

A calculator for the enthalpy of phyllosilicates based on Blanc and others (2015)

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1 Equations for enthalpy calculations

In this section, I rewrite equations 9–14 from Blanc and others (2015) to provide more clarity on the index notation and to remove typos and ambiguities in Blanc and others (2015). The following is only a supplement to the *Enthalpy prediction model development* section in Blanc and others (2015), and likely does not provide a stand alone understanding of the enthalpy calculations. I was not able to create this calculator from reading the paper alone. I had to rely on e-mail communications with P. Vieillard (second author) and P. Blanc, and well as older references such as Chermak and Rimstidt (1989), Vieillard (2000) and Vieillard (1994).

In brief summary to the methods of Blanc and others (2015), the total change in enthalpy of a phyllosilicate with a non-idealized composition at standard state can be estimated through the addition of two enthalpy terms: term 1) the sum of the enthalpies of formation of the oxides for each cation in the clay mineral and term 2) the enthalpy of mixing of cations within a given site for each site in the clay mineral. The contribution from term 1) comprises the bulk of the enthalpy and can be easily calculated given that the enthalpy of formation of oxides is well known from experimental data. To estimate values for a site specific enthalpy (term 2) that is required to calculate the mixing energy, Blanc and others (2015) rely on a polyhedral decomposition method discussed in their *Mathematical formalism* section (p. 16). Together, terms 1) and 2) are written as,

$$\Delta H_f^\circ(\text{phyllo}) = \sum_{i=1}^{n_c} k_i n_i \Delta H_f^\circ(M_i O_{x_i})_{(c)} + \Delta H_{f,Ox}^\circ, \quad (1.1)$$

where n_i is the molar number of the i^{th} cation (M) in the phyllosilicate, $x_i = \frac{z}{2}$ (i.e. the half charge of the cation), and k_i is the number of parts M within an oxide. For example, consider Fe_2O_3 forming the oxide for Fe^{+3} , whereby $k=2$. But for one part Fe, then $M_i O_{x_i}$ is written as $\text{FeO}_{3/2}$. Again, term 1) represents the sum of the enthalpy of formation of the oxide for cation M, while term 2) represents the mixing energy of cations within specific sites, and is written as,

$$\Delta H_{f,Ox}^\circ = -\frac{1}{N} \sum_{k=1}^{n_s-1} \sum_{l=1}^{n_s} \chi_k \chi_l (\Delta_H \text{O}^{\text{site}_l} - \Delta_H \text{O}^{\text{site}_k}) - \delta H_f^\circ(\text{H}_2\text{O}), \quad (1.2)$$

where $\Delta_H \text{O}^{\text{site}}$ is the enthalpy of a given site and $\delta H_f^\circ(\text{H}_2\text{O})$ is water correction (not apparent in Blanc and others (2015), and shown here in section 4). In eq. 1.2 N is the total number of oxygen atoms in the phyllosilicate and χ is the fraction oxygen atoms for a given site, written as,

$$\chi_s = \frac{1}{N} \sum_{i=1}^{n_{cs}} n_i x_i. \quad (1.3)$$

In eq. 1.3, n_{cs} are the number of different cations in a given site, where the sites are octahedral (M), tetrahedral (T), interlayer (I) and (H) hydrogen. Subscripts k and l in 1.2 are dummy variables for the index s in equation 1.3. For consistency, the index i always denotes a specific cation, whereas s denotes a specific site. The cation distribution amongst the site is a function of the clay type, and is outlined below in section 2. The number of oxygen atoms can be verified

by summing all χ_s over the n_s sites as $1 = \sum_{s=1}^{n_s} \chi_s$. Lastly, the enthalpy of a given site can be calculated from the $\Delta_{\text{H}}\text{O}=\text{M}_q^{z+}(\text{clay})$, which is estimated by Blanc and others (2015) from the polyhedral decomposition. The site enthalpy is given as,

$$\Delta_{\text{H}}\text{O}=\text{site}_s = \frac{\sum_i^{n_{cs}} n_i x_i \Delta_{\text{H}}\text{O}=\text{M}_i^{z+}(\text{clay})}{\sum_i^{n_{cs}} n_i x_i} + k_{\text{mix}} \sum_{p=1}^{n_{cs}-1} \sum_{q=p+1}^{n_{cs}} \chi_p \chi_q (\Delta_{\text{H}}\text{O}=\text{M}_p^{z+}(\text{clay}) - \Delta_{\text{H}}\text{O}=\text{M}_q^{z+}(\text{clay})), \quad (1.4)$$

where **p** and **q** are dummy variables to substitute for the index **i**. For example, consider Fe^{3+} , Fe^{2+} and Mg^{2+} sharing the octahedral M2 site. The pairs of interacting terms amongst cations can be thought of as a difference in electronegativity. The interacting terms would be $p=1$ and $q=2$ as $\text{Fe}^{3+} - \text{Fe}^{2+}$, $p=1$ and $q=3$ as $\text{Fe}^{3+} - \text{Mg}^{2+}$, and $p=2$ and $q=3$ as $\text{Fe}^{2+} - \text{Mg}^{2+}$. In eq. 1.4, k_{mix} is a coefficient for the mixing energy for the M2, M3 and I sites. There is no mixing energy for the T, M1 and M4 sites.

2 Distribution of cations

In the following list, total disorder indicates that the ratio of cations in a site is the same for all sites of the same type. For example, $\text{Fe}^{2+}:\text{Mg}^{2+}$ in the M2 site is the same ratio as for the M1 site.

- 7 Å T1 and T2: Total disorder. T1 and T2 get the same quantity of cations.
M1, M2 and M3: Total disorder. M2 is filled first with 2 moles of cation (2/5), then M3 is filled (2/5) and finally M1 takes the remaining 1/5 of the cations.
 H_i and H_e : 1 part H goes into the H_i site while the remaining 3 parts H go into the H_e site.
- 10 Å T1 and T2: Total disorder. T1 and T2 get the same quantity of cations.
M1, M2: M2 is filled first (2/4), then M1 takes the remainder (2/4).
 H_i : Both of the 2 H go into the H_i site.
- 14 Å T1 and T2: Total disorder
M1, M2, M3 and M4: Any Al^{3+} not used on the T sites completely fills the M4 site (Lowenstein's avoidance rule), then the remaining sites are filled with the remaining Al^{3+} and other cations in a disordered fashion following the order for 7 Å clays.
 H_i and H_b : 1 part H goes into the H_i site while the remaining 3 parts H go into the H_b site.

3 Interacting terms

Interactions among cations can be visualized in Blanc and others (2015) Figure 1. In no particular order, the sites that interact are:

I-T1, I-T2

M1-T1, M1-T2

M2-T1, M2-T2

M3-M4

He-T1, He-T2, He-M1, He-M2,

Hb-M3, Hb-M4, Hb-T1, Hb-T2

Hi-M1, Hi-M2

4 Hydrogen correction term

An additional term that does not appear in Blanc and others (2015) corrects for the free energy of hydrogen in the various sites as,

$$\delta H_f^o(H_2O) = \sum_{s=1}^3 n_s x_s \left[\Delta H_f^o(H_2O) - \Delta H_f^o(H_2O)_{(clay)} \right], \quad (4.1)$$

whereby the correction is the sum of the difference in formation enthalpies for water and the n=3 specific hydrogen sites (Hi, He and Hb). This $\delta H_f^o(H_2O)$ correction term is subtracted from the mixing energy in eq. 1.2.

5 Additional considerations

In Blanc and others (2015) there is an error in the k_3 term. As a result the enthalpy for 14 Å clays will be slightly different between the calculator output and the results posted in Blanc et al. (2015).

6 Example of how to use the calculator

Example mineral: nontrite (K) – $\text{K}_{0.34}\text{Fe}_{1.67}^{3+}\text{Al}_{0.67}\text{Si}_{3.66}\text{O}_{10}(\text{OH})_2$

Input cells D3 – D75:

Start by entering the chemical formula into A1 (optional). Enter the number of moles into C1. The number of moles of cations can be entered directly for the interlayer sites (e.g. 0.34 in cell D3). For the octahedral sites, the M2 sites get filled first with up to 2 moles of cations and the remainder gets placed into the M1 sites. For nontrite, no cations will go into the M1 site, because the M2 site will use up all of the Al and Fe. The tetrahedral sites take 4 moles of cations, and all of the Si goes into the tetrahedral sites, leaving $4 - 3.66 = 0.34$ moles of Al for the tetrahedral site, and $0.67 - 0.34 = 0.33$ moles Al for the M2 site. For an example where the M1 site receives cations (M2 overflow), consider Saponite Fe with the octahedral sites as $\text{Mg}_2\text{Fe}^{2+}$. Given that there are 3 moles, and the M2 site can only take 2 moles, the Mg will occupy $(2/3)*2 = 1.33$ moles and the Fe will occupy $(1/3)*2 = 0.67$ moles. The M1 sites will take the remaining $2 - 1.33 = 0.67$ moles of Mg and $1 - 0.67 = 0.33$ moles of Al. Si, Al and Fe are equally shared amongst T1 and T2 sites. For the example of nontrite, the T1 and T2 sites will both receive 1.83 Si and 0.17 Al. The hydrogen sites get filled by the number of moles of H in the hydroxide. For example, with nontrite, there will be 2 moles of H in the Hi site. To verify that the mineral is charge balanced, cell G78 will be highlighted green if the charge on all oxygen atoms is satisfied and highlighted red otherwise.

Column calculations

Sheet 1 (input): A lot of the computations are done in this sheet, but to compute the enthalpy of formation of the oxide in the mineral (Eq. 10) requires knowledge of the site specific interaction terms that are computed through matrix operations in sheets “site Mtx”, with mixing energy between cations in the I, M2 and M3 sites in sheets “I mix”, “M2 mix” and “M3 mix”.

D: number of moles of cation in given site

E: Charge of cation (z)

F: Half charge of cation ($x = \frac{z}{2}$)

G: Number of moles of cation bonded to oxygen ($n*x$)

H: Enthalpy of cation in clay $\Delta_{\text{H}}\text{O}=\text{M}_i^{z+}(\text{clay})$ from minimization of Blanc and others (2015)

I: Enthalpy of formation of oxide. Oxides of major elements taken from Blanc and others (2015) and all other oxides taken from Appendix B in Faure (1998)

J: Computation of first term in Eq. 14

K: Computation Eq. 14, which is column J + mixing energy

L: Number of moles of cation bonded to one oxygen in the oxide

M: First term in Eq. 9.

- O: Sum of first term in Eq. 9
- P: Eq. 10 (second term in Eq. 9)
- Q: Water correction term
- R: The output: ΔH_f° of the mineral

Bibliography

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