The relative stability of stoichiometrically related natural and synthetic double salts

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ABSTRACT

The so-called “simple salt approximation” is used to calculate the lattice energies of double salts (compounds that contain two or more different types of ions). Enthalpies and Gibbs energies of dissolution based upon these lattice energies are then used to estimate the solubilities of hydroxyl sulfates, hydroxyl carbonates, hydroxyl nitrates, hydroxyl chlorides, and hydroxyl phosphates. Based on the solubilities, general rules are postulated for the relative stabilities of double salts that have the same cations and anions, but in different stoichiometries. These observations provide an understanding of the relative stabilities of many minerals and guidance for the design of synthetic methods, and have been used to prepare likasite [Cu₃NO₃(OH)₈·2H₂O], the zinc analog [Zn₃SO₄(OH)₈]₄ of antlerite [Cu₃SO₄(OH)₈], and Cu₃(SO₄)₃(OH)₄·4H₂O.

**Keywords:** Thermodynamics, solubility, stoichiometry, lattice energy

INTRODUCTION

Many minerals contain the same ions but in different stoichiometric ratios. Some simple examples include the copper hydroxyl carbonates, Cu₂CO₃(OH)₂ (malachite) and Cu₃(CO₃)₂(OH)₂ (azurite). The metal hydroxyl double salts, many of which are minerals, provide many examples of these stoichiometric relationships. We have previously used a simple method for the estimation of the solubilities of double salts (Yoder and Rowand 2006). Here we extend this method to provide simple rules that can be used to understand the relative stabilities of double salts that contain the same ions in different ratios. We apply these rules to the design of synthesis methods for compounds that have not been previously prepared.

The thermodynamic principles that govern the relative stabilities of simple “salts” such as FeO and Cu(OH)$_2$ are well known and can be expressed through a Born-Haber type thermodynamic cycle (e.g., Yoder and Flora 2005). The estimation of the relative stabilities of complex materials that contain more than two types of ions requires the knowledge of the lattice energy of the compound, a thermodynamic value that is difficult to approximate. Our recent approximation (Yoder and Flora 2005) allows for the estimation of the lattice energy of these complex materials. We have referred to this approximation as the simple salt method because it uses simple additivity of the lattice energies of the “component” simple salts. For example, the lattice energy of malachite [Cu₂CO₃(OH)₂] can be approximated as the sum of the lattice energies of CuCO$_3$ and Cu(OH)$_2$; that is, Cu₂CO₃(OH)₂ is treated as equivalent to CuCO$_3$ + Cu(OH)$_2$. We have shown that this approximation produces lattice energies generally within 1% of the experimental Born-Haber values (Yoder and Flora 2005). Moreover, the approximation is not limited to ionic compounds, but can be applied to compounds with considerable covalent character.

When combined with other thermodynamic data, such as enthalpies of hydration, these lattice energies can be used to estimate solubilities (Yoder and Rowand 2006), which are crucial to an understanding of the precipitation of many compounds. Compounds with polyatomic anions such as CO$_3^{2-}$, SO$_4^{2-}$, NO$_3^-$, PO$_4^{3-}$, and OH$^-$ frequently precipitate from aqueous solution and consequently their solubilities often determine whether they are found in nature or can be made in aqueous solution in the laboratory.

The purpose of this study is to provide principles that can be used to understand the relative stabilities of many compounds that occur as minerals (more than half of the mineral species can be classified as double salts), and many that do not occur in nature. Our study was motivated by the desire to understand why some compounds exist in nature and others do not. We are also intrigued by the possibility that our observations can be used to synthesize compounds that are currently unknown and may have properties that lead to unusual applications.

EXPERIMENTAL METHODS

Calculations

The simple salt approximation for lattice energy dissects a double salt such as atacamite [Cu₃Cl(OH)$_3$] into its simple salt “components”—CuCl$_2$ and Cu(OH)$_2$. This dissection process should not be interpreted as supposition that the compound is a mixture of the “components”: it is merely valuable as a formalism to approximate the lattice energy. Thus, the lattice energy (LE) of Cu₃Cl(OH)$_3$ can be approximated as 1/2 LE[CuCl$_2$] + 3/2 LE[Cu(OH)$_2$], which produces a value of 6261 kJ/mol using Born-Haber derived lattice energies (Jenkins 1996). With more complex double salts that contain more than one type of cation and more than one type of anion, there is more than one possible combination of simple salt components. For linarite, CuPbSO$_4$(OH)$_3$, one set is CuSO$_4$ + Pb(OH)$_3$, the other is Cu(OH)$_2$ + PbSO$_4$. In these cases, the lattice energy is generally taken as the average of the two or more sets, although there often is little difference between them. After conversion to the lattice enthalpy, this value can be used with the enthalpies of hydration of the gaseous ions (Marcus 1987) and Latimer’s entropy contributions (Latimer 1952) and entropies of aqueous ions (Wagman et al. 1982) to calculate the Gibbs energy of dissolution.

The calculations involved in the simple salt approximation of enthalpies and Gibbs energies of formation and dissolution were performed as discussed previously (Yoder and Flora 2005; Yoder and Rowand 2006). The lattice energies of