Enthalpy calculator

Jeff Crompton

June 12, 2017

1 The equations

In this section, I try to rewrite equations 9–14 from Blanc et al. (2015) to provide more clarity on the index notation and logic of the equations. To briefly summarize the methods of Blanc et al. (2015), the total change in enthalpy of a phyllosilicate with a non-idealized composition at standard state can be estimated throug the addition of two enthalpy terms: 1) the sum of the enthalpies of foramtion of the oxides for each cation in the clay mineral and 2) the enthalpy of mixing of cations within a given site for each site in the clay mineral. The contribution from 1) can be easily calculated because the enthalpy of formation of oxides is well known from experimental data. To estimate values for a site specific enthalpy term that is required to calculate the mixing energy, Blanc et al. (2015) rely on a polyhdra decompostition method discussed in their *mathematical formalism* section on page 16. Together, terms 1) and 2) are written as,

$$\Delta \mathrm{H_f^o(phyllo)} = \sum_{\mathrm{i=1}}^{\mathrm{n_c}} \mathrm{k_i\, n_i\, \Delta H_f^o(M_iO_{x_i})_{(c)}} + \mathrm{\Delta H^o_{f,Ox}}, \tag{1}$$

where $\mathrm{n_i}$ is the molar number of the ith cation (M) in the phyllosilicate, $\mathrm{x_i} = \frac{\mathrm{z}}{2}$ (i.e. the half charge of the cation), and $\mathrm{k_i}$ 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 $\mathrm{M_iO_{x_i}}$ is written as $FeO_{3/2}$. The first term in 1 constitutes the bulk of the enthalpy and represents the sum of the enhtalpy of formation of the oxide for cation M. The second term represents the mixing energy of cations among specific sites as,

$$\mathrm{\Delta H^o_{f,Ox}} = -\frac{1}{\mathrm{N}} \sum_{\mathrm{k=1}}^{\mathrm{n_s-1}} \sum_{\mathrm{l=1}}^{\mathrm{n_s}} \chi_\mathrm{k}\, \chi_\mathrm{l}\, (\Delta_\mathrm{H}\mathrm{O^{=}site_l} - \Delta_\mathrm{H}\mathrm{O^{=}site_k}), \tag{2}$$

where $\Delta_\mathrm{H}\mathrm{O^{=}site}$ is the enthalpy of a given site, N is the total number of oxygen atoms in phyllosilicate and χ is the fraction oxygen atoms for a given site, written as,

$$\chi_\mathrm{s} = \frac{1}{\mathrm{N}} \sum_{\mathrm{i=1}}^{\mathrm{n_{c_s}}} \mathrm{n_i\, x_i}. \tag{3}$$

In 3, $\mathrm{n_{c_s}}$ are the number of different cations in a given site, where the sites are octaherdral (M), tetrahedral (T), interlayer (I) and (H) hydrogen. Subscripts k and l in 2 are dummy

variables for the index s in equation 3. For consistecy, 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... 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

$$\Delta_H O^{=}\text{site}_s = \frac{\sum_i^{n_{cs}} n_i\, x_i\, \Delta_H O^{=} M_i^{z+}(\text{clay})}{\sum_i^{n_{cs}} n_i\, x_i} + \tag{4}$$

$$k_{mix} \sum_{p=1}^{n_{cs}} \sum_{q=p+1}^{n_{cs}-1} \chi_p\, \chi_q \left(\Delta_H O^{=} M_p^{z+}(\text{clay}) - \Delta_H O^{=} M_q^{z+}(\text{clay})\right) \tag{5}$$