

CLAY MINERALS

Thermodynamic properties of clay minerals, as reactive components of clayrock, are important for the understanding/quantification of water-rock interactions in/around a deep disposal (Callovo-Oxfordian). General modeling purposes require stability constants of the initial clay composition, which gives the first geochemical framework. In addition, the chemical disturbances may imply transformations among the initial minerals which suppose to obtain the thermodynamic properties of a large number of clay mineral end members. For example, many experiments have been performed concerning the long term behavior of clay materials, indicating that strong transformations are influenced by the alkaline solutions issued from the cementitious materials (Gaucher and Blanc, 2006). In addition, clay mineral transformations must be modeled in iron rich media or induced by glass dissolution. Dissolved hydrogen may play a role (especially for the iron/clay interactions, together with temperature or the saturation state of the material). It is thus of importance to provide thermodynamic properties of end members that could possibly form, according to the physic-chemical conditions.

A large panel of clay systems has to be studied in a consistent way: 10 Å phases (smectites, illites), 14 Å phase (chlorites) and 7 Å phases (kaolinite, berthierine...).

Thermodynamic properties of clay minerals, which govern the stability of these minerals in solution, are still poorly understood. Indeed, there is only little experimental data available in the literature. However, trying to acquire the thermodynamic data sets covering all the needs is not realistic.

The strategy applied in this work considers that, from a limited number of measurements, it is possible to extend the results to different compositions, by using predictive models. Models are then calibrated using measured data from both the literature and dedicated experiments.

The document is then presenting:

- A selection for the minerals whose properties had been measured
- The experimental measurements performed on selected minerals
- The predictive models, based on previous selection and measurements
- A database for fictive clay minerals end members, which properties are calculated using the models developed here.

1. Short description

Clay minerals belong to the largest family of phyllosilicates, which means that their crystalline cell basically consists in stacking sequences of layers based on silicates and oxide/hydroxides sheets. For example illite, a 10 Å (distance between two layers) phyllosilicate, displays layers formed by two silicates sheets that enclose a third octahedral sheet (TOT sheet, see Figure 1). Between two layers, alkaline or earth alkaline cations compensate the unbalanced, negative charge. The interlayer cations may be anhydrous, for anhydrous clay minerals such as illite or hydrated, case of smectites or vermiculites. For 7 Å phases, the interlayer space is empty whereas it contains an additional octahedral (brucitic) sheet for 14 Å mineral (case of chlorites).

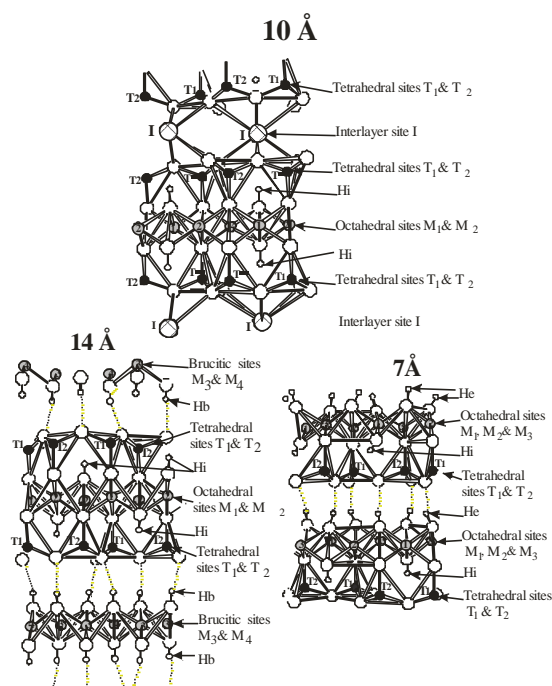


Figure 1. Crystal structures of 10Å, 14Å and 7Å phyllosilicates showing the positions of different crystallographic sites.

Considering the thermodynamic properties of phyllosilicates, data are available for micas and for phases with a structure close to that of talc, kaolinite and for chlorites, to a lesser extent. On the other hand, this is not the case for phases such as smectites, vermiculite or illite. There are measured ΔG_f° for some smectites, based on aqueous solubility experiments (numerous examples in Vieillard, 2000). This is the reason why, for phases that belong to those families, the thermodynamic properties have been planned to be acquired within the frame work of the Thermochimie project.

2. The properties of formation of hydrates, roadmap for thermodynamic studies

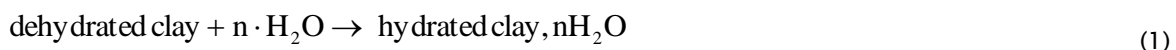
The hydration properties allow to classify clay minerals between hydrous (smectites and vermiculites) and anhydrous minerals (the others). A general pattern thus readily appears for the thermodynamic investigations:

- First to study the hydration reaction energetics
- Then to investigate the formation properties of anhydrous minerals.

By combining the results obtained in both parts, we are then able to provide a general scheme that applied to experimental measurements and predictive modeling.

2.1 Generalities on hydration

Classically, a reaction of hydration may be expressed by the following reaction:



We then consider the property of hydration $\Delta \Xi_{\text{hyd,Tr}}^0$ (per H_2O moles) for a given clay mineral having n bounded molecules per half-cell. In that case, Ξ stands for G, H or S. It is related to the total formation property $\Delta \Xi_{\text{f,Tr}}^0$ of the mineral through the following relation:

$$\Delta \Xi_{\text{f,Tr}}^0(\text{hydrated clay}) = \Delta \Xi_{\text{f,Tr}}^0(\text{dehydrated clay}) + n \cdot \Delta \Xi_{\text{f,Tr}}^0(\text{H}_2\text{O}) + n \cdot \Delta \Xi_{\text{hyd,Tr}}^0 \quad (2)$$

where $\Delta \Xi_{\text{f,Tr}}^0$ (hydrated clay), $\Delta \Xi_{\text{f,Tr}}^0$ (dehydrated clay) and $\Delta \Xi_{\text{f,Tr}}^0$ (H_2O) stand for the formation property for the hydrated mineral, the dehydrated mineral and the bulk water, respectively. Considering that the difference between hydrated and dehydrated mineral is solely due to the presence of interlayer water, the expression may be simplified:

$$\begin{aligned} n \cdot \Delta \Xi_{\text{f,Tr}}^0(\text{interlayer H}_2\text{O}) &= n \cdot \Delta \Xi_{\text{f,Tr}}^0(\text{H}_2\text{O}) + n \cdot \Delta \Xi_{\text{hyd,Tr}}^0 \\ \text{or } \Delta \Xi_{\text{f,Tr}}^0(\text{interlayer H}_2\text{O}) &= \Delta \Xi_{\text{f,Tr}}^0(\text{H}_2\text{O}) + \Delta \Xi_{\text{hyd,Tr}}^0 \end{aligned} \quad (3)$$

In the entropy case for example, the latter even simplifies into:

$$S_{298}^0(\text{interlayer H}_2\text{O}) = S_{298}^0(\text{H}_2\text{O}) + \Delta S_{\text{hyd,298}}^0 \quad (4)$$

The formation properties of the interlayer water may vary depending on the nature of the hydrated cation(s) (Vieillard et al., 2011), the charge deficit of the mineral and its nature (tetrahedral or octahedral).

2.2 Consequences for measuring or estimating thermodynamic properties

For clay minerals, thermodynamics properties will be either measured or estimated. In any cases, the result will be obtained following a pattern that corresponds to reaction and which is illustrated in Figure 2. In that figure, the properties of formation for an hydrated phase are deduced from the properties of formation of the anhydrous phase adding the properties of hydration. The properties of bulk water are supposed to be known.

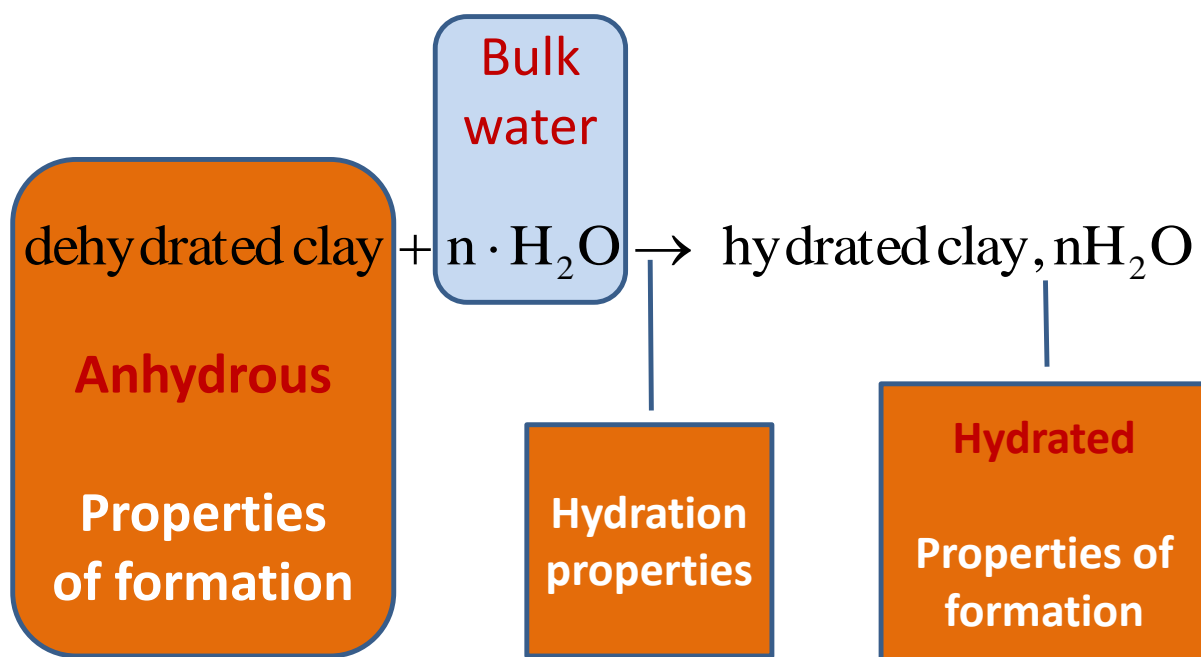


Figure 2. Reaction scheme for studying the thermodynamic properties of hydrated minerals

This implies avoiding to consider directly the properties of formation of the hydrated phase and, rather, to split the studies into the anhydrous phase and the properties of hydration. Several reasons are governing this choice:

- Trying to measure directly the properties of formation of hydrates may lead to questions concerning the hydration state of reference
- It implies to try to perform the different measurements in the same humidity condition which may be not simple since the variation in hydration water amounts can be rather large, especially close to $P/P_0 = 1$ (Gailhanou et al., 2012)
- Experimental methods devoted to hydration properties measurements are specific
- Theoretical treatments for hydration properties are also specific to this matter (see Vieillard et al., 2011).

Finally, in every chapter of the present document, we will distinguish systematically both aspects (properties of formation for anhydrous phases and hydration reactions). The latter will be eventually combine when discussing and predicting the thermodynamic properties of formation of hydrated minerals, in the last part of this document.

3. Critical selection from the literature

A critical selection of phyllosilicates and related phase has been performed for two reasons: first, in order to provide consistent thermodynamic properties for some phases of interest within a deep disposal context and second, in order to provide more accurate and traceable data for predicting models.

Similarly to the parts devoted to cement minerals and zeolites, we are giving here one example of selection, in order to explain the process leading to the thermodynamic data selection from a literature review. Thereafter, the properties gathered for the other phases will be reported into a single table, with specific comments when required.

3.1 Selection guidelines

3.1.1 General considerations

As for zeolites or cement phases, the selection is focused on the collection of direct and traceable measurements. In addition, internal calculations are performed by using the properties already selected within the framework of the Thermochimie project.

On a practical point of view, the selection for the thermodynamic properties of minerals is proceeded considering that:

- when possible, we avoid fitting $\text{LogK}(T)$ functions, as well as averaging equilibrium constants. The aim is to avoid producing some new and perhaps confusing data
- when possible, $\text{LogK}(T)$ function are calculated by using calorimetric data and compared to the results of solution equilibria in order to get a comparison involving different experimental techniques
- solution equilibria results are selected according to the electroneutrality condition, the duration of the experiment, the analysis of final solid products and the experimental protocol
- equilibrium constants extracted from solution equilibria are recalculated by using the Thermochimie Database
- the selection is finally verified by drawing activity diagrams involving the minerals of interest in the chemical sub systems of concern.

3.1.2 Technical aspects

The primary species for expressing equilibria in aqueous solutions are Al^{+++} , Ca^{++} , H_4SiO_4 , Ca^{++} , Mg^{++} , Fe^{+++} , CO_3^{--} , Cl^- , SO_4^{--} , H_2O and H^+ . The convention used to define the standard state of the compounds in the present work, is that proposed by Helgeson et al. (1981). Mineral/solution equilibria are calculated using the PHREEQC (Parkhurst and Appelo, 1999), and the extended Debye-Hückel activity coefficient correction model included in the Thermochimie database.

3.2 Mineral selection: the case of kaolinite, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$

Kaolinite is the most widespread 7 Å phyllosilicate. This case is particularly suitable for a literature review since a lot of calorimetric measurements have been performed to date on this mineral. In addition, it had been used into solution experiments at various temperatures, which allows verifying the parameters selected. Thus, we will first focus on the selection of thermodynamic parameters and a second part will be devoted to the verification against results from solution experiments.

3.2.1 Selection of the thermodynamic constants

For the enthalpy of formation, the following studies could be gathered:

Hemingway et al. (1978), -4120.10 kJ/mol, (HF dissolution calorimetry)

De Ligny and Navrostky (1999), -4120.20 kJ/mol (high temperature lead borate calorimetry)

Fialips et al. (2001), -4115.30 kJ/mol (high temperature lead borate calorimetry)

The first value is corrected from an older experiment (Barany et Kelley, 1961), for a sample containing impurities. The sample used by De Ligny and Navrostky (1999) also contains accessory minerals whose contribution to the total enthalpy ranges, according to the authors, between 6 et 22kJ per mole of kaolinite. In order to avoid impurities, Fialips et al. (2001) have synthesized 6 kaolinites, following 6 different processes. All their measurements fall within the same error interval, ± 4.1 kJ/mol. We have selected the measurements performed by Fialips et al. (2001).

Different authors have used the adiabatic calorimetry in order to obtain directly the entropy of kaolinite:

- King and Weller (1961), 202.92 J/mol.K, acquired from 50 to 300K
- Hemingway et al. (1978), 203.70 J/mol.K (corrected from the previous authors)
- Lipsicas et al. (1986), 183.15 J/mol.K, acquired from 110 to 300K
- Robie and Hemingway (1991), 200.90 J/mol.K, acquired from 20 to 380K.

After Robie and Hemingway (1991), Lipsicas et al. (1986) would have made errors in calibrating their apparatus. In addition, it appears that the measurement from Robie and Hemingway (1991) have been performed over the largest temperature interval, especially concerning the lower temperatures limit. It must be noted that between 0 K and the first measured temperature, the values are always approximated by calculation. According to the selection criteria, we thus retain the experiment from Robie and Hemingway (1991) which are less dependent on calculation results. In addition, we are selecting the $C_p^*(T)$ function acquired by these authors for sake of consistency with the S_{298}° selection and because no other measurements are available (to our knowledge).

Combining selected $\Delta H_{f,298}^\circ$ and S_{298}° and using the elements entropy from Thermochimie 8.0 database provides a $\Delta G_{f,298}^\circ$ of -3793.94 kJ/mol.

3.2.2 Verification of the selection using solution equilibria experiments

The verification is realized by comparing the LogK(T) function calculated from the previously selected thermodynamic parameters with experimental results of solution equilibria experiments, collected from the literature.

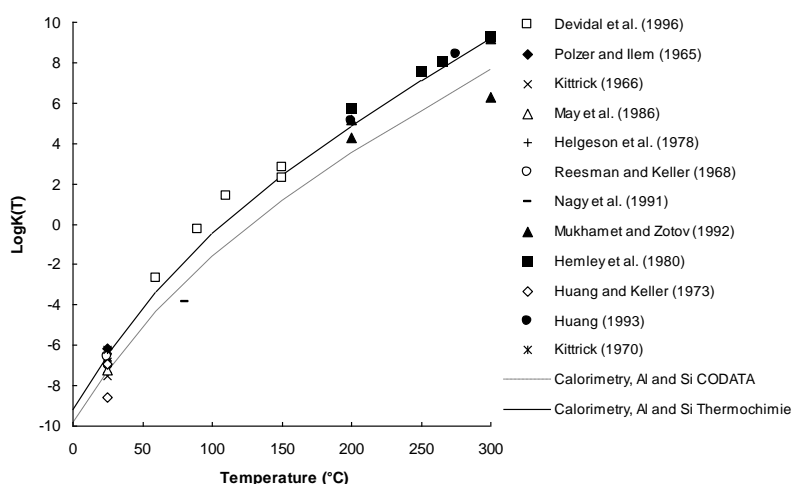


Figure 3. Kaolinite equilibrium constant as a function of temperature

It must be emphasized that the observed values displayed in Figure 3 are extracted from experimental studies by using Thermochimie 8.0 database for the aqueous complexes. All the results are obtained from experimental studies, expected for Helgeson et al. (1978) whose equilibrium constant is calculated from field observations and analyses. In addition, it must be noted that no fitting procedure is involved here. The LogK(T) functions are calculated from the selected thermodynamic properties by using:

Al^{+++} and $H_4SiO_{4,aq}$ thermodynamic properties from Thermochimie 8.0 (continuous curve)

Al^{+++} and $H_4SiO_{4,aq}$ thermodynamic properties from CODATA (Cox et al. 1989, discontinuous curve).

It can be seen from Figure 3 that the function calculated by using aqueous complexes from Thermochimie 8.0 is consistent with results from equilibrated solutions. In addition, by comparing the two calculated LogK(T) functions, it appears that the selection operated for major aqueous complexes actually improve the overall consistency with respect to the former CODATA selection (Cox et al., 1989). However, it must be said that the spread of the solubility values may results in impurities variable crystallinity of the sample. Except for one point, the spread at 25°C is not worse than at higher temperature, implying that the equilibrium achievement is not the main problem here.

3.3 Other phyllosilicates

Full sets of thermodynamic data are available for the following phases: talc, pyrophyllite, muscovite, phlogopite, paragonite, margarite, lizardite, kaolinite and fibrous minerals (chrysotile). In addition, Holland and Powell (1998) and Vidal et al. (2005) did produced data concerning chlorites, by refining phase relations from high temperatures experiments. Some low temperature calorimetry measurements had been performed on clay minerals, like the works of Robie et al. (1976) or Bertoldi et al. (2005), in order to obtain the entropy of illite and berthierine, respectively. In addition, a lot of solution experiments had been performed since the work Reesman and Keller (1968). Their use requires a preliminary selection based on criteria currently used for Thermochimie: duration and reversibility of the experiments, electroneutrality of the solutions and analyses of the final solid products. They are not considered here, at this stage of the selection, owing to these ambiguities.

Following the guidelines previously exposed and illustrated by the kaolinite case, we have selected and collected full sets of thermodynamic constants for a list of phyllosilicates. Hydration properties: experimental measurements

With the exception of Wyoming smectites, experimental data concerning the hydration of smectites are still scarce in the literature. For the Wyoming smectites, we can mention a list of experimental work on hydration properties: Bérend et al. (1995), Cases et al. (1992; 1997), Dios Cancela et al. (1997) and Keren and Shainberg (1975). The list is not complete and only the two last groups of authors have extracted thermodynamic parameters from their experiments. The complete list and discussion about the extracted properties has been discussed extensively by Vieillard et al. (2011). Some additional details are reported here, in the section devoted to the modeling of the hydration reactions.

4. Experimental thermodynamic properties measurements

This section presents the various ways for measuring acquiring thermodynamic properties, from the formation to the hydration reactions, including the solubility experiments.

4.1 Calorimetric methods focused on formation properties

4.1.1 General aspects

The complete thermodynamic dataset of a clay mineral (ΔH_f^0 , ΔG_f^0 , $C_{p,T}$, S^0), at 1 bar and a wide range of temperature, can be determined by calorimetry. This implies the use of several calorimetric techniques, which are listed, for most of them, in the following.

First, some preliminary remarks have to be taken into account before starting calorimetric measurements.

In most cases, a natural or synthetic clay sample contains some impurities, despite physico-chemical treatments which would have been implemented to remove as many impurities as possible. For calorimetric experiments, determining the nature, the chemical composition and the amount of impurities is crucial for assessing the feasibility of measurements on a sample. Those impurities have to be well characterized and their thermodynamic properties, well known. Indeed, for all the following methods, the contribution of impurities has to be subtracted to the measured properties.

The hydration state of the clay mineral is another important point to consider for hydrated minerals. Indeed, hydration energies are not negligible and depend on the nature of the clay, the nature of interlayer cations and the relative humidity. Calorimetric measurements have to be done for a well-known hydration state of the clay which has to be maintained stable during the measurements. For these reasons, the study of a dehydrated clay is easier than a hydrated one. However, an alternative method is to measure hydration energies of a clay mineral *vs* relative humidity (R.H.) and then to calculate the enthalpy of formation and the Gibbs free energy of formation of the hydrated phase by taking into account the corresponding reaction of hydration of the mineral.

Table 1 summarizes the different techniques that have been implemented in order to get a full set of thermodynamic parameter for a given clay mineral. The apparatus for hydration reaction measurements obviously concern only the hydrated minerals. A full description of each technique is provided in the following sections.

CALORIMETRIC TECHNIQUES	MEASURED PROPERTIES	THERMODYNAMIC FUNCTIONS	
Isothermal dissolution calorimetry <i>(IM2NP, Marseille)</i>	Enthalpies of dissolution ΔH_{diss}° at 298,15 K	Standard enthalpies of formation $\Delta H_{f, 298}^{\circ}$	
Low-temperature adiabatic calorimetry (5 - 380K) <i>(Utrecht, Netherlands ; Tsukuba Univ., Japan ; TokyoTech, Japan)</i> PPMS calorimetry <i>(TokyoTech, Japan)</i> DSC (300 K - 500 K) <i>(IM2NP, Marseille)</i>	Low temperature heat capacities $C_p(T)$	Entropies $S(T)$ Heat contents $H_T - H_{298}$	Enthalpies of formation $\Delta H_f(T)$ Entropies $S(T)$ Gibbs free energies of formation $\Delta G_f(T)$
Volumetric or gravimetric adsorption isotherm + calorimetric measurements <i>(Mons, Belgique; LCP, Marseille)</i>	Amounts of adsorbed water and Heats of adsorption ^(*) vs. RH	Enthalpies ^(*) and Gibbs free energies of hydration vs. RH	

Table 1 Summary of the calorimetric techniques implemented in the measurements

4.1.2 Enthalpy of formation

The standard enthalpy of formation of a clay mineral is obtained indirectly from reaction-solution calorimetry. Two methods may be implemented, acid solution calorimetry at low temperature (room temperature or less than 100°C) and drop solution calorimetry at high temperature (close to 700°C for lead borate) in molten oxides. For both methods, apparatus are Tian-Calvet heat-flux microcalorimeters (Ganteaume et al. 1991, Navrotsky 1997). In this document, we will discuss only the acid solution calorimetry which is the method used for the measurement on clay minerals.

For solution calorimetry at 298.15 K, the method implements several reactions of dissolution of (i) clay sample (= clay mineral + impurities), (ii) formative constituents of the clay mineral in appropriate stoichiometry and (iii) impurities present in the clay sample. An appropriate combination of these reactions leads to the reaction of formation of the clay mineral from its formative constituents at 298.15 K and 1 bar. The acid solution is generally a hydrofluoric and nitric acid solution, with a composition optimized to dissolve totally the clay samples and the formative constituents in a reasonable time (a few hours). Formative constituents, which contain elements constitutive of the clay mineral, are generally oxides or hydroxides, and may be also nitrates and fluorides (Gailhanou et al., 2012). It is recommended to dissolve a mixture of formative constituents and impurities rather than each phase independently, in order to obtain a final state as close as possible to the one obtained for the dissolution of the clay sample. Moreover, the uncertainty associated with the enthalpy of formation of the clay mineral will thus be minimized. An example of application of this method is given for an illite further on.

4.1.3 Heat capacity

The heat capacity of a clay mineral may be measured in a very wide range of temperatures, from 2 K to 1000 K, using several complementary techniques. Among available techniques, adiabatic calorimetry is especially suitable for measuring heat capacities at low temperature. Low temperature adiabatic calorimetry (low-TAC) is commonly used and allows C_p measurements from 10 - 15 K to about 350 K (Gailhanou et al. 2007, 2009). It requires an important amount of sample (about 10 g) to optimize the C_p contribution of the sample compared to that of the cell, especially at low temperature. This technique presents a very good accuracy on the measurements, assessed using a standard reference material, with deviations on C_p values generally lower than 0.1% above 100 K. The relative uncertainties (scattering) of the C_p measurements have been estimated on three clay minerals to be lower than 0.3% between 150 K and 350 K (Gailhanou et al., 2007).

Recently, a heat-pulse calorimeter has been commercialized by Quantum Design® and allows measuring heat capacities of minerals at low temperatures (heat capacity option of the Physical Properties Measurement System (PPMS)). One of the main differences with low-TAC is the amount of sample, as only a few milligrams are necessary for PPMS measurements. Consequently, a high purity and homogeneity of the sample are required for the measurement to be representative of the whole sample. The reliability of this technique has been assessed by Dachs and Bertoldi (2005) for three synthetic minerals, between 5 K and 300 K. According to the authors, the precision and accuracy of C_p measurements depend on the preparation and the amount of sample and are better for single-crystals and sintered powder than for sealed powders in Al-pans. Thus, Dachs and Bertoldi (2005) obtained relative errors lower than 0.5% between 100 and 300 K for single-crystal and sintered-powder samples and underestimated of about 1-2% the C_p of sealed powder samples. The relative uncertainties (scattering) were estimated to be lower than 0.3% for $T > 50$ K, in the best conditions of preparation of the sample.

Finally, the third complementary technique, commonly used for higher temperatures, is differential scanning calorimetry (DSC). By this technique, heat capacities of clay samples may be measured from 143 K to high temperatures. The amount of sample is a few hundreds of milligrams. Standard deviations on C_p values are lower than 1% at $T > 200$ K (Bertoldi et al., 2005; Gailhanou et al., 2007, 2009). For clay minerals, they are strong limits to this technique:

- the highest temperature, for anhydrous clay minerals, are reached when deshydroxylation begins (depending on the mineral, from 300 to 600°C);
- for hydrated phases, this technique is difficult to apply since the loss of water may begin close to room temperature.

Afterwards, heat capacities of the mineral $C_{p, \text{miner}}$ are determined by subtracting the contribution of impurities, according to a relation based on an additivity law:

$$C_{p, \text{miner}} = \frac{C_{p, \text{sample}} - \sum_i x_i C_{p, i}}{x_{\text{miner}}} \quad (5)$$

where x_{miner} is the mass fraction of the mineral, $C_{p, \text{sample}}$ is the heat capacity of the sample, x_i is the mass fraction of impurity i and $C_{p, i}$ is the heat capacity of impurity i (in $\text{J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$).

4.1.4 Residual entropy

A part of the total entropy of a mineral cannot be measured. It is called residual and, for clay minerals, it originates from two main sources: the configurational and the magnetic entropy.

Configurational entropy. It is associated to the disorder that occurs when mixing different cations in the same crystallographical site (octahedral, tetrahedral and interlayer sites). This entropic term is not negligible in the case of clay mineral, but its determination requires specific analyses and structural modeling. Usually it is estimated to its maximum value using Ulbrich and Waldbaum (1976) method. However several investigations have been done to improve the knowledge of cationic distribution in the different crystallographic sites of clay minerals, based on spectroscopic analyses (^{29}Si NMR, ^{27}Al NMR) and mechanistic calculations (Cuadros et al., 1999; Sainz-Diaz et al., 2001; Sainz-Diaz et al., 2003) or X-ray diffraction (Drits et al., 2006). Until now, these studies concern mainly illites, smectites and interstratified illite-smectites. Some studies are trying to generalize such spectroscopic works, like the model of Vinograd (1995) for the tetrahedral sites of layered silicates.

Magnetic entropy. In the case of clay minerals containing paramagnetic elements (generally Fe, Mn), a magnetic transition, associated with the order/disorder transition of magnetic spins of paramagnetic ions, may appear and generate an anomaly on the C_p curve, at very low temperatures (Ulbrich and Waldbaum, 1976). For instance, for iron-rich chlorites (chamosite), magnetic transition occurs at temperatures lower than 7 K (Towsend et al., 1986). Magnetic entropy can be included in the calorimetric entropy when C_p is measured starting from those very low temperatures.

In most cases, when magnetic transition happens, it concerns only a part of the paramagnetic ions, so that the calculation of maximum magnetic entropy according to Ulbrich and Waldbaum (1976) formula $S_{spin}^0 = R \sum_i x_i \ln(2s_i + 1)$, with x_i the molar fraction and s_i the spin quantum number of paramagnetic ion i in the clay mineral, leads to an overestimation (Gailhanou et al., 2009).

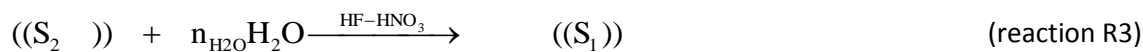
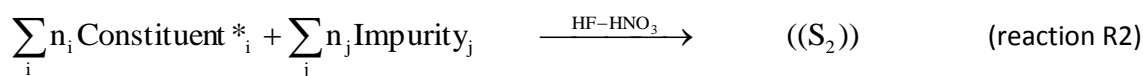
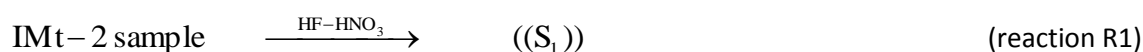
4.1.5 Illustration: the case of illite

The complete thermodynamic dataset of an illite has been determined using the preceding calorimetric methods. The procedure and the results are detailed in Gailhanou et al. (2012). A brief summary is given here, for illustration purposes.

The studied sample is an international reference sample, the illite IMt-2, obtained from the Source Clay Project of the Clay Minerals Society. It originates from Silver Hill (Montana, USA, Hower and Mowatt, 1966; Vogt et al., 2002). The illite sample has undergone chemical treatments and purification, described by Gailhanou et al. (2007). The impurities in the dehydrated sample (in wt%) have been determined as being quartz 7.65%, microcline 2.04%, rutile 0.89% and kaolinite 0.31%. Chemical analyses provide the structural formulae of the illite as: $K_{0.762} Na_{0.044} (Si_{3.387} Al_{0.613})(Al_{1.427} Mg_{0.241} Fe^{3+}_{0.292} Fe^{2+}_{0.084})O_{10}(OH)_2$. The calorimetric measurements performed on the dehydrated sample are presented next.

4.1.5.1 Enthalpy of formation

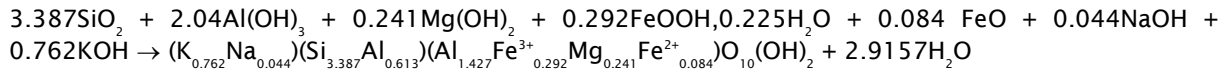
The enthalpy of formation of illite has been determined by solution calorimetry at 298.15 K, using a Calsol calorimeter (Ganteaume et al., 1991). The composition of the acid solution was HF(13M)-HNO₃(2M) and the amount of sample was about 40-50 mg. The following reactions, expressed for one mole of clay (O₁₀(OH)₂ unit) were experimented:



For reaction (R2), the sample was a mixture of the constituents and impurities in appropriate proportions. Thus, constituent_i* refers to formative constituents of the clay mineral (* = except H₂O), which was selected among oxides and hydroxides, n_i is the number of moles of constituent_i* with the same stoichiometry than in one mole of illite (except for O and H). Impurity_j refers to impurities identical to those in IMt-2 sample and n_j is the number of moles of impurity_j calculated for one mole of illite. The symbol (()) represents a solution; ((S₁)) and ((S₂)) refers to the final state of the solutions after dissolution of the samples. The combination of reactions (R2) – (R1) + (R3) leads to the reaction of formation of illite from the constituents:



In this case, (R4) corresponds to:



Hence, the enthalpy of formation per mole of illite from the constituents is obtained according to:

$$\Delta H_{f/constit}^0 = m_{mixt} \Delta H_{diss,mixt} - m_{sample} \Delta H_{diss,sample} + m_{H_2O} \Delta H_{dil} \quad (6)$$

where $\Delta H_{diss,mixt}$, $\Delta H_{diss,sample}$ and ΔH_{dil} are respectively the enthalpy of dissolution of the constituents* (* = all constituents except H_2O) and the impurities mixture, the enthalpy of dissolution of the clay sample, and the enthalpy of dilution of the solution ((S_2)). m_{mixt} , m_{sample} and m_{H_2O} are respectively the masses of the constituents* and impurities mixture, of the clay sample, and of the H_2O constituent, for one mole of clay mineral. After measuring the heat released during the dissolution reactions, the enthalpy of formation from constituents $\square \Delta H_{f/constit}^0$ for the dehydrated illite is found to be $-57.05 (\pm 7.40) \text{ kJ}\cdot\text{mol}^{-1}$. Combining this value with the standard enthalpies of formation of the constituents, Gailhanou et al. (2012) obtained the standard enthalpy of formation $\square \Delta H_f^\circ$ of illite IMt-2 as $-5711.25 \pm 8.49 \text{ kJ}\cdot\text{mol}^{-1}$.

4.1.5.2 Heat capacity

Heat capacities of the dehydrated IMt-2 sample have been measured, between 6 and 400 K by low-TAC and from 380 to 520 K by DSC (Gailhanou et al., 2007). Heat capacities have been extrapolated between 0 and 6 K, using the Debye approximation $C_p \sim C_v = \alpha T^3$ at very low temperatures. Afterwards, C_p values have been interpolated at every degree, between 0 and 520 K. Then, the correction for impurity contribution (5) has been applied, in order to obtain the heat capacities of the dehydrated illite. All the details are given in Gailhanou et al. (2007).

4.1.5.3 Entropy

Entropy of dehydrated illite has been determined by integrating the $C_p(T)/T$ low temperature function up to 298.15K, using the trapezoid method. No C_p anomaly was detected at very low temperatures. From analytical results previously published, the configurational entropy has been estimated by Gailhanou et al. (2012), taking into account the mixing into the octahedral and tetrahedral sites and within the interlayer space.

4.2 Experimental measurements of hydration properties

This section is devoted to the description of apparatuses specific to the measurement of hydration energies. As previously seen, it applies to clay minerals whose interlayer is open to the solution and filled by cations able to hydrate in contact with a solution.

4.2.1 Gibbs energy of adsorption by volumetry

The Gibbs energy of hydration is classically measured either by gravimetry or volumetry. The basic principles remain the same except on the property measured: the mass increase for gravimetry (using a balance) and the pressure increase for volumetry (using a pressure gauge) Thereafter, we are describing the volumetry apparatus that we are currently using.

Figure 4 is representing the apparatus used for obtaining the water vapour adsorption isotherm a point by point volumetric method. The apparatus and the experimental method are described in Denoyel et al. (2002). The sample is first dehydrated (150°C for 12 h under vacuum). Afterwards, the vessel is hermetically closed and placed in the apparatus at 25°C for acquiring the isotherm. A variable number of injections of H₂O is realized according to the precision required for the isotherm. The stabilization period is close to 2 hours after each injection. It may increase, especially close to the vapour saturation. The pressure variations, measured by the gauge, are related to the increase in adsorbed water. The heat exchanged during the reaction is also measured by mean of the thermopile, surrounding the sample cell.

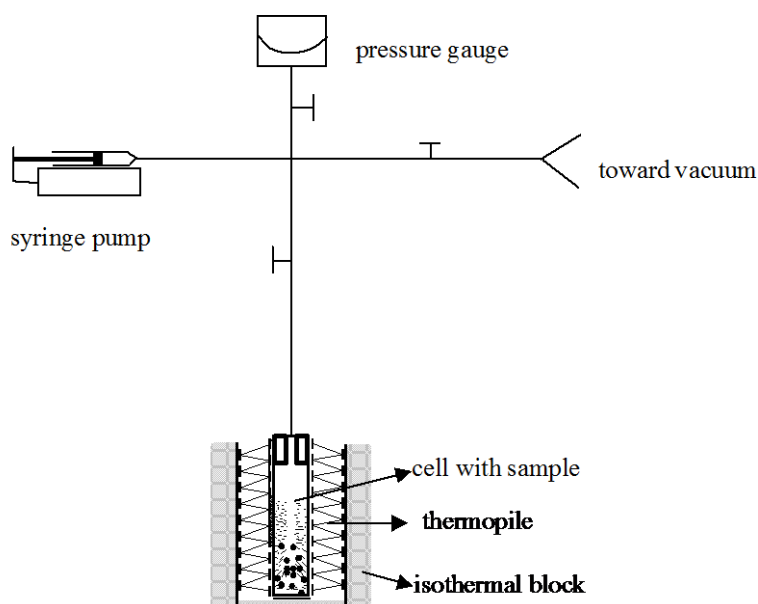


Figure 4. Apparatus used for obtaining the vapour adsorption isotherm and the isotherm for the heat of adsorption.

From the measured adsorbed amounts, the free enthalpy of adsorption ΔG_{Hyd}° may be determined by the following expression (Barshad, 1960):

$$\Delta G_{ads}^0 = RT \int_{n=0}^{n=n_1} \ln\left(\frac{P}{P_0}\right) dn - \Delta G_{cond}^0 \quad (7)$$

where R is the ideal gas constant, n is the amount of adsorbed water, P is the partial water vapor pressure, P_0 , the saturated water vapor pressure at temperature T ($P/P_0 = RH/100$) and ΔG_{cond}^0 is the Gibbs free energy of condensation of water vapor.

4.2.2 Enthalpy and entropy of adsorption

As adsorption proceeds in the vapour state, it is impossible to measure temperature variations during the slow adsorption of water molecules. It is easier to obtain independently the heat and the entropy variations. These functions may be obtained by two different ways:

(1) by determining adsorption isotherms at more than one temperature as suggested by Hill, (1949, 1950) (Sharma et al. 1969);

(2) by combining calorimetric heat of immersion data with one adsorption isotherm at the same temperature (Jura and Hill, 1951) and applied to Wyoming (Cases et al., 1992; Bérend et al., 1995; Cases et al., 1997).

In these conventional approaches, the adsorbent (only one phase) is supposed to be inert so that the functions derived represent the energy variations formally occurring between water (liquid) and the swelling clay (adsorbing material). The formalism for the first case consists in an adaptation of the Clausius- Clapeyron's equation:

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_L}{R} * \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad (8)$$

This equation is used to calculate a pressure P_2 at a T_2 temperature if water vapor pressure P_1 is known at the temperature T_1 and if the enthalpy of vaporization, ΔH_L is known. If pressure measurements of water vapour P_1 and P_2 determined at two temperatures T_1 and T_2 selected verify the Clausius - Clapeyron equation, the difference in enthalpy of vaporization can appear either in the same number of moles of adsorbed water n (expressed in g/g) (differential quantities):

$$dh = \left(\frac{T_1 * T_2}{T_2 - T_1}\right) * R * \ln\left(\frac{P_2}{P_1}\right)_n + (H_g - H_L) \quad (9)$$

or to the same surface energy \cdot (mJ/m²) (integral quantities):

$$\Delta H_1 = (H_s - H_l) = \frac{T_1 * T_2}{(T_2 - T_1)} * R * \ln\left[\frac{P_1}{P_2}\right]_{\Phi} \quad (10)$$

In Eq 9 the suffix n indicates that P_1 and P_2 and the corresponding temperature T_1 and T_2 are taken at a constant moisture content (n), $(H_g - H_l)$ is the latent heat of vaporization at some temperature T and the terms dh represent the differential enthalpy or partial molar enthalpy. In Eq 10, H_s et H_l are respectively the average molar enthalpy of the adsorbed phase and pure bulk water, respectively ; P_1 et P_2 are the vapor pressure at temperatures T_1 et T_2 . To calculate the integral quantities from isotherms, an evaluation of the spreading pressure alternatively known as the surface tension difference and given by Bangham(1937)

$$\Phi = R * T / (M * A) * \int_{P=0}^P \theta * d(\ln P) \quad (11)$$

and required the knowledge of specific surface A at low vapor pressures. As the Clausius- Clapeyron equation requires that the surface area for the two isotherms to be constant, the calculation of integral quantities can be erroneous and the differential quantity (Eq. 9) obtained at a constant number of water moles is preferred and used this study.

Considering the initial state of clay as the dehydrated state, the formalism for the second case shows a combination of heats of adsorption of water vapor versus the number of moles of adsorbed water, at temperature T . The partial molar enthalpy dh is obtained by the following expression

$$dh = (H_{ads\ 1} - H_{ads\ 2}) / (m_1 - m_2) - (m_1 - m_2) * H_{cond} \quad (12)$$

where $H_{ads\ 1}$ and $H_{ads\ 2}$ are respectively the heats of adsorption of n_1 and n_2 water vapor amounts measured at a same relative humidities, H_{cond} is the enthalpy of condensation of water vapor at temperature T .

The enthalpy of adsorption ΔH_{hyd}^0 is finally obtained by integrating the partial molar enthalpy:

$$\Delta H_{ads}^0 = \int_{n=0}^{n=n_i} dh \cdot dn \quad (13)$$

The entropy of adsorption may then be calculated:

- either by combining ΔH^0_{ads} and ΔG^0_{ads} .

- or by considering the approach of Clausius- Clapeyron law that provides the differential entropy calculated from isotherms measured a two temperatures T_1 and T_2 at a constant number of moles of adsorbed water (Keren et Shainberg, 1980; Sharma et al. ,1969) :

$$\Delta \bar{S}_1 = R / 2 * \left[\frac{T_1 + T_2}{(T_2 - T_1)} * \ln \left[\frac{P_1}{P_2} \right] - R * \ln(P_1 * P_2) \right]_n \quad (14)$$

4.2.3 Remarks on the measurement of adsorption properties from vapour isotherms

Rather few studies are dealing with both adsorption and desorption isotherms. Yet, this question of importance since, as shown by Bérend et al. (1995), adsorption and desorption isotherms display a hysteresis loop. The question to which reaction path to consider for thermodynamic calculations has not been satisfactory addressed, up to now.

In addition, complementary measurements by XRD are essential to detect the mechanisms of hydration by steps and to compare with other measurements. BET measurements carried out by Bérend et al., 1995; Cases et al., 1992; Cases et al., 1997, are also necessary to evaluate specific surface area and to determine the amount of recovering water during the hydration.

4.3 Equilibrium in solutions

Numerous attempts of solubility experiments have been conducted so far on clay minerals:

- Kaolinite (Kittrick, 1966; Reesman and Keller, 1968; May et al., 1986; Nagy et al., 1991; Mukhamet-Galeev and Zotov, 1992; Devidal et al., 1996);
- Dickite (Reesman and Keller, 1968);
- Illite (Kittrick, 1984; Sass et al., 1987; Rosenberg et al., 1990; Aja, 1991; Aja et al., 1991; Yates and Rosenberg, 1996, 1997, 1998);
- Smectite (Reesman and Keller, 1968; Kittrick, 1971; May et al., 1986; Kittrick and Perya, 1988, 1989; Cama et al., 2000; Metz et al., 2005);
- Vermiculite (Kalinowski and Scheveda, 2007);
- Chlorite (Kittrick, 1982; Aja and Dyar, 2002).

In these experiments, some specific pitfalls await for the researcher and this can be worsened by the complexity of clay minerals. In addition to the classical uncertainties arising from analytical uncertainty or experimental monitoring, attention must be paid to the clay mineral sample, its compositional variability, the presence of impurities even in the finest size-fraction, all of which may lead to misinterpretation of the experiment results (Metz et al., 2005; May et al., 1986; Mermut and Cano, 2001). The equilibrium achievement remains the main issue. For example, Rimstidt (1997) has shown that 2 years of equilibration was not a long enough reaction time to reach equilibrium for quartz. Instead, he has proposed the results of his own experiments, with a 13 years reaction time, at 25°C.

Such difficulties may explain why the results of these experiments are generally not integrated into geochemical databases. However, the Thermochimie project includes a series of such experiments, for verification purposes.

5. Developments of models for thermodynamic properties prediction

This section is devoted to the development of models able to extend the experimental results to different compositions of clay minerals.

As previously explained, the development is splitted into 1) models for the properties of formation of the anhydrous clay minerals and 2) models for the hydration reaction when the mineral requires it.

5.1 Predictive modeling of the thermodynamic properties of formation of anhydrous clay minerals

5.1.1 Existing models

To determine the missing thermodynamic parameters of a clay phase whose chemical composition is known, different methods were developed using thermodynamic data of silicates to estimate the major thermodynamic parameters (V , ΔG_f° , ΔH_f° , S° , Cp_f).

Most of the predicting models are based on the assumption that the thermodynamic properties of a mineral can be obtained by combining the properties of its constituents. They may be simple elements (Latimer, 1951), oxides (Karpov and Kashik, 1968), or hydroxides (Sposito, 1986). This technique has been significantly improved by taking into account the coordination polyhedron of cations in mineral structures (polyhedral decomposition models: Hazen, 1985, 1988; Chermak and Rimstidt 1989, Holland 1989, Van Hinsberg et al. 2005). In any case, basic principles remains, that is: 1) to collect a set of calibration phases; 2) to decompose those phases into the base units retained and 3) to calibrate the properties of each base unit by minimizing the sum of squared differences between observed and predicted values for the calibration set of minerals.

A different type of model is based on the approach developed by Vieillard, (1994a and b). The principle of calculation relies on the difference in electronegativity between two cations around a common oxygen atom.

The latter is especially efficient in predicting formation enthalpy, the reason why it was retained. Then the other thermodynamic functions are completed by using the polyhedral approach.

The following sections are related to:

- The development of the model based on the electronegativity scale for the enthalpy of formation
- The development of the polyhedral model for the other thermodynamic functions
- The development of the model for the hydration reactions.

5.1.2 Method of prediction for the enthalpy of formation based on the electronegativity difference

5.1.2.1 Fundamental developments

The methods tested on phyllosilicates are essentially based on the concept of the electronegativity of Pauling (1960) which is the power of an atom in a molecule to attract electrons from another atom. Let us consider a binary oxide compound ABO_N , (where A and B are different cations), that may decompose in a sum of two oxides AO_{n1} and BO_{n2} , the energy of formation of ABO_N can be written as:

$$E(ABO_N) = E(AO_{n1}) + E(BO_{n2}) + kX_A X_B (\chi_A - \chi_B)^2 \quad (15)$$

The third term, representing the energy of formation of the compound from AO_{n1} and BO_{n2} oxides, is proportional, in the first hand, to the molar fraction of oxygens atoms respectively related to the cations A (X_A) and B (X_B) of the oxides AO_{n1} and BO_{n2} in the formation of binary compound, and, in the second hand, to the difference in electronegativity between the cations A and B on a common oxygen atom. Greater is the difference in electronegativity between the cations on oxygen, stronger will be the energy of formation of the compound. If two cations linked to the same atom of oxygen, have a same electronegativity or are identical, the energy of formation from the oxides is null. If two cations have different electronegativities and are not bound by a common oxygen atom, the energy of formation is zero or negligible. Zuyev (1987) has proposed a method of prediction of enthalpies of formation based on the electronegativity of a constant and single ion, while Vieillard (1994a and b) has developed a prediction model of enthalpies of formation from experimental data of many compounds (silicates, aluminates and ferrites) in which the electronegativity of an ion is as a function of the interatomic distance between the ion and oxygen involving the so-called energy of Born-Haber. For both hydrated and dehydrated clay minerals, Vieillard (2000; 2002) has developed a methodology of estimation based on the difference of electronegativity by considering three scales of values of the parameter $\Delta_{\text{H}}\text{O}^-\text{M}^{z+}(\text{clay})$ in the three sites of phyllosilicates.

The model of computation was tested for micas (pyrophyllite, talc, phlogopite, annite, muscovite 1M, 2M, paragonite, margarite, illite, phengite, ferri-annite), chlorites (clinochlore, cookeite) and phyllosilicates 7Å (kaolinite, dickite, lizardite) for which the crystalline structures are refined and measured optical properties are available (Vieillard, 1994b).

5.1.2.2 Application: the $\Delta H_{f, 298}^\circ$ of anhydrous phyllosilicates

Thanks to recent measurements of the enthalpies of formation of the anhydrous phyllosilicates developed within the framework of Thermochimie, (Vieillard, 2007) propose to build a model for the prediction of the enthalpies of formation of the anhydrous phyllosilicates including the three structural families (7, 10 and 14Å). This model, based on the (Vieillard, 1994a)'s algorithm, will be simplified by assuming that the parameter $\Delta_{\text{H}}\text{O}^-\text{M}^{z+}(\text{clay})$, characterizing the electronegativity of the cation M^{z+} in a specific site is constant and independent of the interatomic variations of distances in the various sites. The 28 selected minerals (given previously) will be used as a basis in the determination of a set of parameters $\Delta_{\text{H}}\text{O}^-\text{M}^{z+}(\text{clay})$ of sixteen cations distributed in the various structural sites of the phyllosilicates: Na^+ , K^+ , Ca^{2+} in the interlayer sites, Mg^{2+} , Fe^{2+} , Fe^{3+} , Al^{3+} in octahedral sites on the one hand and in brucitic sites on the other hand, Al^{3+} and Si^{4+} in tetrahedral sites, H_o^+ , H_b^+ and H_e^+ in the different sites, i.e. 16 unknown parameters.

Contrary to the model of estimate of the free enthalpy developed by (Vieillard, 2000) and (Vieillard, 2002) on the anhydrous smectites and phyllosilicates respectively, the model developed here presents an originality based on the true organization of the cations within the various sites. The second originality of this model, which is a direct application of the formalism based on (Vieillard, 1994A), (Vieillard, 1994b) is the use of energies of interactions between the cations occupying a same site.

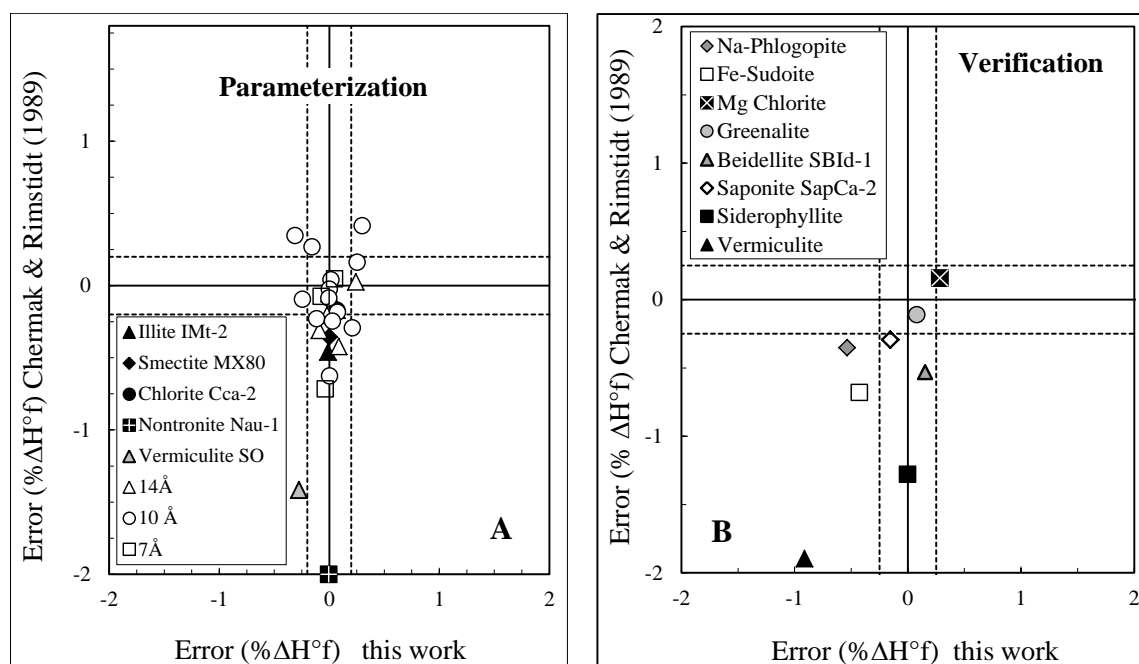


Figure 5. Enthalpy of formation of phyllosilicates: comparison of the discrepancy of the estimates, calculated either with the present model or with the method of Chermak and Rimstidt (1989). A- Parameterization phases; B- Verification phases.

The set newly scaled $\Delta_{\text{H}}\text{O}=\text{M}^{2+}(\text{clay})$ parameters is used to calculate the enthalpy of formation from constituent oxides. From enthalpies of oxides and water in different states (Thermochimie database), the enthalpy of formation of a phyllosilicate can be evaluated and compared with the Chermak and Rimstidt (1989) model (Figure 5). It can be seen that the present model gives better results for calibration phases belonging to the three families of phyllosilicates (Fig. 5A). The high deviation observed on vermiculite and nontronite by the polyhedral model (-1.42 and -2%, respectively) are completely resolved in this model. This improvement is explained by the fact that a better consideration of the octahedral ferric iron, on the one hand and a high tetrahedral aluminium content on the other hand.

On the whole, the agreement with respect to experimental values is quite satisfactory and the results are still better than those obtained by using the Chermak and Rimstidt (1989) method.

5.1.3 Polyhedral method for entropy and heat capacity

The polyhedral model developed here has been designed in order to predict the main thermodynamic properties S , V , and Mayer-Kelley coefficients a , b , c for the $C_p(T)$ function.

For the polyhedral decomposition, we are considering the following base units: $^{[8-12]}Na_2O$, $^{[8-12]}K_2O$, $^{[6-8]}CaO$, $^{[6]}Mg(OH)_2$, $^{[6]}Fe(OH)_2$, $^{[6]}Al(OH)_3$, $^{[6]}Al_2O_3$, $^{[6]}FeO$, $^{[6]}MgO$, $^{[6]}Fe_2O_3$, $^{[4]}Al_2O_3$ and $^{[4]}SiO_2$. In addition, we have followed Holland and Powell (1998) rules for chlorite polyhedral decomposition and Chermak and Rimstidt (1989) for 2 :1 phyllosilicates. The latter technique were improved in order to be consistent with a $O_{10}(OH)_2$ based chemical formula. Following Holland (1989) or Van Hinsberg et al. (2005), our model does only predict the entropy part that corresponds to S_{net}° (without spin or configurational contributions). Using Holland (1989) method provides, for group 1 minerals, a mean discrepancy of 6.0% or 20.6 J/mol.K for the absolute discrepancy against 2.1% and 7.0 J/mol.K for our method, which is displayed on Figure 6. With respect to Holland (1989) work, the method developed here thus represents a significant improvement.

Results obtained for $C_p(25^{\circ}C)$ and the molar volume are also displayed on Figure 7 and Figure 8. For the heat capacity, the results are comparable to that obtained with the Berman and Brown (1985) method and, for the volume, the agreement is quite satisfactory with respect to experimental results.

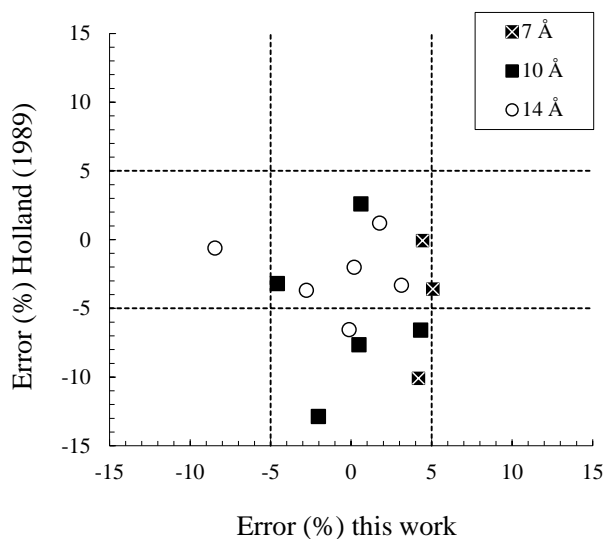


Figure 6. Predicted entropy values for anhydrous phyllosilicates (relative differences).

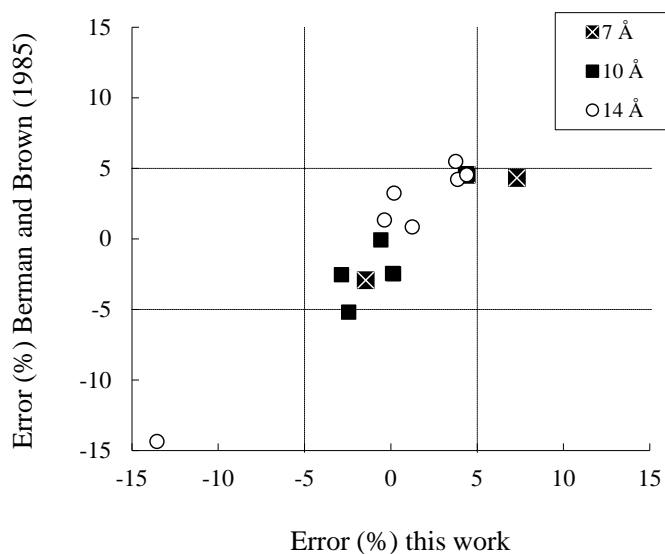


Figure 7. Predicted $C_p(25^\circ\text{C})$ values for anhydrous phyllosilicates (relative differences)

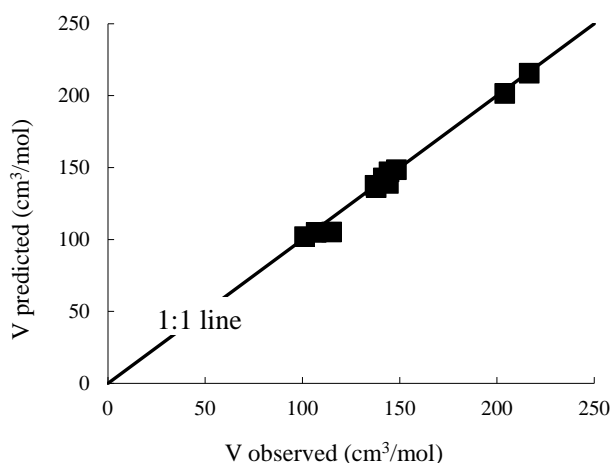


Figure 8. Comparison between the predicted and observed molar volume values of the phyllosilicates.

Finally, the polyhedral decomposition model developed here improves the results for predicting entropy values, and allows to predict $C_p(25^\circ\text{C})$ and molar volumes of the minerals consistently with the prediction of entropy since the set of parameterization minerals is the same in all cases.

5.1.4 Predicting the Gibbs energy of anhydrous phases

This section shows that by associating the two predictive models developed here, we are able to calculate an estimated Gibbs free energy for some anhydrous phyllosilicates.

By combining the estimates of the enthalpy of formation and the entropy, it is possible to predict the Gibbs free energy values. Since the accuracy of predictions for ΔH_f^0 and S^{lat} have already been checked, the main question arises from the additional entropy terms S^{mag} and S^{conf} . For chamosite for example, S^{mag} reaches 66.91 J/mol.K which contributes up to -20 kJ/mol to the final value of $\square G_f^0$ and modifies it by -0.28%. Such modification is far from negligible and has to be tested. Calculations are then performed by combining S^{mag} and S^{conf} and the estimates for $\square H_f^0$ and S^{lat} . In figures 9A and 9B, the results are compared to the experimentally measured $\square G_f^0$.

From these figures, it is clear that introducing the configurational and magnetic entropy terms does not significantly increase the discrepancies with respect to experimental data. These remain of the same order of magnitude as discrepancies observed for ΔH_f^0 predictions. In fact, for the verification minerals, the combination of predicted enthalpies and entropies tends to reduce the overall uncertainty for ΔG_f^0 estimates.

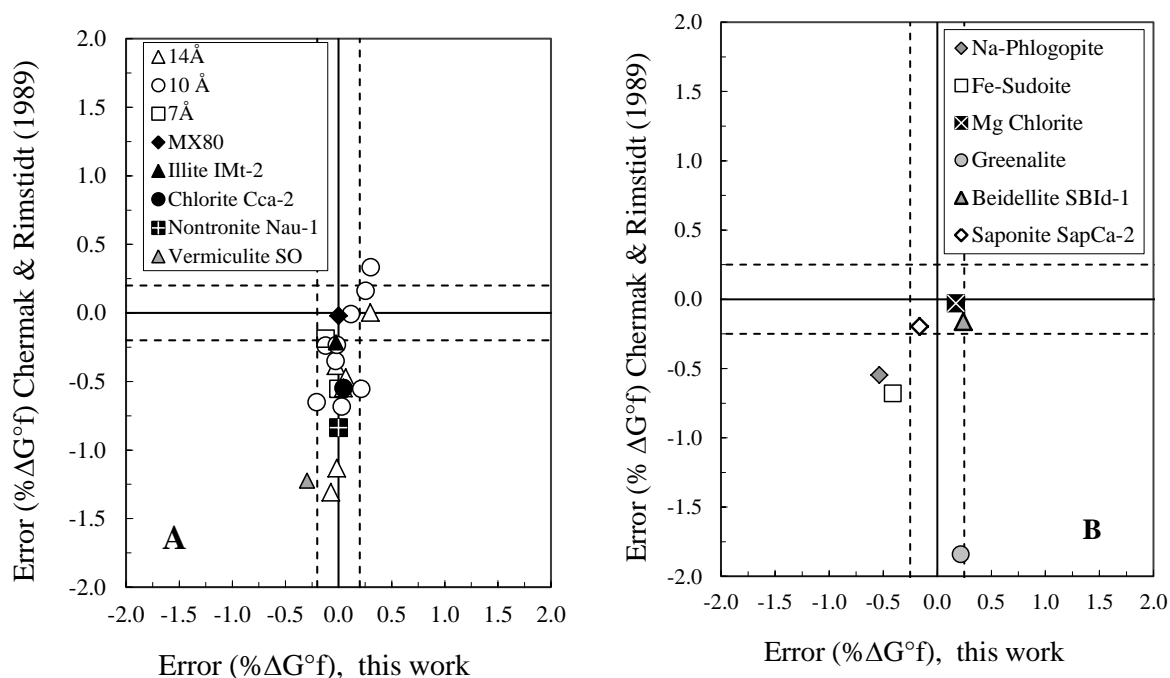


Figure 9 – Predicted ΔG_f^0 for phyllosilicates: comparison of the discrepancy between experimental measurements and values calculated either with the present model or with the method of Chermak and Rimstidt (1989). A) Phases for parameterization; B) Verification phases.

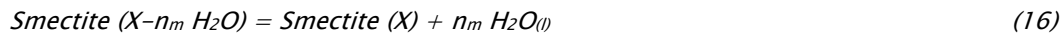
5.2 Predictive modeling of the thermodynamic properties of the hydration of clay minerals

In terms of stability, the measurements performed by Gailhanou (2005) indicate that hydration reactions may modify the stability of smectite by up to 2 logK units per mole, which is far from negligible. Those reactions are thus of importance, even for long term disposal concerns.

5.2.1 Development of a solid solution model

A tentative for modelling an adsorption-desorption isotherm had been proposed by Ransom and Helgeson (1994). The development reported here is an improvement of it and is described in more details by Vieillard et al. (2011). A more complex solid-solution had also been proposed by Vidal and Dubacq (2009), Dubacq et al. (2010).

Ransom and Helgeson (1994) consider the system hydrated smectite – anhydrous smectite + bulk water as a binary solid solution. The dehydration of a smectite is considered through the following reaction between hydrated and dehydrated end members:



where n_m represents the maximum number of moles of water that can be included in the smectite on the basis of an half-cell (*i.e.*, $\text{O}_{10}(\text{OH})_2$). This reaction is considered as a binary solid solution between an anhydrous end member, smectite – (X), and a fully hydrated end member, smectite – (X. $n_m \text{ H}_2\text{O}$), with an interlayer cation, X, bonded to a maximum of n_m moles of water.

The amount of interlayer water in a smectite is proportional to the mole fraction of hydrated end-member: $x \text{ H}_2\text{O} = n_m * x_{hs} = n_m * (1-x_{as})$, *i.e.* to the mole fraction of the hydrous end-member, x_{hs} or the anhydrous end-member, x_{as} . The mass action law for reaction (16) can be written as:

$$K = \frac{a_{as} * a_{\text{H}_2\text{O}}^{n_m}}{a_{hs}} \quad (17)$$

where K is the equilibrium constant for reaction (16), $a_{\text{H}_2\text{O}}$ is the activity of H_2O in the aqueous phase, and a_{hs} and a_{as} represent the activities of the hydrous and anhydrous smectite end-members of the solid solution, respectively. The activities of the hydrous (hs) and anhydrous (as) end members can be expressed in terms of mole fractions (x_{hs} and x_{as}) and activity coefficients (λ_{hs} and λ_{as}):

$$a_{as} = x_{as} * \lambda_{as} \quad (18)$$

$$a_{hs} = x_{hs} * \lambda_{hs} \quad (19)$$

Substituting the preceding equations into (17), the equilibrium constant, K, can be written as:

$$\log_{10} K = \text{Log} \left(\frac{x_{hs}}{1-x_{hs}} \right) + \log(\lambda_{hs}) - \log(\lambda_{as}) - n_m * a_{\text{H}_2\text{O}} \quad (20)$$

The solubility constant $\text{Log}_{10} K$ can be calculated from the enthalpy of hydration ΔH_{hyd}^0 and the entropy of hydration ΔS_{hyd}^0 at standard temperature and pressure:

$$\log_{10} K = \frac{(\Delta H_{\text{hyd}}^0 - T\Delta S_{\text{hyd}}^0)}{RT \ln(10)} \quad (21)$$

In that context, Vieillard et al. (2011) proposes an asymmetrical sub-regular binary solid solution where the excess molal Gibbs free energy of mixing (G_{xs}) is expressed as:

$$G_{xs} = x_{as} * (1 - x_{as}) * [W_{G_1} * x_{as} + W_{G_2} * (1 - x_{as})] \quad (22)$$

G_{xs} is described by two Margules parameters W_{G_1} and W_{G_2} . Since measured data are available for the enthalpy of hydration, the excess enthalpy of mixing and excess entropy of mixing can also be introduced:

$$H_{xs} = x_{as} * (1 - x_{as}) * [W_{H_1} * x_{as} + W_{H_2} * (1 - x_{as})] \quad (23)$$

$$S_{xs} = x_{as} * (1 - x_{as}) * [W_{S_1} * x_{as} + W_{S_2} * (1 - x_{as})] \quad (24)$$

where W_{H_1} , W_{H_2} , W_{S_1} , and W_{S_2} are temperature independent Margules parameters for the enthalpy and entropy.

5.2.2 Model results

Vieillard et al. (2011) have validated their asymmetric sub-regular model by (1) comparing the behavior of hydration-dehydration with experimental measurements on hetero-ionic and homo-ionic SWy-1 smectite samples at different temperatures; (2) comparing experimental integral enthalpy and entropy of hydration of the SWy1 smectite samples with calculated values; and (3) comparing the new results with those obtained for various smectites with different layer charges (Upton, MX80, Arizona).

Table 2. Number of hydrated water molecules and integral hydration properties (enthalpy, entropy and Gibbs free energy) in four homoionic SWy-1 montmorillonites.

P/P _o	0.1	0.2	0.4	0.6	0.8	1.0
K						
Nb H ₂ O	0.03	0.26	0.76	1.17	1.52	1.87
$\Delta\tilde{H}_{Hyd}$ (kJ mol ⁻¹)	-0.38	-3.53	-8.53	-11.13	-12.56	-13.28
$\Delta\tilde{S}_{Hyd}$ (JK ⁻¹ mol ⁻¹)	-1.2	-11.4	-27.3	-34.5	-37.6	-38.1
$\Delta\tilde{G}_{Hyd}$ (kJ mol ⁻¹)	-0.03	-0.12	-0.40	-0.83	-1.34	-1.93
Na						
Nb H ₂ O	0.00	0.12	1.25	2.49	3.51	4.28
$\Delta\tilde{H}_{Hyd}$ (kJ mol ⁻¹)	-0.03	-1.23	-9.41	-14.00	-16.25	-18.08
$\Delta\tilde{S}_{Hyd}$ (JK ⁻¹ mol ⁻¹)	0.0	-2.4	-19.1	-26.8	-30.8	-36.0
$\Delta\tilde{G}_{Hyd}$ (kJ mol ⁻¹)	-0.02	-0.52	-3.72	-6.01	-7.07	-7.34
Ca						
Nb H ₂ O	1.51	2.20	3.02	3.58	4.03	4.40
$\Delta\tilde{H}_{Hyd}$ (kJ mol ⁻¹)	-31.16	-39.75	-46.19	-48.65	-49.67	-50.00
$\Delta\tilde{S}_{Hyd}$ (JK ⁻¹ mol ⁻¹)	-67.2	-83.0	-92.9	-96.0	-97.1	-97.7
$\Delta\tilde{G}_{Hyd}$ (kJ mol ⁻¹)	-11.13	-15.01	-18.48	-20.03	-20.72	-20.88
Mg						
Nb H ₂ O	1.48	2.09	2.85	3.42	3.93	4.43
$\Delta\tilde{H}_{Hyd}$ (kJ mol ⁻¹)	-37.01	-45.66	-52.45	-55.33	-56.81	-57.64
$\Delta\tilde{S}_{Hyd}$ (JK ⁻¹ mol ⁻¹)	-88.3	-105.1	-115.4	-118.5	-119.8	-121.6
$\Delta\tilde{G}_{Hyd}$ (kJ mol ⁻¹)	-10.67	-14.32	-18.03	-20.01	-21.09	-21.39

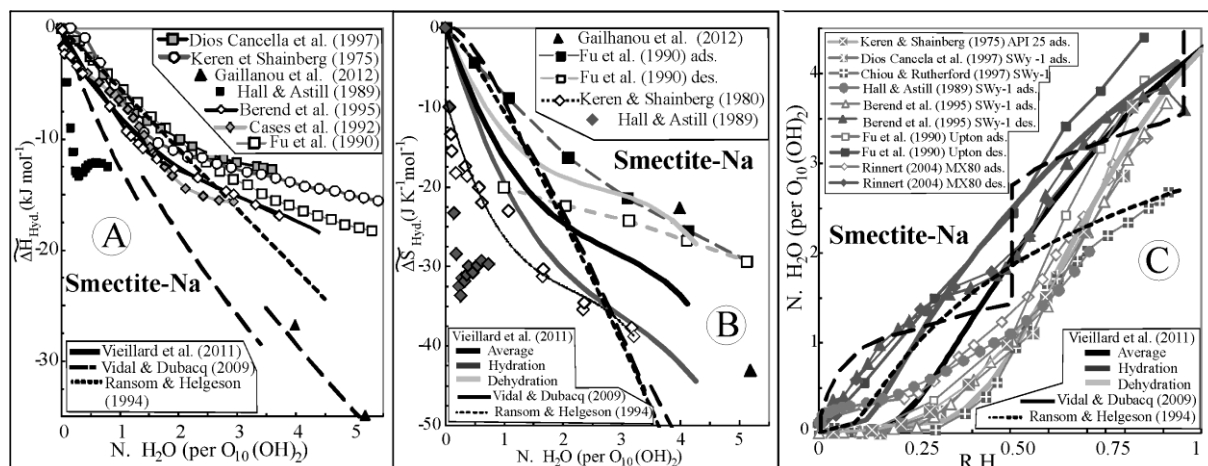


Figure 10. Integral thermodynamic entities of hydration versus the number of interlayer cations for different dioctahedral smectites saturated by Na: A) Integral enthalpy of hydration; B) Integral entropy of hydration; C) Experimental adsorption-desorption isotherms (symbols) and modelled isotherms (lines).

The predicted number of moles of water at any given relative humidity, the integral enthalpy, entropy and free energy of hydration for four homoionic SWy-1 montmorillonites (K, Na, Ca and Mg) are defined. In addition, the hydration thermodynamic properties and adsorption-desorption isotherms available for Na-smectites, from different sources, are displayed and compared with thermodynamic properties (enthalpy and entropy) and isotherms calculated using the models of Ransom and Helgeson (1994), Vidal and Dubacq (2009) and Vieillard et al. (2011).

Integral enthalpies of hydration modelled by Vieillard et al. (2011) is based on experimental measurements of heat of adsorption from Bérend et al. (1995) and Cases et al. (1992) encompasses nearly all experimental data with a slight overestimation. As the standard entropy of hydration is assumed constant in the models of Ransom and Helgeson (1994) and Vidal and Dubacq (2009), integral hydration enthalpy provided by these two previous models are nearly linear. Those obtained by Vidal and Dubacq (2009) exhibits three sections of curves corresponding to the three states of hydration (1, 2 and 3 water layers). Experimental data of Gailhanou et al. (2012) come from heat dissolution calorimetry measurements on MX80 sodic smectite exhibit a greater hydration enthalpy because of its high tetrahedral layer charge.

The integral hydration entropy modelled by Ransom and Helgeson (1994) and Vidal and Dubacq (2009) are the same. In the model by Vieillard et al. (2011), three calculated integral entropies of SWy1-Na-water system were plotted corresponding to the adsorption (dark greyed line), the desorption (light greyed line) and the theoretical equilibrium water-SWy1-Na (thick black line). The comparison of hydration-dehydration curve calculated in this work with those provided by Fu et al. (1990) shows opposite behaviors. Integral entropy values measured by Fu et al. (1990) during adsorption are less negative than those acquired during desorption. Using the model of Vieillard et al. (2011), this is the contrary. This difference is explained by the fact that in the experimental study of Fu et al. (1990), adsorption did follow desorption, while in the study by Vieillard et al. (2011), desorption did follow adsorption. However, the average integral hydration entropy curve calculated in this work (dark line) exhibits larger (more negative) values than those of Fu et al. (1990) but matches well with the two calorimetric values of entropy measured by Gailhanou et al. (2012) at two different hydration states (3.989 H₂O and 5.189 H₂O).

All adsorption - desorption isotherms measured on different sodic smectites are provided: MX80-Na , Na-Upton and Na-SWy-1. All these experimental isotherms have been corrected assuming a same amount of surface covering water molecules analogous to those of Na-SWy-1 given by Bérend et al. (1995) and Cases et al. (1992). It can be seen that the couple of calculated isotherms (adsorption - desorption) performed by Vieillard et al. (2011) matches well with the corrected experimental isotherms in the full range of relative humidity. The theoretical curve of equilibrium between water and Na-Smectite provided by Vidal and Dubacq (2009) encompasses the dehydration isotherm and exhibits three steps of hydration, while those proposed by Ransom and Helgeson (1994) displays a low number of moles of water close to saturation.

Given the dispersion of isotherm, the solid solution model of Vieillard et al. (2011) is able to reproduce rather correctly the isotherms of a Wyoming smectite.

6. Prediction of the thermodynamic properties of fictive end members

Modeling cement-clay interactions in the context of radioactive waste deep disposal implies to take advantage of a large database of clay minerals end-members in order to leave the reactions pathways as free as possible. In order to provide such a large database, we have used the predictive models detailed before. The latter are largely relying on directly measured thermodynamic constants, providing a rather secure predictive ability for this exercise.

The calculations are processed the following way:

- first formation enthalpies, entropies, the $C_p(T)$ functions and volumes are calculated for different compositions of clay minerals
- then formation enthalpies and entropies are combine in order to provide the Gibbs free energy
- finally, the equilibrium constant $\text{Log}K(T)$ is calculated as a function of temperature, using primary basic species included into the ThermoChimie 8.0 database.

The properties are listed in ThermoChimie data base, where estimated entropies are including a configurational term, calculated according to the method of Ulbrich and Waldbaum (1976). The thermodynamic properties of the hydrated clay mineral end members are also reported in ThermoChimie. Those have been calculated from the properties of the anhydrous end members. We then have used the hydration model from Vieillard et al. (2011) to calculate the number of H_2O moles, the enthalpies and entropies of hydration, for $P/P_0 = 1$ (water saturation). For the moment, the hydration model does not take into account the charge and its location in the TOT sheet.

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