

## Estimation of thermodynamic properties of hydroxides, oxides and layered double hydroxysalts from the electronegativities of the elements

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### Electronegativity of ions as a microscopic energy suitable to correlate with macroscopic thermodynamic properties

Many minerals are isostructural and only differ by the nature of a cation or an anion in the layer or the interlayer. In hydroxides of the group of pyroaurite-hydrotalcite, such as green rusts (GRs) and in synthetic compounds known as layered double hydroxysalts (LDHs), the mineral consists of a brucitic layer with both divalent and trivalent cations in the octahedra, the net positive charge being compensated in the interlayer by anions.

This is the case of natural minerals such as pyroaurite-hydrotalcite and related Mg-Al, Mg-Cr(III), Mg-Fe(III), Ni(II)-Al compounds (Table 1) and of synthetic compounds (LDHs) studied for their catalytic properties. Green Rusts are the Fe(II)-Fe(III) LDHs and can be synthesized as chloride-, carbonate- or sulphate-Fe(II)-Fe(III) hydroxysalts. Blue-green colour of soils has long been ascribed to GRs (Taylor and Mackenzie, 1980; Taylor, 1981) and fougérite (International Mineralogical Association 2004, Trolard *et al.*, 2007) is the natural GR responsible for the gleyic properties. However, it is a ternary Mg-Fe(II)-Fe(III) compound, so it is a Layered Ternary Hydroxide (Bourrié *et al.*, 2004). In Fougères (France), the most likely anion is OH<sup>-</sup>, as evidenced by considering soil/solution equilibria and by XRD decomposition (Trolard and Bourrié, 2008), but in other environments Cl<sup>-</sup> or CO<sub>3</sub><sup>2-</sup> could be present too, as they are compatible with the GR1 structure.

Table 1. Structural formulae of natural minerals of the fougérite group and nature of the interlayer anion, from Trolard *et al.* (2007).

Mineral	Structural Formula	Interlayered Anion
Fougérite	[(Fe <sup>2+</sup> , Mg) <sub>1-x</sub> Fe <sub>x</sub> <sup>3+</sup> (OH) <sub>2</sub> ][x/n A <sup>n</sup> , mH <sub>2</sub> O], 1/4 ≤ x ≤ 1/3	Possible: OH <sup>-</sup> , Cl <sup>-</sup> , CO <sub>3</sub> <sup>2-</sup>
Meixnerite	[Mg <sub>6</sub> Al <sub>2</sub> (OH) <sub>16</sub> ][(OH) <sub>2</sub> , 4H <sub>2</sub> O]	OH <sup>-</sup>
Woodallite	[Mg <sub>2</sub> Cr <sub>2</sub> (OH) <sub>16</sub> ][Cl <sub>2</sub> , 4H <sub>2</sub> O]	Cl <sup>-</sup>
Iowaite	[Mg <sub>4</sub> Fe <sup>III</sup> (OH) <sub>10</sub> ][Cl <sub>2</sub> , H <sub>2</sub> O]	Cl <sup>-</sup>
Takovite	[Ni <sub>6</sub> Al <sub>2</sub> (OH) <sub>16</sub> ][(OH, CO <sub>3</sub> ), 4H <sub>2</sub> O]	OH <sup>-</sup> , CO <sub>3</sub> <sup>2-</sup>
Hydrotalcite	[Mg <sub>6</sub> Al <sub>2</sub> (OH) <sub>16</sub> ][CO <sub>3</sub> , 4H <sub>2</sub> O]	CO <sub>3</sub> <sup>2-</sup>
Pyroaurite	[Mg <sub>6</sub> Fe <sub>2</sub> <sup>III</sup> (OH) <sub>16</sub> ][CO <sub>3</sub> , 4H <sub>2</sub> O]	CO <sub>3</sub> <sup>2-</sup>

Thermodynamic properties of minerals mainly depend on the chemical composition of the mineral, and at a lesser degree on its structure. Evidence for this is the fact that nesosilicates include very soluble compounds such as olivine and quasi-insoluble minerals *e.g.* zircon. Considering isostructural compounds, thermodynamic properties can thus be related with a suitable parameter related with the chemical properties of ions. As the interaction between layer and interlayer is mainly electrostatic, we

proposed to consider the electronegativity of the ion (Bourrié *et al.*, 2004). Pauling's electronegativity scale is not suitable, as it refers only to elements. Jolivet (1994) developed a partial charges model based upon Allred and Rochow's electronegativity scale. The electronegativities of elements  $\chi_i^*$  are derived from the electronic affinity and first ionization energy of the element and are independent of  $P$  and  $T$ . Following Jolivet (1994), the electronegativity of any ion can be computed as:

$$\chi = \frac{\sum_i \sqrt{\chi_i^*} + 1.36Z}{\sum_i \frac{1}{\sqrt{\chi_i^*}}}, \quad (1)$$

where  $Z$  is the global charge of the molecule or ion, and the summation is carried upon all elements of the ion. With  $\chi_i^* = 2.50$  for C, 3.50 for O, 2.83 for Cl, 2.48 for S (Jolivet, 1994) the values obtained for the anions are  $\chi_i = 0.5421$  for  $\text{Cl}^-$ , 2.007 for  $\text{CO}_3^{2-}$  and 2.2856 for  $\text{SO}_4^{2-}$  (the value for  $\text{SO}_4^{2-}$  in Bourrié *et al.*, 2004 was in error).

### Gibbs free energies of formation of Green Rusts

The Gibbs free energies of formation of synthetic green rusts, are plotted versus the Allred-Rochow electronegativities of the interlayer anions in Figure 1. The value of the Gibbs free energy of formation of  $\text{Fe}(\text{OH})_2$  is plotted at  $\chi = 0$ , as the interlayer is empty. Both Gibbs free energies and electronegativities are normalized to 2 structural OH per mole formula, *i.e.* for one third of the unit cell of a brucitic layer  $\text{Mg}_3(\text{OH})_6$  or  $\text{Fe}(\text{II})_3(\text{OH})_6$ .

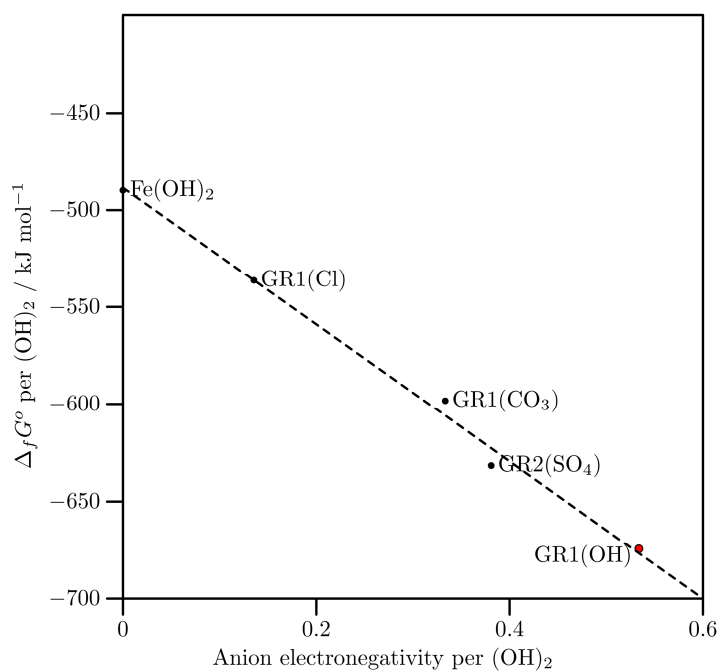


Fig.1. Correlation between Gibbs free energy of formation of Green Rusts, and the Allred-Rochow electronegativity of the anion, both normalized to 2 OH in the layer per mole formula. The correlation is then used to estimate the Gibbs free energy of formation of Green Rust1-OH, with 2 OH in the layer and 1 OH<sup>-</sup> as interlayer compensating anion.

### Enthalpies of formation of hydroxides and oxyhydroxides

Similar correlations are obtained between enthalpies of formation of hydroxides  $M(II)(OH)_2$  and oxyhydroxides  $M(III)OOH$  and electronegativities of respectively bivalent and trivalent metals (Fig. 2).

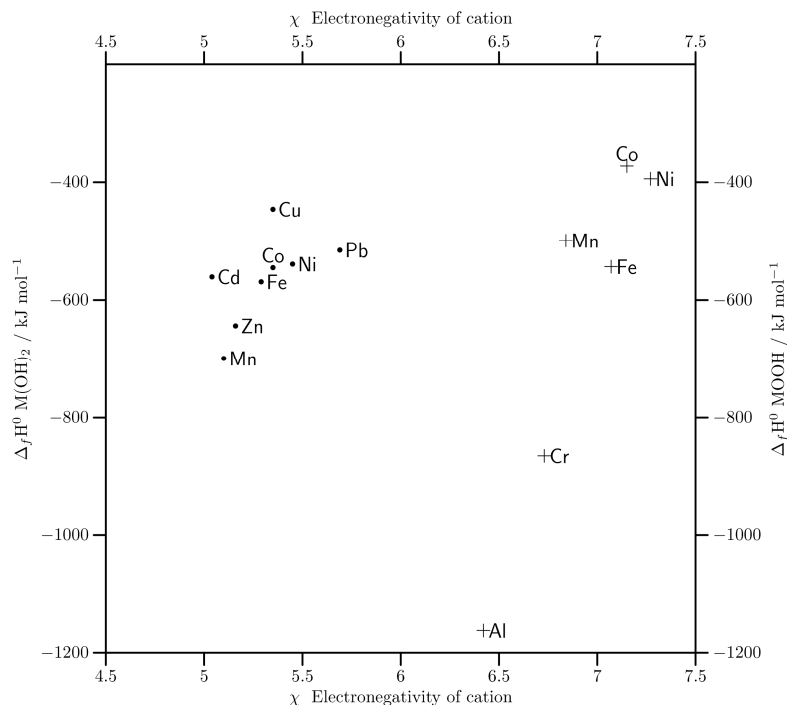


Fig. 2. Correlation between  $\Delta_f H^0$  of  $M(OH)_2$  (•) and  $MOOH$  (+), and the Allred-Rochow electronegativity of the cation, normalized to 2 O in the layer per mole formula.

### Enthalpies of formation of LDHs

Enthalpies of formation of synthetic Ni(II)-Al LDHs were measured by Peltier *et al.* (2006), for different anions, sulphate, carbonate, nitrate and mixed carbonate-silicate. The range of composition of LDHs is very narrow and they differ mainly by the nature of the interlayered anion (Allada *et al.*, 2002). Same as above, the value of the enthalpy of formation of  $Ni(OH)_2$  is plotted at  $\chi = 0$ , as the interlayer is empty. A large decrease is observed when LDHs form (Fig. 3a) but the values are very close to each other for all LDHs without silicate anion; for this latter, the value is more negative. The main  $\Delta_f H^0$  decrease can be ascribed to the opening and hydration of the interlayer as soon as the net charge of the layer is not zero. It is about  $-340 \text{ J mol}^{-1} \text{ K}^{-1}$ .

The contribution of the anion can be obtained by multiplying the electronegativity by the Faraday constant, to transform the microscopic energy  $\chi$  into a macroscopic energy, and by the number of anions in the interlayer. The residual is then plotted against the number of water molecules (Fig. 3b). The further decrease observed with silicate can be ascribed to condensation of silicate anion with the LDH layer with elimination of water molecules, hence to nucleation of Ni(II)-Al clay mineral by polymerization of silica within the interlayer following the anion exchange carbonate / silicate (Peltier *et al.* 2006; Bourrié *et al.*, 2006).

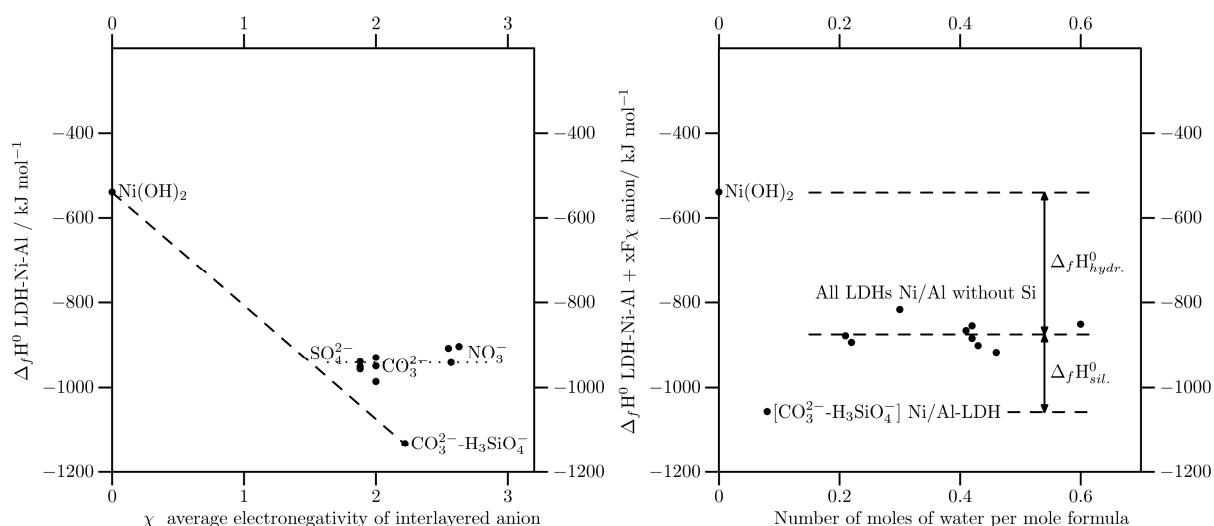


Fig. 3: Correlation between enthalpies of formation of Ni-Al LDHs and the electronegativity of the interlayered anion (left). Variation of the residual  $\Delta_f H^0 + x \cdot F \cdot \chi_{anion}$  with the number of moles of water in the interlayer.

## Conclusion

Electronegativities of ions, computed following the model of partial charges by Jolivet (1994) is a suitable parameter to correlate macroscopic thermodynamic properties of isostructural compounds when interactions are mainly electrostatic. It is of special value for small sized natural minerals that cannot be isolated and purified, and to assess consistency between experimental data sets.

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