

Charge Distributions in Polyatomic Ions

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The determination of charge distributions in polyatomic ions through both energetic and quantum mechanical (CNDO/2) methods is discussed. Results from both methods are shown to be in good agreement.

In an earlier paper [1], a method for evaluating the charge distribution in polyatomic ions in inorganic salts was presented. The purpose of this note is to consider an extension of that work, and to give an indication of the precision of the method through a comparison with quantum mechanical calculations.

In a study of alkali-metal cyanides [1], the various factors involved in bringing two polymorphs on to a common internal energy basis were discussed. It seems possible to relax these requirements slightly, and yet retain a reasonably precise result.

Early calculations of the cohesive energies of inorganic salts containing polyatomic ions treated the polyatomic ion as a point charge at the centre of gravity of the ion-group (the point-charge model). More refined calculations consider the distribution of the total ionic charge among the atomic species present in the ion (the distributed-charge model).

In the cyanides, the decrease in cohesive energy for the distributed-charge model is 5–10% of that found for the point-charge model. The change occurs mainly in the electrostatic part of the cohesive energy. From those and other (including the present) studies, it seems that provided $\sum |z_i| \simeq Z$, where z_i are the charges on the atoms in a polyatomic ion of total charge Z , the greater the spread of the charge, the lower is the numerical value of the electrostatic energy. This takes place through a decrease in the value of the Madelung constant. If, however, $\sum |z_i| > Z$, while $|\sum z_i| = Z$ (necessarily), then wider variations in the Madelung term may be obtained.

Calculations have been carried out on the calcite (c1), aragonite (c2) and vaterite (c3) forms of calcium carbonate. The Madelung terms $A(L)/L$, where L is the shortest interatomic distance in the crystal, have been evaluated by the Bertaut-Templeton expressions [2–4], as a function of z_o , the charge, including sign, on the oxygen atom; the charge z_c on the carbon atom is $(-2 - 3z_o)$. A linear distribution function was employed together with a summation limit of about 1.2 reciprocal space units. The results are illustrated by Fig. 1. The curves are approximately parabolic and may be represented by the similar Eqs. (1)–(3),

Table 1. Energy parameters and charge distributions for polymorphs of calcium carbonate

	$q/L, \text{\AA}^{-1}$	$-U, \text{kcal mol}^{-1}$	$-U', \text{kcal mol}^{-1}$	$A(L)/L, \text{\AA}^{-1}$	$Z_0, e. \text{ units}$
Calcite (c1)	0.10	640	589	1.97	-0.763
Aragonite (c2)	0.11	624	574	1.93	-0.755
Vaterite (c3)	0.11 ^a	642	591	2.00	-0.794
					Mean $z_0 = -0.77$

^a Estimated value.

with average r.m.s. errors ϵ_i ($i = 1, 2, 3$):

$$c1 : A(L)/L = 2.1422 + 4.5391 z_0 + 5.6546 z_0^2 \quad (1)$$

$$\epsilon_1 = 3.7 \times 10^{-3}$$

$$c2 : A(L)/L = 2.1068 + 4.3201 z_0 + 5.4193 z_0^2 \quad (2)$$

$$\epsilon_2 = 6.3 \times 10^{-3}$$

$$c3 : A(L)/L = 2.1679 + 4.6551 z_0 + 5.5989 z_0^2 \quad (3)$$

$$\epsilon_3 = 3.1 \times 10^{-3}$$

Crystal cohesive energies have been calculated from Eqs. (4) and (5), where the terms used have their usual significances.

$$U(L) = - (A(L)e^2/L) \{1 - (q/L)\} , \quad (4)$$

$$(q/L) = (A(L)e^2/L) / \{ (9V/\beta) + (2A(L)e^2/L) \} . \quad (5)$$

Crystal data were taken from Wyckoff [5] and compressibilities from the International Critical Tables [6]. The point-charge model values of U are listed in Table 1. If we accept a decrease of about 8% of the cohesive energy U , as suggested by the work on the cyanides, then the energies, U' , for the distributed-

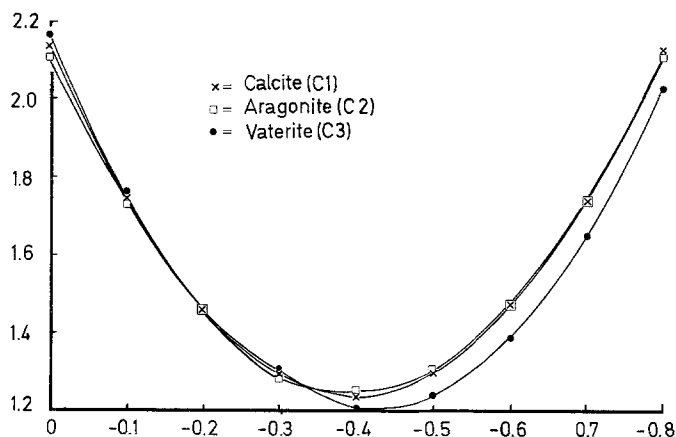


Fig. 1. Variation of the Madelung term, $A(L)/L$, with charge, z_0 , on oxygen in three polymorphs of CaCO_3

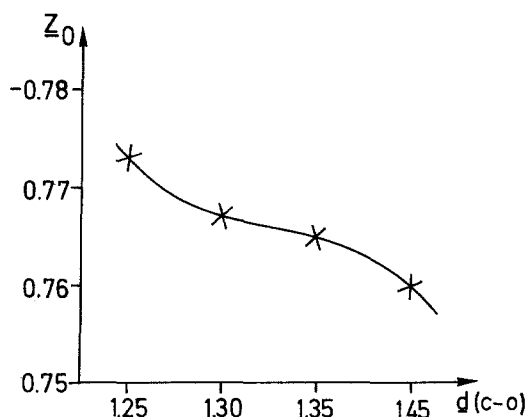


Fig. 2. Variation of z_0 with bond distance $d(\text{C-O})$ in the carbonate ion

charge model may be obtained through Eqs. (4) and (5). The appropriate Madelung terms are obtained and from Fig. 1, the corresponding values of z_0 ; all of these values are listed in the table. The alternative values for z_0 , lying between -0.03 and -0.05 electron units, are rejected as unrealistic.

Quantum mechanical calculations of the charge distribution in the carbonate ion (symmetry, $\bar{6}m2$) have been carried out by the CNDO/2 method [7, 8] as a function of the C-O distance, d . The results are illustrated in Fig. 2. For the calcium carbonate structures, d is approximately 1.26 \AA , whence z_0 is -0.771 .

The agreement between the values of z_0 obtained by these two independent procedures is very good, and leads one to place reliance upon these methods of calculating charge distributions in simple polyatomic ions.

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