaolinite ≡ Na₂[Si₂O₅] + {Mg₂ + (OH)₄} need additional explanation. These compounds possess atoms that are not involved in the charge transfer of the Zintl polyanions, and therefore these ‘non-Zintl’ atoms are inserted in brackets and are added to the moiety that contains the potential Zintl anion. The calculation of I is carried out for both moieties, as is quoted in the corresponding entries in Table 1.

All values of the stability enhancement ratio $S = (\Psi\text{-}I)/I$ of equation (3) indicate that the ionic strength of the Zintl polyanion is higher than that of the original compound. This result agrees with the first finding in (NH₄)₂Ge[Ge₆O₁₅] (Vegas & Jenkins, 2017) and gives support to the idea that the EZKC – as used so far to explain other similar structures – is reinforced by the application of the thermodynamically related ionic strength, I .

4. Concluding remarks

As discussed above, this paper illustrates the fact that the classical description of inorganic structures in terms of cation-centred anionic polyhedra is now outdated, since it provides poor insight into the chemical interactions occurring in the crystal.

The joint application of the EZKC and the ionic strength concept not only accounts for the structural changes occurring

in the [TO₄] networks, but it also seems to be the driving force that compels the structure towards its greatest thermodynamic stability as predicted from the respective I values (strictly speaking, $I^{4/3}$ values), representing a new era in the way of understanding the role that atomic species can play. A much fuller description of these ideas is due to appear in a text currently in preparation (Vegas, 2017).

APPENDIX A

Examination of the increase in lattice energy (and hence of stability) to support the ‘higher stability hypothesis’ arising when the EZKC is considered

Firstly we consider the lattice energies.

Consider K₆[Si₂O₇], whose crystal structure volume is given by

$$V_m = V_{\text{cell}}/Z = 0.51145/Z = 0.51145/2 = 0.2557 \text{ nm}^3. \quad (4)$$

The charge balance is

$$(6\text{K}^+) + (2\text{Si}^{4+}) + 7(\text{O}^{2-}) = 14 + +14 - \quad (5)$$

and the ionic strength, $I(\text{K}_6\text{Si}_2\text{O}_7)$

$$I(\text{K}_6\text{Si}_2\text{O}_7) = \frac{1}{2}[6(1^2) + 2(4^2) + 7(-2^2)] = \frac{1}{2}[66] = 33. \quad (6)$$

Under the EZKC, K₆[Si₂O₇] transforms into Cl₂O₇. In Cl₂O₇ the charge balance is

$$(2\text{Cl}^{7+}) + (7\text{O}^{2-}) = 14 + +14 - . \quad (7)$$

Given this and the ionic strength of Cl₂O₇, $I(\text{Cl}_2\text{O}_7)$

$$I(\text{Cl}_2\text{O}_7) = \frac{1}{2}[2(7^2) + 7(-2^2)] = \frac{1}{2}[126] = 63 \quad (8)$$

the pseudo-lattice energy calculated from equation (1) will be

$$\begin{aligned} U_{\text{POT}}(\text{pseudo-formula}) &= U_{\text{POT}}(\text{pseudo Cl}_2\text{O}_7) = AI(2I/V)^{1/3} \\ &= 121.4(63)[(2)(63)/(0.2557)]^{1/3} \\ &= 60409 \text{ kJ mol}^{-1}. \end{aligned} \quad (9)$$

Cl₂O₇ would, in its normal form, have a lattice energy

$$\begin{aligned} U_{\text{POT}}(\text{Cl}_2\text{O}_7) &= 121.4(63)[(2)(63)/(0.1279)]^{1/3} \\ &= 76101 \text{ kJ mol}^{-1}. \end{aligned} \quad (10)$$

The reason for this large lattice energy is, likely, the very small value of the enthalpy of formation of solid Cl₂O₇, $\Delta_f H^\circ(\text{Cl}_2\text{O}_{7,\text{s}})$, when compared with that of the liquid and gaseous forms: $\Delta_f H^\circ(\text{Cl}_2\text{O}_{7,\text{l}}) = 238.1 \text{ kJ mol}^{-1}$ (NIST, <http://webbook.nist.gov/chemistry/>) and $\Delta_f H^\circ(\text{Cl}_2\text{O}_{7,\text{g}}) =$

272.0 kJ mol⁻¹ (NIST). The ‘experimental’ result from the Born–Haber cycle, obtained using the thermochemical cycle which involved the target compound K₆{Si₂O₇}, the component gaseous ions, K⁺(g), Si⁴⁺(g) and O²⁻(g), and the elements in their standard states, K(s), Si(s) and O₂(g), yields the formula

$$\begin{aligned}
 U_{\text{POT}}(\text{experimental}) &= U_{\text{POT}}(\text{K}_6\{\text{Si}_2\text{O}_7\}) \\
 &= 6\Delta_f H^\circ(\text{K}^+, \text{g}) + 2\Delta_f H^\circ(\text{Si}^{4+}, \text{g}) \\
 &\quad + 7\Delta_f H^\circ(\text{O}^{2-}, \text{g}) - \Delta_f H^\circ(\text{K}_2\text{Si}_2\text{O}_7, \text{s}) \\
 &\quad + (15/2)RT.
 \end{aligned}
 \tag{11}$$

The (15/2)RT term arises in order to convert the lattice *energy* into a lattice *enthalpy* (see Jenkins, 2005). An immediate problem arises because there are no data in the literature for $\Delta_f H^\circ(\text{K}_2\text{Si}_2\text{O}_7, \text{s})$. However, it can be observed that the enthalpy of formation of compounds having just one additional O atom in their formula has comparable enthalpies of formation to the compounds having one less O atom. A couple of examples showing this feature are given below.

$\Delta_f H^\circ(\text{KIO}_3, \text{s}) = -503.3 \text{ kJ mol}^{-1}$ (Wu *et al.*, 1963) and $\Delta_f H^\circ(\text{KIO}_4, \text{s}) = -472.0 \text{ kJ mol}^{-1}$ (Shidlovskii & Voskresenskii, 1965); $\Delta_f H^\circ(\text{Na}_2\text{SeO}_3, \text{s}) = -963.6 \text{ kJ mol}^{-1}$ (Klushina & Selinova, 1960) and $\Delta_f H^\circ(\text{Na}_2\text{SeO}_4, \text{s}) = -1093.4 \text{ kJ mol}^{-1}$ (Selinova & Sazykina, 1964); $-1093.2 \text{ kJ mol}^{-1}$ (Karapet'yants & Karapet'yants, 1970); thus the standard enthalpy of formation of K₆Si₂O₇ should be comparable with the standard enthalpy of formation of K₆Si₂O₅ which has the value $-2483.2 \text{ kJ mol}^{-1}$ (Matveev *et al.*, 1965). This is used in the above formula together with other data for $\Delta_f H^\circ(\text{K}^+, \text{g})$ and $\Delta_f H^\circ(\text{Si}^{4+}, \text{g})$ from the NIST database and data for $\Delta_f H^\circ(\text{O}^{2-}, \text{g}) = 838 \text{ kJ mol}^{-1}$ from Glasser & Jenkins (2000).

Accordingly

$$\begin{aligned}
 U_{\text{POT}}(\text{experimental}) &= U_{\text{POT}}(\text{K}_6\{\text{Si}_2\text{O}_7\}) \\
 &= 6(514.3) + 2(10428.5) + 7(838) \\
 &\quad - (-2483.2) + (18.6) \\
 &= 32311 \text{ kJ mol}^{-1}.
 \end{aligned}
 \tag{12}$$

One of the referees for this paper said that to believe our contention he/she would need to see that: ‘for a certain compound the classical formula gives $U_{\text{POT}} = X$, the pseudo-formula gives $U_{\text{POT}} = 1.5X$ and the experimental value is $1.4(2)X$; this will then prove the issue’.

From the above $U_{\text{POT}}(\text{classical}) = 25508 \text{ kJ mol}^{-1}$ from equation (1), so $X = 25508$, $U_{\text{POT}}(\text{pseudo-formula})$ from equation (1) = 60409 = 2.36 X and finally $U_{\text{POT}}(\text{experimental}) = 32311 \text{ kJ mol}^{-1} = 1.27X$ which matches our theory:

$$U_{\text{POT}}(\text{classical}) < U_{\text{POT}}(\text{experimental}) < U_{\text{POT}}(\text{pseudo-formula}).
 \tag{13}$$

In this example we have chosen the compound in Table 1 that has the smallest difference in ionic strength between the classical and pseudo structures and the assumption is that materials with a larger difference are more likely to obey relationship (13).

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