



# The Equivalence of the Charge Interaction Sum and the Ionic Strength

Leslie Glasser

Curtin Institute for Computation, Discipline of Chemistry, Curtin University, GPO Box U1987, Perth, WA 6845, Australia

## ABSTRACT

The electrostatic interaction among a neutral and finite set of point charges is based on the sum of their *pairwise* charge products,  $z_i z_j$ , yet many analyses yield terms which simply contain a sum of the squares of the *separate* charges, corresponding to the ionic strength,  $\frac{1}{2} \sum m_i z_i^2$ .

This submission collects together a number of important instances of this result and explains their equivalence. In effect, the ionic strength-like terms provide conveniently calculated coulomb sums for systems with finite collections of charges.

## 1. Introduction

It has often been observed, but seldom noted and perhaps never queried that, while the electrostatic interaction among a neutral finite set of point charges is based on the sum of their *pairwise* charge products,  $z_i z_j$ , based on Coulomb's Law, yet analysis yields terms (such as the ionic strength,  $\frac{1}{2} \sum m_i z_i^2$ ) which are simply a sum of the squares of the *separate* charges. It is the purpose of this brief contribution to collect together a number of important instances of this result and to explain its occurrence, independent of the mathematical complexities in which it may be cloaked in particular instances of its appearance. A general review of ionic strength applications was published in 2004. [1-2]

Perhaps the earliest well-known appearance of such a sum is in Ewald's accelerated convergence method [3] (1921) for calculating lattice energies. Three terms appear in the Ewald sum: one arises as a smoothed sum of the short-range interactions of the contents of the origin unit cell with the direct lattice, a second from a corresponding reciprocal lattice sum, while the third arises from the charge interactions within the origin unit cell itself – this has the form  $\sum z_i^2$ , where the  $z$ 's represent the charges of the  $n$  species within the unit cell.

Ionic strength,  $I$ , was introduced (also in 1921) by Lewis and Randall [4] as a purely empirical quantity which correlated (surprisingly successfully) the thermodynamic activities of different strong electrolytes in dilute solution; in their words "In dilute solutions the activity coefficient of a given strong electrolyte is the same in all solutions of the same ionic strength". They defined ionic strength on a molality basis as:

$$I = 1/2 \sum m_i z_i^2 \quad (1)$$

where  $m_i$  represents the molality of ions of type  $i$  with integer charge,  $z_i$ . The factor  $\frac{1}{2}$  is introduced in order that the ionic strength of a 1:1 electrolyte (e.g., NaCl) equals its molality. In practice, it is more common to use a related term,  $\Gamma_c$ , also called ionic concentration, where concentra-

tion,  $c$ , replaces molality; the two expressions are proportional to one another in sufficiently dilute solution: [5]

$$\Gamma_c = 1/2 \sum_i c_i z_i^2 \quad (2)$$

Lewis and Randall refer admiringly to earlier work by Ghosh [6] on strong electrolytes which uses the same charge-squared factor as appears in their ionic strength term.

A related term,  $\sum n_i z_i^2$ , appeared independently in Debye and Hückel's (1923) development of a theory of electrolytes [7] where  $n_i$  represents the number of ions per  $\text{cm}^3$ . Later, in 1924, Debye [8] acknowledged the prior definition by Lewis and Randall of the ionic strength, and the afore-mentioned proportionality of these two quantities to one another in dilute solution. He then proceeded to use ionic strength in his treatment of ionic activity.

The Madelung energies of ionic solids relate to their geometry and electrostatic interactions, [9] with the electrostatic term consisting of a sum of pairwise ion charge products. In 1955 Templeton [10] introduced a related factor,  $S$  ( $= 2I$ ), as a normalizing factor for Madelung energies but this seems to have been applied [11] only occasionally.

In 1995, Glasser [12] noted the appearance of a similar ionic strength-like term (now including the factor  $\frac{1}{2}$ ) in the Kapustinskii equation, [13] an equation which provides good estimates of the lattice energies,  $U$ , of binary ionic crystalline solids. By detailed calculation, he established that the sum of the *pairwise charge interactions* was equal to the *sum of the squares* of the individual charges in a unit cell. On the basis of this recognition, it proved possible to generalize the Kapustinskii equation beyond its purely binary form to predict the lattice energies of complex ionic crystals. The generalized equation has the form:

$$U = - \frac{A}{\langle r \rangle} \left( 1 - \frac{\rho}{\langle r \rangle} \right) I \quad (3a)$$

E-mail address: [l.glasser@curtin.edu.au](mailto:l.glasser@curtin.edu.au)

<https://doi.org/10.1016/j.ctta.2022.100059>

Received 9 March 2022; Accepted 7 April 2022

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where $I$	=	$\frac{1}{2} \sum n_i z_i^2$
$n_i$	=	number of ions of species $i$ in the formula unit
$\langle r \rangle$	=	weighted mean cation-anion Goldschmidt radius sum
$A$	=	conversion factor between charge and energy units; $121.4 \text{ kJ mol}^{-1} \text{ nm}$
$\rho / \langle r \rangle$	=	a Born-Mayer correction term for ion repulsion, where $\rho$ is commonly assigned the value $0.0345 \text{ nm}$ .

The mean radius is a rather nebulous quantity but can be substituted by the cube-root of the formula unit volume,  $V_m^{1/3}$ , having the necessary dimension of length. Actual use of the revised equation [14] is most conveniently in terms of a linear fit to data sets, with fitted constants  $\alpha$  and  $\beta$

$$U = 2I \left( \frac{\alpha}{V^{1/3}} + \beta \right) \quad (3b)$$

Such a relation between the continuum approximation of the Debye-Hückel theory and the necessarily discrete ion treatment of the Kapustinskii equation was earlier foreshadowed by Fuoss and Accascina [15] in their remarks on the likely form of the radial distribution function as one proceeds from dilute electrolyte solutions to fused salts to ionic crystals.

Appearing in these various situations, ionic strength (in its various guises) seems simply to be a correlation factor of somewhat obscure origin. This does not mean, however, that the ionic strength concept is underplayed; it is of importance in all electrolyte experimentation where, for example, in order to reduce extraneous electrolyte concentration effects, solutions are generally made up to constant ionic strength by adding inactive strong electrolyte to the active ion constituents, and it remains as an essential term in the important Debye-Hückel theory of electrolytes.

We here provide a more fundamental interpretation of this quantity.

### 1.1. Analysis

For an arbitrary but finite neutral system of  $n$  charges:

$$\sum_{i=1}^n z_i = 0 \quad (4)$$

then:

$$\sum_{i=1}^n z_i \cdot \sum_{j=1}^n z_j = 0 \quad (5)$$

Expanding this product, and separating it into diagonal and off-diagonal elements:

$$\sum_i^n z_i \cdot \sum_j^n z_j = \sum_{i=1}^n z_i^2 + \sum_i^n \sum_{j \neq i}^n z_i z_j = 0 \quad (6)$$

thus, rearranging:

$$\sum_i^n \sum_{j \neq i}^n z_i z_j = - \sum_i^n z_i^2 \quad (7)$$

By symmetry, since  $z_i z_j = z_j z_i$ , the above equation becomes:

$$\sum_i^n \sum_{j>i}^n z_i z_j = 1/2 \sum_i^n \sum_{j \neq i}^n z_i z_j = -1/2 \sum_i^n z_i^2 \quad (8)$$

We may now classify the ions into  $t$  types, with  $n_k$  ions of each type,  $k$ , such that:

$$n = \sum_{k=1}^t n_k \quad (9)$$

then:

$$\sum_i^n \sum_{j>i}^n z_i z_j = -1/2 \sum_k^t n_k z_k^2 \quad (10)$$

or, briefly:

$$\sum_{j>i} z_i z_j = -1/2 \sum_k n_k z_k^2 \quad (11)$$

The system of  $n$  charges considered here might consist of: the charges contained in a kilogram of solvent (so that the last term corresponds to the ionic strength,  $I$ ); or the charges in a liter of solution (leading to the ionic concentration,  $\Gamma_c$ ); or the charges in a formula unit of a solid (leading to the generalised Kapustinskii term,  $I$ ).

Thus, the ionic strength, and its related terms, simply provide conveniently-calculated sums of systems of charges. This accords with the only specific comment, [16] rather than “hand-waving” generalisations, that I have found on the nature of ionic strength.

### Declaration of Competing Interest

There are no conflicts of interest.

### Acknowledgements

I wish to acknowledge, with appreciation, that the form of the derivation of Eq. (11) given above was supplied to me by an anonymous referee in support of my calculations and intuitive identification where Eq. (11) was developed [12] but its proof was not provided, nor were its implications explored.

### References

- [1] M.E. Sastre de Vicente, The Concept of Ionic Strength Eighty Years after Its Introduction in Chemistry, *J. Chem. Educ.* 81 (2004) 750–753.
- [2] L. Glasser, Reaction to “the concept of ionic strength eighty years after its introduction in chemistry”, *J. Chem. Educ.* 82 (2005) 212.
- [3] B.P. Van Eijck, J. Kroon, Coulomb Energy of Polar Crystals, *J. Phys. Chem. B* 101 (1997) 1096–1100.
- [4] G.N. Lewis, M. Randall, The activity coefficient of strong electrolytes.1, *J. Amer. Chem. Soc.* 43 (1921) 1112–1154.
- [5] T. Solomon, The Definition and Unit of Ionic Strength, *J. Chem. Educ.* 78 (2001) 1691.
- [6] J. Ghosh, The abnormality of strong electrolytes: I-IV, *J. Chem. Soc.* 113 (1918) 449–458 627-638, 707-715, 790-788.
- [7] P. Debye, E. Hückel, Zur Theorie der Elektrolyte, *Phys. Zeits.* 24 (1923) 185–206.
- [8] P. Debye, Osmotic constitutive equation and activity of diluted strong electrolytes, *Phys. Zeits.* 25 (1924) 97–107.
- [9] L. Glasser, Solid-State Energetics and Electrostatics: MADELUNG Constants and Madelung Energies, *Inorg. Chem.* 51 (2012) 2420–2424.
- [10] D.H. Templeton, Prediction of Madelung Constants, *J. Chem. Phys.* 23 (1955) 1826–1829.
- [11] J.B. Torrance, P. Lacorre, C. Asavaroengchai, R.M. Metzger, Why are some oxides metallic, while most are insulating? *Physica C* 182 (1991) 351–364.
- [12] L. Glasser, Lattice Energies of Crystals with Multiple Ions - a Generalised Kapustinskii Equation, *Inorg. Chem.* 34 (1995) 4935–4936.
- [13] A.F. Kapustinskii, Lattice energy of ionic crystals, *Quart. Rev. Chem. Soc.* 10 (1956) 283–294.
- [14] H.D.B. Jenkins, H.K. Roobottom, J. Passmore, L. Glasser, Relationships among Ionic Lattice Energies, Molecular (Formula Unit) Volumes, and Thermochemical Radii, *Inorg. Chem.* 38 (1999) 3609–3620.
- [15] R.M. Fuoss, F. Accascina, in: *Electrolytic Conductance*, 106, Interscience, New York, 1959, pp. 101–102.
- [16] S. Glasstone, in: *An Introduction to Electrochemistry*, van Nostrand, Princeton, 1942, p. 140.