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Thermodynamics of Hydration in Minerals: How to Predict These Entities

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Additional information is available at the end of the chapter

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1. Introduction

Many papers have suggested that several specific “types” of H₂O exist. These have been labelled variously as “zeolitic”, “loosely held”, “structural”, “crystal”, “tightly bound” and “external” [1-3]. These labels suggest both the differing apparent energies of H₂O as well as their differing apparent structural roles. Three useful distinctions can be made about H₂O in compounds:

1. H₂O that varies in content as a continuous function of temperature and pressure
2. H₂O that changes discontinuously at a unique temperature for a given pressure
3. H₂O that is sorbed to external surfaces

The first type (continuously varying H₂O) is characteristic of the zeolites and clay minerals and considers that most of the zeolites and clay minerals lose or gain H₂O in response to small changes in temperature and pressure over an extended temperature, relative humidity or the nature of cations in exchanged sites.

The second type of H₂O is similar in nature to that found in hydrates of salts and considers that dehydration occurs over narrow temperature intervals in some compounds. Some zeolites, like analcime and laumontite, do not exchange water at room temperature. This type can be called “hydrate” H₂O and has a specific position in the crystal structure. Hydroxides are excluded from this chapter because the H₂O molecule is not identified but is only virtually present as a hydroxyl OH.

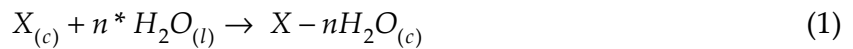
The third type of H₂O is externally sorbed to the crystal and may be referred to as external. This type is present in quantities much smaller than the H₂O present within the structure of any zeolite grain size. In the clay minerals, whose specific surfaces are greater than those of zeolites, the water located in inter-particle spaces, in inter-aggregate spaces and at the

surface of uncharged clays minerals indicates that a special status of H₂O may be different in the regimes of adsorption or of capillary condensation, and this is not considered in this chapter.

2. Definition of thermodynamic entities of hydration

In evaluating the thermodynamic quantities, it is important to define the standard state chosen for a given constituent. In the present study, the standard state for water is chosen as pure water at a temperature of 25°C with a vapour pressure of P_o, and for the minerals, the dry compound is at a temperature of 25°C with a vapour pressure of P=0.

The reaction of hydration may be expressed by the following reaction:

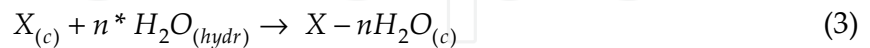


If we consider any standard thermodynamic entity of hydration $\Xi_{hyd,298}^{\circ}$ (enthalpy $\Delta H_{hyd,298}^{\circ}$, free energy $\Delta G_{hyd,298}^{\circ}$, entropy $\Delta S_{hyd,298}^{\circ}$, heat capacity $C_{p,hyd}$ and molar volume V_{Hyd} .) for a given mineral having n bounded molecules, the entity of hydration is related to the total formation entity $\Xi_{f,298}^{\circ}$ (enthalpy $\Delta H_{f,298.15}^{\circ}$, free energy $\Delta G_{f,298.15}^{\circ}$, entropy S_{298}° , heat capacity $C_{p,298.15}$ and molar volume V_{298}) of the mineral by the following:

$$\Xi_{hyd,298}^{\circ} = \Xi_{f,298}^{\circ}(X - nH_2O) - \Xi_{f,298}^{\circ}(X) - n * \Xi_{f,298}^{\circ}(H_2O_{liq}) \quad (2)$$

where $\Xi_{f,298}^{\circ}(X - nH_2O)$ and $\Xi_{f,298}^{\circ}(X)$ are the thermodynamic entity of formation of the mineral in the hydrated and dehydrated states, respectively, and $\Xi_{f,298}^{\circ}(H_2O_{liq})$ stands for the thermodynamic entity of formation of bulk water. The unit of the entity $\Xi_{hyd,298}^{\circ}$ is based per n moles of bound water or per mole of an anhydrous compound X.

The standard thermodynamic parameters of the hydration water can be calculated if the thermodynamic entities of formation (enthalpy $\Delta H_{f,298.15}^{\circ}$, free energy $\Delta G_{f,298.15}^{\circ}$, entropy S_{298}° , heat capacity $C_{p,298.15}$ and molar volume V_{298} .) of the anhydrous and hydrous end members are available in thermochemical tables or calculated from calorimetric measurements. However, the thermodynamic properties of the hydration water can be estimated by considering the hypothetical intra-crystalline reaction:



where H₂O_(hyd) represents the hydration water. The thermodynamics of the intra-crystalline reaction can be written as follows:

$$\Xi_{r,298}^{\circ} = \Xi_{f,298}^{\circ}(X - nH_2O) - \Xi_{f,298}^{\circ}(X) - n * \Xi_{f,298}^{\circ}(H_2O_{hydr}) \quad (4)$$

By assuming that the standard thermodynamic entities of the intra-crystalline reaction are equal to zero, *i.e.*, $\Xi_{r,298}^{\circ} = 0$, the standard values of the molar thermodynamic entity of the hydration water, $\Xi_{f,298}^{\circ}(H_2O_{Hyd})$, is finally obtained from eqs (2) and (4):

$$\Xi_{f,298}^0(H_2O_{Hyd}) = \left(n * \Xi_{f,298}^0(H_2O_{liq}) + \Xi_{hyd,298}^0 \right) / n \quad (5)$$

The aim of this chapter is to determine how the thermodynamic entity $\Xi_{f,298}^0(H_2O_{Hyd})$ of the hydration water varies in all inorganic compounds, such as minerals, salts, zeolites and clays. There are two main questions: 1) Is the thermodynamic entity of the hydration water strongly related to the physical-chemical properties of the inorganic compound or does it remain constant within a structural family of inorganic compounds? and 2) What are the adequate relationships that can predict the thermodynamic entity of the hydration water in any mineral?

3. Measurements of thermodynamics of hydration in minerals

Different methods of measurements of thermodynamic entities of hydration are presented in this section:

- Hydrofluoric acid solution calorimetry. The calorimetric measurements of the heat of dissolution of anhydrous and hydrated compounds provide the enthalpy of formation to form elements. The enthalpies of hydration are obtained by measuring the difference in the enthalpy of the solution in HF acid at approximately 70°C, of a hydrated and a dehydrated zeolite [4-6] or at 25°C in a HF - HNO₃ solution for clay minerals [7].
- Transposed-temperature drop calorimetry. The enthalpy of hydration data are obtained by measurements of the heat evolved from a sample dropped at room temperature into a calorimeter maintained at 700–800°C [8], [9-12]. One of the difficulties associated with this measurement includes the enthalpy effects because of the irreversible structural changes at 700–800°C.
- Adiabatic low temperature calorimetry. This is performed on the anhydrous and hydrated compounds to determine the third law of entropy for the zeolites [4-6] and clay minerals [7, 13].
- Heat of adsorption combined with adsorption-desorption isotherms. This method provides measurements of integral enthalpies of hydration as a function of the degree of hydration. Some of the difficult parameters to control include the amount of H₂O adsorbed by the sample (requires knowledge of the amount of H₂O in the sample while immersed in water), the accurate measurement of the initial state of dehydration and the potential for irreversible change in the zeolite structure during dehydration such that the sample does not re-adsorb its full capacity of H₂O during immersion [14]. For clays, the measurements of heat of adsorption were performed on eight homoionic SWy-1 montmorillonites [15-17] [18] [19] [20] and on vermiculites [21]. One advantage of the method is that it is a direct measurement of the enthalpy of hydration.
- Phase equilibria. The enthalpy of hydration can be determined from the phase equilibrium measurements of the isothermic method, which are plotted as Ln P (or Ln K) versus 1/T at a constant hydration state. The slopes of these lines give the enthalpy of hydration for zeolites [22], [23] and for montmorillonites [24-26].

- Gas-adsorption calorimetry. The enthalpies of hydration data are obtained by exposing a bed of zeolite to differing vapour pressures within a calorimeter [27]. One of the difficulties of this method is the kinetic limitations on attainment of equilibrium (slow kinetics requires a very sensitive and stable calorimeter). An advantage of the method is the capacity to measure partial molar enthalpies of hydration directly.
- Adsorption-desorption isotherms measured at different temperatures. With the Clausius-Clapeyron relationships, the ability to extract the integral and partial thermodynamic entities of hydration from isotherms at any two temperatures was developed by [28, 29] and applied on montmorillonite in [30] and [31]
- Thermochemistry and Raman spectroscopy. A combined study of thermochemistry and raman spectroscopy has been tested on zeolites [32] and clays [33] [34].

4. Inventory of different values from prediction methods of thermodynamic entities of hydration water

The thermodynamic data of liquid water and ice are displayed in Table 1. The formation properties of the hydration water may vary depending on the nature of the physical-chemical properties of the anhydrous compound [35]. In any case, when the minerals exist as hydrated phases, the presence of water molecules stabilises them. Thermodynamically, this corresponds to $\Delta G^0_{\text{hyd}} < 0 \text{ kJ mol}^{-1}$ or $\Delta G^0_f(\text{H}_2\text{O}_{\text{Hyd}}) < -237.14 \text{ kJ mol}^{-1}$, the value for bulk water at 25°C and 1 bar [36]. Additionally, the maximum entropy is for bulk water and implies that $S^0(\text{H}_2\text{O}_{\text{Hyd}}) < 69.95 \text{ J K}^{-1} \text{ mol}^{-1}$ [36]. The minimum entropy may be assessed by considering the entropy of Ih ice, as refined by Tardy et al. [37] (44.77 $\text{J K}^{-1} \text{ mol}^{-1}$). To give a minimum value for $\Delta G^0_f(\text{H}_2\text{O}_{\text{Hyd}})$ is more complicated. Ice cannot be of use, for example, because it is not stable at room temperature, and on the contrary, $\Delta G^0_f(\text{Ice Ih}) > \Delta G^0_f(\text{bulk water})$, with $-236.59 \text{ kJ mol}^{-1}$. For the enthalpy term $\Delta H^0_f(\text{H}_2\text{O}_{\text{Hyd}})$, because $\Delta G^0_{\text{hyd}} < 0 \text{ kJ mol}^{-1}$ and $S^0(\text{H}_2\text{O}_{\text{Hyd}}) < S^0(\text{bulk H}_2\text{O})$ for hydrated minerals, then ΔH^0_{hyd} must be negative or $\Delta H^0_f(\text{H}_2\text{O}_{\text{Hyd}}) < \Delta H^0_f(\text{bulk H}_2\text{O})$ with $-285.83 \text{ kJ mol}^{-1}$ [36]. For the heat capacity of hydration water, very few measurements have been actually performed so far.

| Families | Ref. | ΔH^0_f (kJ mol ⁻¹) | ΔG^0_f (kJ mol ⁻¹) | S^0 (J K ⁻¹ mol ⁻¹) | C_p (J K ⁻¹ mol ⁻¹) | V cm ³ mol ⁻¹ |
|--------------|------|---|---|---|---|--|
| Liquid water | 1 | -285.84±0.04 | -237.18±0.05 | 69.923±0.03 | 75.576 | 18.064 |
| Ice | 2,3 | -292.75±0.1 | -236.59±0.1 | 44.771±0.05 | 42.008 | 19.228 |

References: 1 – [36]; 2 – [37]; 3 – [35].

Table 1. Average thermodynamic entities (ΔH^0_f , ΔG^0_f , S^0 , C_p and V) of liquid water and ice.

Among the numerous methods of prediction of thermodynamics entities of compounds (salts, and minerals), only twelve are retained and exhibit different values of the thermodynamic entities of ice-like water obtained from the statistical results from the anhydrous and hydrated compounds (Table 2).

| Families | Ref. | Nb. comp | ΔH°_f (kJ/mole) | ΔG°_f (kJ/mole) | S° (J/K/mole) | C_p (J/K/mole) | V cm ³ /mole |
|-----------------------|------|-------------|-----------------------------------|-----------------------------------|---------------------------|---------------------|----------------------------|
| Sulphates & sulphites | 1 | 41 | -301.4±7.7 | -244.4±7.9 | 41.5±6.0 | 39±5.2 | 14.5±1.2 |
| Chlorates & Chlorides | 1 | 34 | -308.3±8.6 | -251.8±8.5 | 43.7±5.9 | 42±2.7 | 14.1±2.3 |
| Zeolites | 2 | 15 | | | 59.1 | | |
| Hydrates | 3 | 342 | -298.6±20.5 | -242.4 | 40.9 | 42.8 | 14.75 |
| Silicates | 4 | ? | | | 39.3±4.2 | | 13.7±0.5 |
| Silicates | 5 | 3 | | | 54.123 | | |
| Hydrates | 6 | ? | -297.06 | | | | |
| RE chlorides | 7 | 8 | -297 | | 46.4 | | |
| Binary comp. of Na | 8 | 42 | -297±8.3 | | | | |
| Silicates | 9 | 7 | | | | 43.5 | 14 |
| Silicates | 10 | 7 | -306.99±12.8 | | 44.1±2.0 | | 14.6±0.09 |
| Silicates | 11 | 6 | -292.37±4.6 | -239.91±5.7 | | | |
| Borates | 12 | 23 | -290.42 | -237.28 | 54.86 | | |
| U bearing minerals | 13 | 14 | -295.58 | -241.1 | | | |

References: 1 - [35]; 2 - [38]; 3 - [39]; 4 - [40]; 5 - [41]; 6 - [42]; 7 - [43]; 8 - [44]; 9 - [45]; 10 - [46]; 11 - [47]; 12 - [48]; 13 - [49].

Table 2. Average thermodynamic entities (ΔH°_f , ΔG°_f , S° , C_p and V) of hydration water obtained in different prediction models.

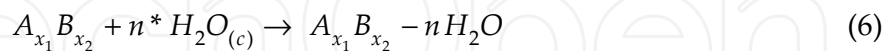
All of these models of predictions are built on a simple additive scheme and require knowledge of the thermodynamic entity of the anhydrous compound, the number of water molecules and the thermodynamic entity of formation of “ice-like” water or of hydration water obtained by statistical regressions. For each thermodynamic entity (enthalpy, free energy, entropy, heat capacity and molar volume), the values are significantly different within the nature of the compounds or minerals. For each prediction model, the nature of family, number of compounds and statistical errors are provided to check the extent and the validity of the model. There appear to be few models of prediction of free energies of hydration, which is the most useful parameter in geochemical modelling. The best way to reach this target is to combine the enthalpy and entropy of hydration. Despite the great diversity of the enthalpy of formation of the hydration water and its great error within different families of compounds, some recent and accurate models of prediction of the enthalpy of hydration are important to introduce for compounds such as salts, zeolites and clays minerals.

To improve the accuracy of prediction, the next section develops several models of prediction based on different kinds of minerals displaying recent measurements of the thermodynamic entities of the hydration water closely related either to the environmental conditions and or to the nature and chemical formulas of the anhydrous compounds.

5. Recommended models of prediction of thermodynamic entities

5.1. Enthalpy of formation

Salts: A model of the prediction of hydration enthalpy has been developed and tested on 349 different hydrates salts [50-52]. By considering the following reaction defining the hydration of a salt $A_{x_1}B_{x_2}$:



the enthalpy of hydration of the reaction (6) becomes

$$\Delta H_{hyd,298}^{\circ} = \Delta H_{f,298}^{\circ} (A_{x_1}B_{x_2} \cdot nH_2O) - \Delta H_{f,298}^{\circ} (A_{x_1}B_{x_2}) - n * \Delta H_{f,298}^{\circ} (H_2O_{(c)}) \quad (7)$$

where n is the number of molecules of crystalline water contained in the hydrate under consideration and $\Delta H_{f,298}^{\circ} (H_2O)_{(c)}$ represents the enthalpy of formation of ice. A parameter $\Delta_H(B^{z_2^-})A^{z_1^+}$ characterising the anhydrous salt $A_{x_1}B_{x_2}$, was defined as follows [50-52]:

$$\Delta_H(B^{z_2^-})A^{z_1^+} = \frac{1}{z_1 * z_2} \left[\Delta H_{f,298}^{\circ} (A_{x_1}B_{x_2}) - x_1 * \Delta H_{f,298}^{\circ} (A^{z_1^+}) - x_2 * \Delta H_{f,298}^{\circ} (B^{z_2^-}) \right] \quad (8)$$

This parameter is analogous to the enthalpy of dissolution of an anhydrous salt per equivalent (characterised by the product of charges of the cation and anion). The relationships of the enthalpy of hydration of a salt to the number of the molecules of water and to the nature of the salt is:

$$\Delta H_{hyd,298.15} = \alpha_{A^{z_1^+}} * (n)^a * \left[\Delta_H(B^{z_2^-})A^{z_1^+} + b \right] + \beta \quad (9)$$

where $\alpha_{A^{z_1^+}}$ and β are constants that depend on the nature of the cation $A^{z_1^+}$ present in the hydrate, n is the number of molecules of the water of crystallisation in the hydrate, and a and b are constants for all hydrates and respectively equal to 0.791 and -80.0 kJ mol⁻¹ [50-52]. Eq. (9) shows that the enthalpy of hydration is closely related to the nature of the cation in the anhydrous salt, to the number of water molecules in the chemical formula and to the nature of the anhydrous salt.

The enthalpy of the formation of ice used in Eq. (7) [50-52] comes from Robie & Waldbaum [53] and is equal to -279.8 kJ mol⁻¹. As this value is very different from those given in table 1, the values of coefficients ($\alpha_{A^{z_1^+}}$, β , a and b) of Eq. (9) need to be determined with $\Delta H_{f,298}^{\circ} H_2O_{(ice)} = -292.75$ kJ mol⁻¹ by a minimisation technique of the square difference between the measured and calculated heat of hydration. The values of a and b are assumed constants for all hydrated salts and are a= 0.612 and b= 17.07; Eq (9) becomes:

$$\Delta H_{hyd,298.15} = \alpha_{A^{z_1^+}} * (n)^{0.612} * \left[\Delta_H(B^{z_2^-})A^{z_1^+} + 17.07 \right] + \beta \quad (10)$$

The values of $\alpha_{A^{z+}}$ and β for the different salts of cation A^{z+} are given in table 3 with the respective standard deviations and % errors of the predicted enthalpy of formation of the hydrated salts.

An example is given by considering the data of all of the sodium salts displayed in Figure 1A and shows the great variation of the enthalpy of hydration having the same number as the crystalline water. The different straight lines are obtained from Eq. (10) with values of $\alpha_{A^{z+}}$ and β for Na^+ and are plotted for the different values of the number of crystalline water molecules and the nature of the crystalline salts ($\Delta_H(B^{z-})A^{z+}$). For a given anhydrous salt (same value of $\Delta_H(B^{z-})A^{z+}$), the enthalpy of hydration per mole of water appears to not be constant but decreases when the number of molecules of the crystalline water increases. Figure 1B displays the enthalpy of crystalline water versus the nature of the anhydrous salt showing the great disparity and shows that the enthalpy of the crystalline water in all of the sodic salts is more negative than those of the hexagonal ice. When the number of crystalline water molecules of any salt increases, the enthalpy of formation of the crystalline water decreases from large values ($\text{NaOH} \cdot \text{H}_2\text{O}$; $\Delta H_{f,298}^\circ \text{H}_2\text{O} = -309.25 \text{ kJ mol}^{-1}$) to values close to those of ice ($\text{Na}_2\text{Se} \cdot 16 \text{ H}_2\text{O}$; $\Delta H_{f,298}^\circ = -297.22 \text{ kJ mol}^{-1}$) and are different from the average value for 61 Na salts ($\Delta H_{f,298}^\circ = -297.74 \text{ kJ mol}^{-1}$).

| Cations | $\alpha_{A^{z+}}$ | β | Nb. of data | % error ¹ | Std dev. (kJ/mol H ₂ O) |
|-------------------------------|-------------------|---------|-------------|----------------------|---------------------------------------|
| Li ⁺ | -0.277 | -0.341 | 19 | 0.34 | ± 3.58 |
| Na ⁺ | -0.294 | 1.759 | 61 | 0.29 | ± 3.44 |
| K ⁺ | -0.115 | -9.168 | 15 | 0.66 | ± 10.70 |
| Rb ⁺ | -0.360 | -6.769 | 6 | 0.29 | ± 3.38 |
| Cs ⁺ | -0.577 | 18.954 | 4 | 0.48 | ± 6.35 |
| Be ⁺² | -0.485 | -3.068 | 7 | 0.25 | ± 3.48 |
| Mg ⁺² | -0.312 | -10.708 | 21 | 0.43 | ± 5.39 |
| Ca ⁺² | -0.270 | -3.892 | 25 | 0.44 | ± 4.64 |
| Sr ⁺² | -0.349 | -1.894 | 20 | 0.32 | ± 5.93 |
| Ba ⁺² | -0.327 | -4.637 | 19 | 0.80 | ± 5.31 |
| Zn ⁺² | -0.211 | -16.461 | 12 | 0.44 | ± 6.57 |
| Cd ⁺² | -0.322 | 2.266 | 8 | 0.33 | ± 4.29 |
| Cu ⁺² | -0.433 | -1.791 | 11 | 0.65 | ± 4.22 |
| Ni ⁺² | -0.176 | -18.056 | 10 | 0.46 | ± 2.81 |
| Co ⁺² | -0.260 | -2.296 | 11 | 0.36 | ± 3.60 |
| Fe ⁺² | -0.136 | -17.806 | 6 | 0.18 | ± 1.58 |
| Mn ⁺² | -0.238 | -5.144 | 15 | 0.25 | ± 6.14 |
| Cr ⁺² | -0.478 | 31.459 | 3 | 0.28 | ± 1.77 |
| UO ₂ ⁺² | -0.247 | -7.945 | 18 | 0.35 | ± 4.80 |

1: the % error weighs the difference (in %) between the measured and predicted enthalpy of the formation of the hydrated salts.

Table 3. Values of $\alpha_{A^{z+}}$, β , number of data, % error and statistical error per moles of crystalline water.

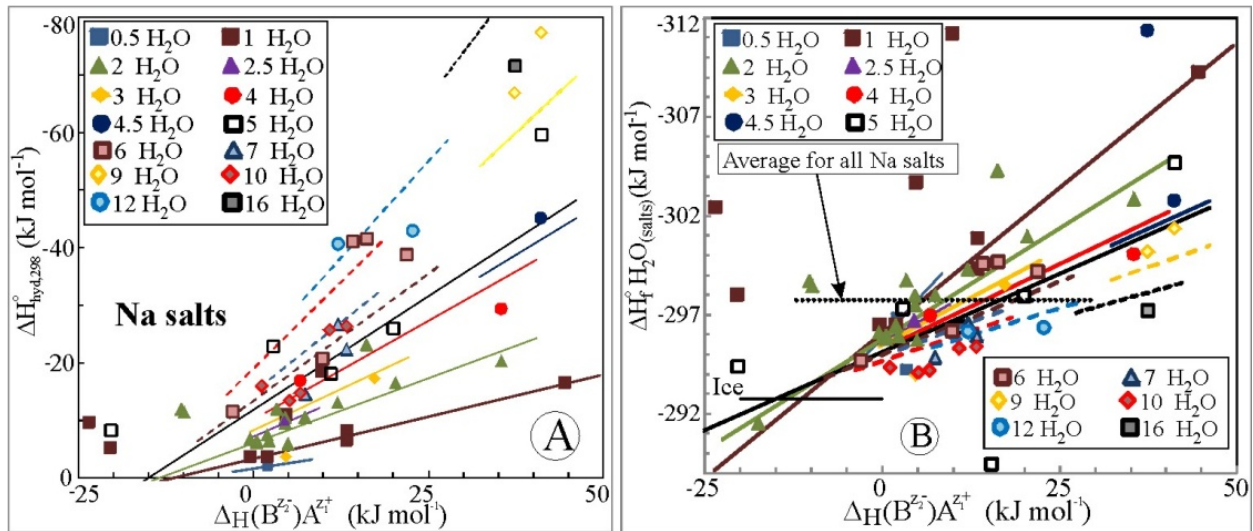


Figure 1. A – Hydration enthalpy of sodium salts versus the parameter $\Delta_H(B^{2-})A^{z+}$; B – Enthalpy of the formation of the crystalline water versus the parameter $\Delta_H(B^{2-})A^{z+}$.

Zeolites: The anhydrous compound X (reaction 1) is a zeolite with the following formula:

$$\left(\sum_{i=1}^{i=n_c} A_i \right) (Al_{n_{Al}} Fe_{n_{Fe}} Si_{n_{Si}}) O_N, \text{ in which Al, Fe and Si represent the framework with different}$$

channels occupied by various exchangeable cations present, which are represented by A^{z+} . A compilation of the average hydration enthalpies per mole of water of 145 diversely originating zeolites measured using different technical methods [54] provided 76 data points from the transposed-temperature drop calorimetry (TTDC), 57 data points from the immersion calorimetry (IC), 6 data points from the phase equilibriums (PE), 5 data points from the gas-adsorption calorimetry (GAC) and 3 data points from the hydrofluoric acid calorimetry (HF).

From the selected average enthalpies of hydration of the different zeolites with their chemical formulas (145 data points), a regression equation for the enthalpy of hydration per mole of water is proposed [54]:

$$\Delta H_{Hyd-W} = - \left(\frac{Al}{Si} \right)^* e^{[a + b * WP]} \quad (11)$$

where coefficients a and b are

$$a = 4.664 - 2.787 * \left(\frac{Al}{(Al + Si)} \right) + 0.056 * FD_{anh.} - 0.003 * \left(\Delta_H O^- \text{site } A \right) \quad (12)$$

$$b = -1.52 + 0.0047 * \left(\Delta_H O^- \text{site } A \right)^* \left(\frac{Al}{Si} \right) \quad (13)$$

Coefficients of Eqs. (11) (12) and (13), such as the ratio Al/Si , $Al/(Al+Si)$, $FD_{anh.}$, $\Delta_H O^- \text{(site } A)_{(aq)}$ and WP , represent the extra-framework charge, the ratio of tetrahedral

substitution, the framework density of the anhydrous zeolite, the average cation electronegativity in the exchange site and the intracrystalline water porosity, respectively. All of these parameters can be calculated from the chemical formula and the unit cell volume for any zeolite.

The framework density (FD) [55, 56] represents the number of tetrahedral atoms per 1000 Å³ and are obtained as:

$$FD_{anh.} = \left[(n_{Al} + n_{Fe} + n_{Si}) / Unit\ cell\ Vol \right] * 1000 \quad (14)$$

The electronegativity of site A^{z+}, defined by ΔH^oO⁼ (site A), represents the weighed average of ΔH^oO⁼ M^{z+}(aq) of n_c different cations in the exchanged site A:

$$\Delta_H O^{\circ} (site.A) = \frac{\sum_{i=1}^{i=n_c} n_i * x_i * (\Delta_H O^{\circ} M_{aq}^{z_i+})}{x_A} \quad (15)$$

The number of oxygens balancing site Mz+ (in extra-framework sites) is then:

$$x_A = \sum_{i=1}^{i=n_c} n_i * x_i \quad (16)$$

The parameter ΔH^oO⁼ Mz+ (aq) characterises the electronegativity for a given cation M^{z+} and is defined as the difference between the enthalpy of formation of the corresponding oxides ΔH_f^o(M_iO_{x_i})_(c) and the enthalpy of formation of the corresponding aqueous cation ΔH_f^o(M_i^{z_i+})_(aq):

$$\Delta_H O^{\circ} M_{aq}^{z_i+} = \frac{1}{x_i} \left[\Delta H_f^{\circ} (M_i O_{x_i})_{(c)} - \Delta H_f^{\circ} (M_i^{z_i+})_{(aq)} \right] \quad (17)$$

where z is the charge of the cation M^{z+} and x is the number of oxygen atoms combined with one atom of M in the oxide (x = z/2), such that the difference in Eq. (17) refers to one oxygen atom. A set of internally consistent values was presented by Vieillard & Mathieu [54] and is given in Table 4.

The total intracrystalline pore volume, WP, was introduced by Barrer [57] for determining the volume of liquid water that can be recovered thorough the outgassing of the fully hydrated zeolite. Assuming that the unit cell volume of zeolitic water is the same as that of liquid water (V_{u.c. H₂O} = 29.89 Å³), during the hydration-dehydration processes, the water porosity (WP) can be calculated as the volume of liquid water in 1Å³ of crystal and is expressed as follows:

$$WP = \frac{29.89 * n_{H_2O}}{(V_{u.c. hydr.})} \quad (18)$$

where $V_{u.c. hyd.}$ represents the unit cell volume of a hydrated zeolite containing n_{H_2O} water molecules. Assuming that the number of water molecules n_{H_2O} varies from 0 to $n_{H_2O max}$, the unit cell volume of a zeolite can be directly related to the number of water molecules. Although such variations in the unit -cell volume do occur, let us assume a linear variation in the unit-cell volume as a function of the number of water molecules:

$$V_{u.c. hyd.} = V_{u.c. anh.} + k * n_{H_2O} \quad (19)$$

where $V_{u.c. anh.}$ represents the unit-cell volume of the anhydrous zeolite. Parameter k weights the variation in the unit-cell volume between an anhydrous zeolite and a fully hydrated zeolite per one water molecule. This parameter can be calculated from the available unit-cell volumes of anhydrous and fully hydrated zeolites. Thus, knowledge of the number of water molecules and the unit-cell volume of anhydrous and hydrated zeolites is required for the calculation of the water porosity:

$$WP = \frac{29.89 * n_{H_2O}}{(V_{u.c. anh.} + k * n_{H_2O})} \quad (20)$$

| Ions | $\Delta_{H^+}O=M^{z+}(aq)$ (kJ mol ⁻¹) | Ions | $\Delta_{H^+}O=M^{z+}(aq)$ (kJ mol ⁻¹) |
|-----------------------|---|-----------------------|---|
| Li ⁺ (aq) | -40.90 | Ca ⁺² (aq) | -92.1 |
| Na ⁺ (aq) | 65.80 | Mg ⁺² (aq) | -134.6 |
| K ⁺ (aq) | 141.00 | Fe ⁺² (aq) | -181.58 |
| Rb ⁺ (aq) | 163.24 | Mn ⁺² (aq) | -164.4 |
| Cs ⁺ (aq) | 170.0 | Zn ⁺² (aq) | -197.07 |
| Ba ⁺² (aq) | -15.6 | La ⁺³ (aq) | -124.8 |
| Sr ⁺² (aq) | -40.4 | H ⁺ (aq) | -285.83 |

Table 4. Parameter $\Delta_{H^+}O=M^{z+}(aq)$ of selected cations [54].

By eliminating 9 erroneous data points [54], the regression coefficient for 136 data is $R^2=0.880$, with a standard error of ± 3.46 kJ mol⁻¹ for all data, regardless of the nature of the experimental data. Figure 2 displays the predicted enthalpy of hydration of zeolitic water calculated from Eqs. (11) (12) and (13) versus the experimental enthalpy of hydration coming from the different technical measurements. Regression coefficients and standard errors are different within the two main groups: $R^2=0.88$ and std. err. = ± 3.41 kJ mol⁻¹ for TTDC data (67 data points), $R^2=0.658$ and std. err. = ± 2.66 kJ mol⁻¹ for the "IC" data (57 data points).

When Al/Si and $Al/(Al+Si) = 0$, the hypothetical integral enthalpy of water in zeolites obtained by the extrapolation of Eq. (11) is 0, which corresponds to the enthalpy of hydration of water in cordierite (2.2 ± 1.6 kJ mol⁻¹ from Carey [58]). Unlike zeolites, the water in cordierite is not coordinated by cations, so the molecular environment of H₂O in cordierite is similar to that of H₂O in water.

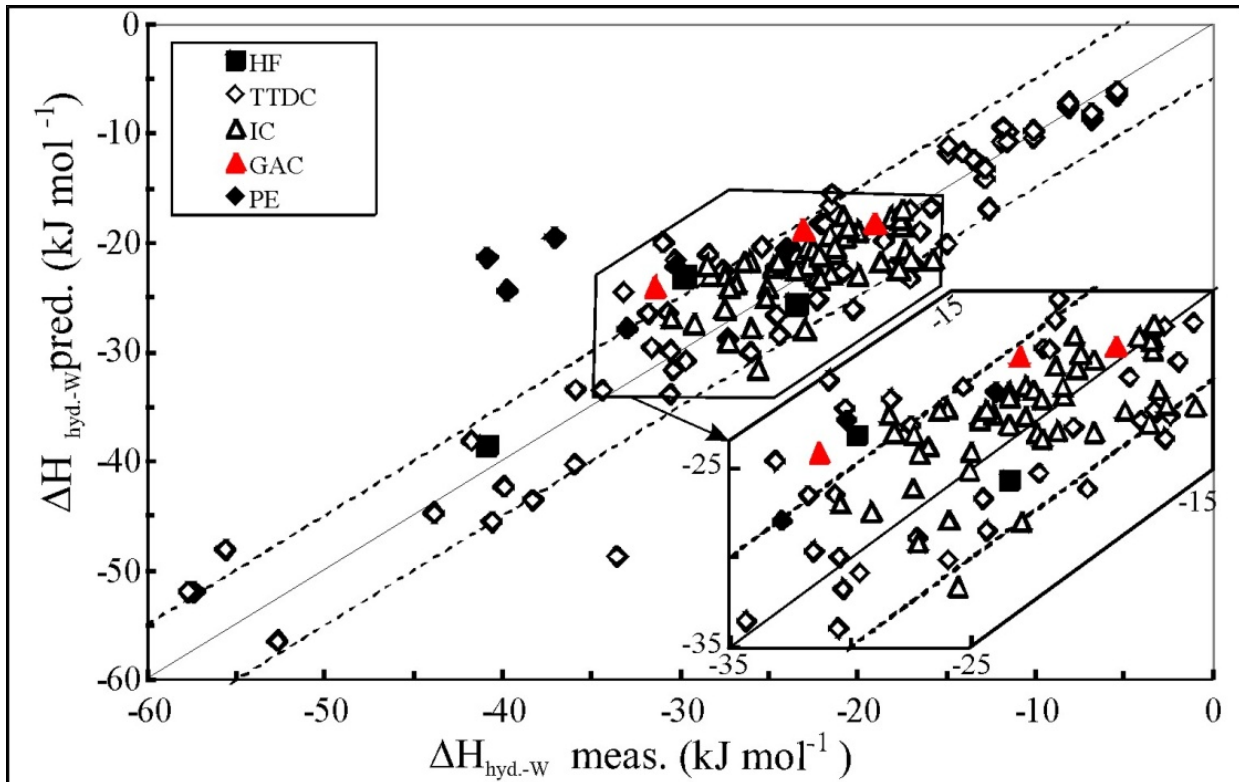


Figure 2. Predicted enthalpy of the hydration of zeolitic water calculated from Eq. (11) versus the experimental enthalpy of hydration using different technical measurements.

A detailed computation of the enthalpy of hydration is given as an example for three natural clinoptilolites (-Ca, -Na and -K) with the following chemical formula given by [22]:

- Clinoptilolite-Na: $(\text{Ca}_{0.12}\text{Mg}_{0.29}\text{K}_{0.75}\text{Na}_{5.21})(\text{Al}_{6.78}\text{Fe}_{0.06}\text{Si}_{29.2})\text{O}_{72.05}-21.3\text{H}_2\text{O}$
- Clinoptilolite-K: $(\text{Ca}_{0.13}\text{Mg}_{0.25}\text{K}_{5.84}\text{Na}_{0.27})(\text{Al}_{6.85}\text{Fe}_{0.1}\text{Si}_{29})\text{O}_{71.9}-18.5\text{H}_2\text{O}$
- Clinoptilolite-Ca: $(\text{Ca}_{2.34}\text{Mg}_{0.57}\text{K}_{0.9}\text{Na}_{0.18})(\text{Al}_{6.7}\text{Fe}_{0.017}\text{Si}_{29})\text{O}_{71.8}-21.9\text{H}_2\text{O}$

The values of the ratio Al/Si yield a constant value of 0.235. The electronegativity of the exchangeable site A^{z+} for clinoptilolite-Na is, for example, the average electronegativity of four cations (Na^+ , K^+ , Ca^{2+} and Mg^{2+} (table 4)) as follows:

$$\Delta_{\text{H}}\text{O}^-(\text{site.A}) = \frac{2.607 * (\Delta_{\text{H}}\text{O}^-\text{Na}_{\text{aq}}^+) + 0.375 * (\Delta_{\text{H}}\text{O}^-\text{K}_{\text{aq}}^+) + 0.12 * (\Delta_{\text{H}}\text{O}^-\text{Ca}_{\text{aq}}^{2+}) + 0.29 * (\Delta_{\text{H}}\text{O}^-\text{Mg}_{\text{aq}}^{2+})}{3.39} \quad (21)$$

i.e., $\Delta_{\text{H}}\text{O}^-(\text{site.A}) = 51.42 \text{ kJ mol}^{-1}$.

The unit-cell volume of the anhydrous clinoptilolite-K (V u.c.) is 2019.51 \AA^3 [59]. This means that there are 35.95 tetrahedral atoms ($6.95+0.1+29$) in 2019.51 \AA^3 ; which indicates that $\text{FD}_{\text{anh.}} = 17.8$ tetrahedral atoms in 1000 \AA^3 . The unit-cell volume of the hydrated clinoptilolite-K (at saturation or fully hydrated) with 18.5 moles of zeolitic waters is 2089.50 \AA^3 [54], which is slightly greater than the anhydrous form and allows the setting of the relationship of water porosity versus the number of hydration water moles:

$$WP = \frac{29.89 * n_{H_2O}}{(2019.51 + 3.78 * n_{H_2O})} \quad (22)$$

From these previous examples, the parameters requested for the prediction of the enthalpy of hydration are displayed in table 5 for the three clinoptilolites (-Na, -K and -Ca).

| Zeolite minerals | V u.c. anh. (Å ³) | Vu.c. hydr. (Å ³) | k | Δ _H O ⁼ Site A kJmol ⁻¹ | FD. Anh. | WP | Al/Si |
|--------------------|----------------------------------|----------------------------------|------|--|-------------|------|-------|
| Clinoptilolite -Na | 2000.00 ¹ | 2140.00 ¹ | 6.35 | 51.39 | 18.02 | 0.31 | 0.23 |
| Clinoptilolite -K | 2019.51 ² | 2089.50 ² | 3.78 | 109.16 | 17.80 | 0.26 | 0.24 |
| Clinoptilolite -Ca | 2019.51 ² | 2089.50 ² | 3.20 | -64.60 | 17.78 | 0.31 | 0.23 |

1 - [60]; 2 - [59]

Table 5. Unit-cell volume of hydrated and anhydrous clinoptilolite, factor k (eq. 20), mean Δ_HO⁼A^{z+} (site A), framework density and ratio Al/Si for 3 clinoptilolites (-Na, K and -Ca).

From the values given in table 5, the enthalpy of hydration of the zeolitic water, Δ_HH_{yd-W}, can be computed with Eqs. (11), (12) and (13) and are close to experimental values from [22] (Table 6).

The model of the computation of the enthalpy of hydration of the hydration water represents a very useful tool and contributes to the knowledge of enthalpies of formation of hydrated zeolites from anhydrous ones [61].

A useful method for avoiding complications at the outset of a thermodynamic analysis is to emphasise the H₂O rather than the zeolite structure. Using such an approach, the equilibriums can be considered as the equilibrium between the H₂O in the fluid-vapour phase and the H₂O in the zeolite. According to the definition of equilibrium, the chemical potential of H₂O in the vapour phase must equal the chemical potential of the H₂O component in the zeolite. Any series of measurements of the amount of H₂O in zeolite at a known fugacity (or partial pressure of H₂O under ideal gas conditions) provides the basis for the thermodynamic description of the system. The most elegant approach to develop a thermodynamic formulation is to know the partial molar enthalpy of hydration, Δ \bar{H} , and the partial molar entropy Δ \bar{S} . A constant partial molar enthalpy of hydration indicates an ideal mixing of the H₂O.

| Zeolite minerals | Δ _H H _{yd-W} | Δ _H H _{yd-W} | References |
|--------------------|---|---|------------|
| | predicted (kJ mol ⁻¹ H ₂ O) | measured (kJmol ⁻¹ H ₂ O) | |
| Clinoptilolite.-Na | -22.20 | -30.17 | [22] |
| Clinoptilolite -K | -20.24 | -23.97 | [22] |
| Clinoptilolite-Ca | -29.03 | -32.87 | [22] |

Table 6. Predicted and experimental enthalpy of hydration, Δ_HH_{yd-W} of clinoptilolites -Na, -K and -Ca.

The bulk enthalpy of hydration or the integral enthalpy of hydration can be used as the product of the enthalpy of hydration of the water times the number of zeolitic water:

$$\Delta\tilde{H}_{Hyd-Z} = (\Delta H_{Hyd-W}) * n_{H_2O} = \left[-\left(\frac{Al}{Si}\right)^* e^{(a+b*WP)} \right] * n_{H_2O} \quad (23)$$

As the integral hydration enthalpy $\Delta\tilde{H}_{Hyd-Z}$ is the integral function of the partial molar enthalpy hydration from $n_{H_2O} = 0$ (corresponding to an anhydrous zeolite) to a maximum value of $n_{H_2O,max}$ (corresponding to the fully hydrated zeolite), the partial molar enthalpy of hydration relative to the liquid water, $\Delta\bar{H}$, which is the derivative function of $\Delta\tilde{H}_{Hyd-Z}$, becomes:

$$\Delta\tilde{H}_{Hyd-Z} = \frac{1}{n_{H_2O}} \int_{n=0}^{n=n_{H_2O}} \Delta\bar{H} * dn \quad (24)$$

$$\Delta\bar{H} = \left[-\left(\frac{Al}{Si}\right)^* e^{\left(a + b * \left(\frac{29.89 * n_{H_2O}}{(V_{u.c.anh.} + k * n_{H_2O})} \right) \right)} * \left(1 + \frac{29.89 * b * V_{u.c.anh.} * n_{H_2O}}{(V_{u.c.anh.} + k * n_{H_2O})^2} \right) \right] \quad (25)$$

The fractional water content can be obtained if the maximum number of zeolitic waters is known at the saturation state and is equal to:

$$\theta = \frac{n_{H_2O}}{n_{H_2O,max.}} \quad (26)$$

From values of table 5, the partial molar enthalpy of clinoptilolites K, Na and Ca can be calculated versus the fractional water content and plotted in Figure 3 with the experimental partial molar enthalpies measured from immersion calorimetry [62] and from thermogravimetry [22]. The modelled values of the partial molar enthalpy for the three clinoptilolites appear to be closer to the data from the immersion calorimetry than from thermogravimetry. The second important point is the fact that the calculated and experimental partial molar enthalpy of hydration has a similar behaviour.

The partial molar enthalpy of hydration per mole of H₂O increases smoothly from low water content to high θ and indicates that the H₂O in clinoptilolites occupies a continuum of energetic states. This is not the case for chabazite-Ca [23], which exhibits three energetically distinct types of H₂O.

This shows that, within different zeolites with the same exchangeable cation, the partial molar enthalpy as a function of the hydration degree may display different functions. This is the reason why the fundamental relationship verifying the enthalpy of hydration by means

of the chemical composition and the accurate knowledge of the unit-cell parameters of anhydrous and hydrated zeolites needs to be improved with new data of hydration enthalpy of the partially hydrated zeolites on the one hand and a better fit of the effective water porosity as a function of the hydration degree on the other hand. Then, the thermodynamic description of the hydration-dehydration process can be modelled as a function of pressure and temperature with the contribution of predicted enthalpies of hydration and entropies of hydration.

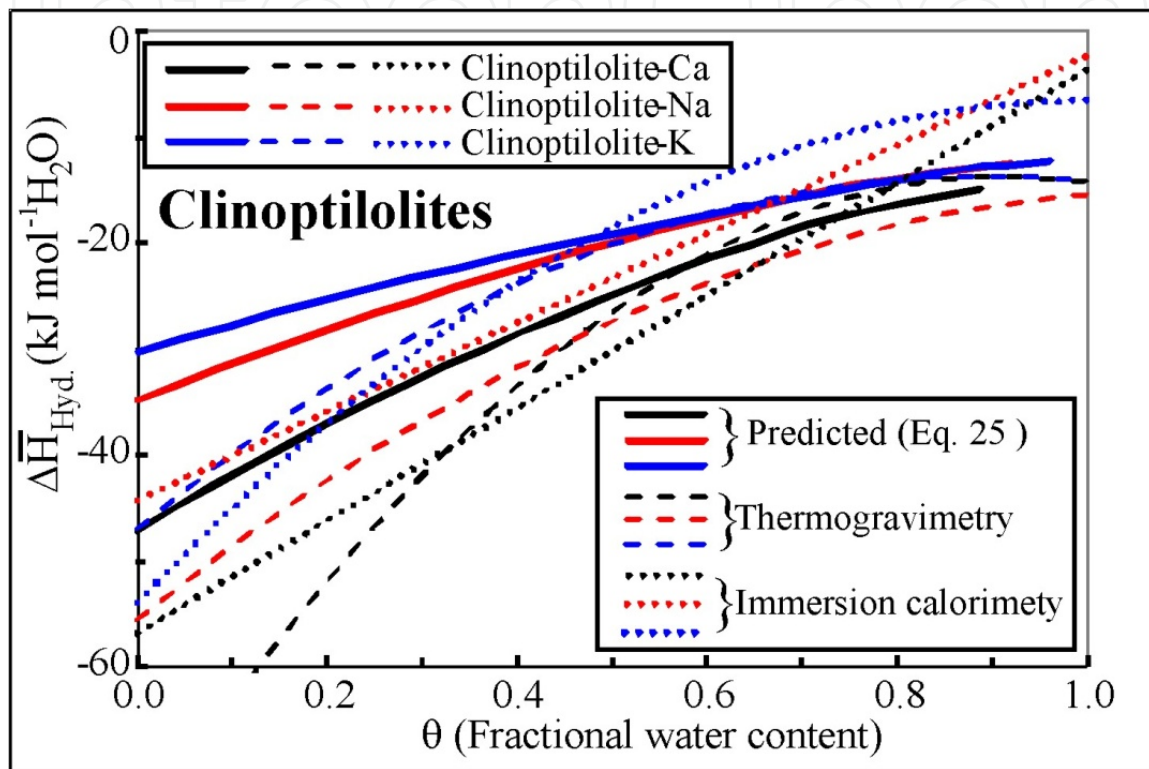


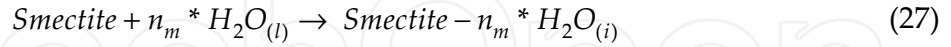
Figure 3. Partial molar enthalpy of hydration of K-, Na- and Ca- clinoptilolites derived from a model in [54], immersion calorimetry [62] and thermogravimetry results [22]

Clay minerals:

Unlike zeolites, smectites are clearly not inert phases, as the particles size increases with the relative humidity [15]. Adsorbed water is distributed throughout the interlayer space, the outer surfaces of particles and the open pores space in the sample. [15-17] provided measured values of the surface covering waters for both the hydration and dehydration reactions of a set of eight homo-ionic SWy-1 montmorillonites saturated by alkali and alkaline-earth cations from their BET specific surface area (Table 1) and their basal spacing variations with relative humidity. To quantify the effective amount of water involved in the hydration reaction, the amount of poral H₂O must be quantified and subtracted from the total amount of H₂O taken up by the clay sample. The number of external surface water molecules (expressed in mmol/g dry clay) can be expressed as a function of relative humidity [63]. There are numerous papers about the adsorption-desorption isotherms performed on various clays minerals, but few are devoted to the acquisition of enthalpy of

hydration-dehydration on SWy-1 [15-17, 64] [18, 19, 30] [20] [34] [24, 26, 65] [25] and on vermiculites [21].

All recent predictive models of the hydration of smectites are based on an approach that uses the solid solution initiated by Ransom & Helgeson [66]. The hydration of a smectite is considered through the following reaction between hydrated and dehydrated end-members:



where n_m represents the maximal number of moles of water that can be included in the smectite on the basis of a half-cell (i.e., $\text{O}_{10}(\text{OH})_2$). One considers the interlayer water $\text{H}_2\text{O}_{(i)}$ (where subscript i stands for interlayer) as a variable weighing the hydration ratio. The amount of interlayer water in a smectite is proportional to the mole fraction of hydrated end-member: $x * \text{H}_2\text{O} = n_m * x_{hs} = (1 - n_m) * x_{as}$; to the mole fraction of the hydrous end-member, x_{hs} or to the anhydrous end-members x_{as} . Ransom & Helgeson [66] considered the system hydrated smectite – anhydrous smectite + bulk water as a strictly regular binary solid solution by considering the free energy only. Thus, the excess free energy of mixing can be expressed as follows:

$$G_{xs} = x_{as} * (1 - x_{as}) * W_G \quad (28)$$

where W_G is an excess mixing constant. The integral Gibbs free energy of hydration is:

$$\Delta \tilde{G}_{Hyd} = x_{hs} * \Delta G_{Hyd,298}^\circ + x_{hs} * (1 - x_{hs}) * W_G \quad (29)$$

in which $\Delta G_{Hyd,298}^\circ$ is the standard free energy of hydration. The previous parameter and W_G are determined only from adsorption isotherms by assuming a maximal number of moles of interlayer water fixed to 4.5 moles. As there are no experimental measurements of heat of adsorption, the standard enthalpy of hydration, $\Delta H_{Hyd,298}^\circ$, is determined from $\Delta G_{Hyd,298}^\circ$ by assuming a constant value of $S_{298}^\circ \text{H}_2\text{O}_{(i)}$ equal to $55.02 \text{ J K}^{-1} \text{ mol}^{-1}$ [67]. From calculated $\Delta H_{Hyd,298}^\circ$, the standard enthalpy of formation of the interlayer water, $\Delta H_{f,298}^\circ(\text{H}_2\text{O})_i$, is given in table 7.

Vidal et al. [68-69] have assumed that a smectite could be considered strictly regular solid solutions between four end-members with 0.7 H_2O , 2 H_2O , 4 H_2O , and 7 H_2O . Those compositions correspond to four different hydrated states (with 0, 1, 2, and 3 water sheets, respectively). For any strictly regular solid solution, the integral enthalpy of hydration is expressed as the following:

$$\Delta \tilde{H}_{Hyd} = x_{hs} * \Delta H_{Hyd,298}^\circ + x_{hs} * (1 - x_{hs}) * W_H \quad (30)$$

with

$$\Delta H_{hyd,298}^0 = n_m * \left[\Delta H_{f,298}^0(\text{H}_2\text{O}_{(i)}) - \Delta H_{f,298}^0(\text{H}_2\text{O}_{liq}) \right] \quad (31)$$

The hydration enthalpy is retrieved from data of [24] for montmorillonite –Na and –K and derived from differential heats of adsorption obtained from the measurements of the heat of immersion [18, 20] for Na-, Ca- and Mg- montmorillonite. Thus, an integral enthalpy of hydration $\Delta H_{f,298}^{\circ}(H_2O)_i$ is provided for each of the four solid solutions with n_m equal to 0.7, 2, 4 and 7 and is given in table 7. Vieillard et al. [63] consider the hydration of a smectite to be an asymmetrical regular solid solution between anhydrous and hydrated smectite.

| Units (kJ mol ⁻¹) | H ₂ O | Cs | Rb | K | Na | Ba | Sr | Ca | Mg |
|---|------------------|---------|---------|---------|---------|---------|---------|---------|---------|
| $\Delta H_{f,298}^{\circ}(H_2O)_i$ ¹ | 4.5 | -289.93 | -290.23 | -290.45 | -291.25 | -294.14 | -294.57 | -294.86 | -295.71 |
| $\Delta H_{f,298}^{\circ}(H_2O)_i$ ² | 0-0.7 | | | -295.50 | -299.71 | | | -301.43 | -302.86 |
| W_{H^2} | | | | 0. | 0. | | | 0. | 0. |
| $\Delta H_{f,298}^{\circ}(H_2O)_i$ ² | 0-2 | | | -293.58 | -295.90 | | | -298.60 | -300.05 |
| W_{H^2} | | | | -10. | -10. | | | -10. | -10. |
| $\Delta H_{f,298}^{\circ}(H_2O)_i$ ² | 0-4 | | | -291.96 | -293.83 | | | -296.25 | -297.62 |
| W_{H^2} | | | | -10. | -10. | | | -10. | -10. |
| $\Delta H_{f,298}^{\circ}(H_2O)_i$ ² | 0-7 | | | -291.05 | -292.33 | | | -293.86 | -294.69 |
| W_{H^2} | | | | -10. | -10. | | | -10. | -10. |
| $\Delta H_{f,298}^{\circ}(H_2O)_i$ ³ | 5.5 | -287.47 | -288.01 | -288.16 | -290.01 | -292.10 | -292.65 | -294.72 | -296.56 |
| W_{H_1} ³ | | 16.0 | 19.0 | 15.0 | 8.0 | -60.0 | -55.0 | -60.0 | -49.0 |
| W_{H_2} ³ | | -90.0 | -95.0 | -68.0 | -33.0 | -75.0 | -90.0 | -100.0 | -129.0 |

1 –[66]; 2 – [68]; 3 – [63].

Table 7. Standard thermodynamic enthalpy $\Delta H_{f,298}^{\circ}(H_2O)_i$ (in kJ mol⁻¹) of interlayer water and Margules interaction parameters for the system H₂O – smectite.

The integral hydration enthalpy is obtained by the following relationships:

$$\Delta \tilde{H}_{Hyd} = x_{hs} * \Delta H_{Hyd,298}^{\circ} + x_{hs} * (1 - x_{hs}) * [W_{H_1} * x_{hs} + W_{H_2} * (1 - x_{hs})] \quad (32)$$

in which $\Delta H_{Hyd,298}^{\circ}$ and Margules parameters W_{H_1} and W_{H_2} are determined by a minimisation procedure applied to the difference between computed and calorimetric integral enthalpies on eight homoionic montmorillonite SWy-1 [15-17] and given in table 7. The maximum number of moles of interlayer water was set to 5.5 moles. Figure 4A displays the comparison of integral enthalpy of hydration of a smectite- Na computed from the three models developed previously with different experimental values.

The curve 1 in Figure 4A (yellow dotted line) comes from model of Ransom & Helgeson [66], is linear and is obtained from the following equation of integral enthalpy of hydration:

$$\Delta \tilde{H}_{Hyd,298} = -24.39 * x_{hs} \quad (33)$$

where the coefficient -24.39 is computed from $\Delta H_{f,298}^\circ(H_2O)_i$ given in Table 7. The curves 2b, 2c and 2d (green dotted lines) displayed in Figure 4A come together from the model of Vidal et al. [68] and are graphically represented by four truncated lines with their respective equations:

$$0 \text{ layer } (0 < x_{hs} < 0.7): \Delta \tilde{H}_{Hyd,298} = -9.716 * x_{hs} \quad (34)$$

$$1 \text{ layer } (0 < x_{hs} < 2.0): \Delta \tilde{H}_{Hyd,298} = -20.14 * x_{hs} + x_{hs} * (1 - x_{hs}) * 10.0 \quad (35)$$

$$2 \text{ layers } (0 < x_{hs} < 4.0): \Delta \tilde{H}_{Hyd,298} = -32.0 * x_{hs} + x_{hs} * (1 - x_{hs}) * 10.0 \quad (36)$$

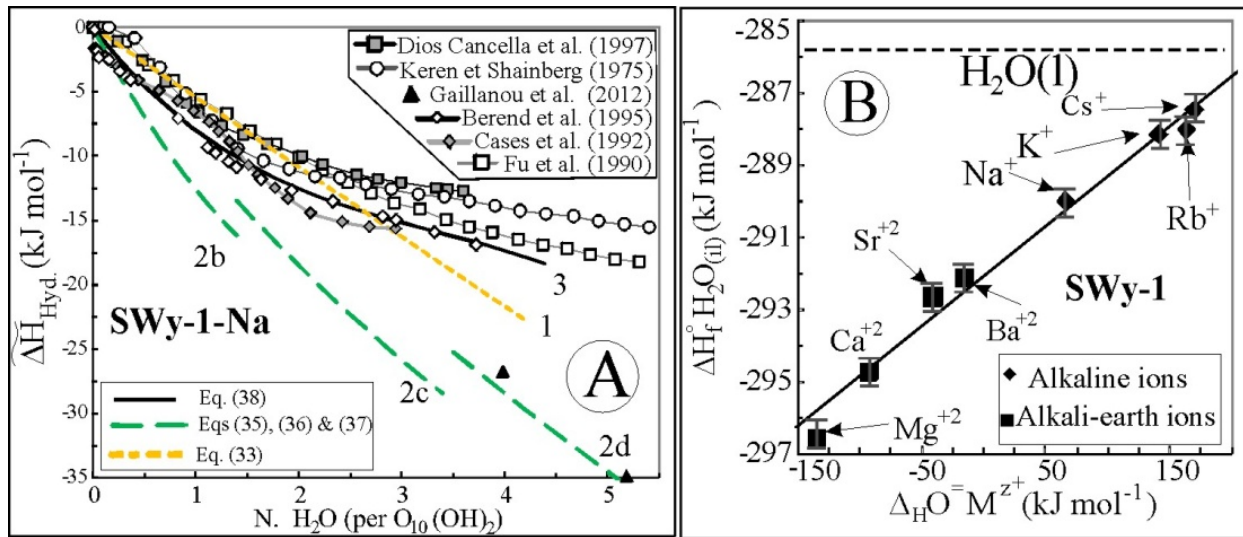


Figure 4. A – Integral enthalpy of hydration versus the number of interlayer cation; B – Standard enthalpy of formation of interlayer water versus the nature of the interlayer cation.

$$3 \text{ layers } (0 < x_{hs} < 7.0): \Delta \tilde{H}_{Hyd,298} = -45.5 * x_{hs} + x_{hs} * (1 - x_{hs}) * 10.0 \quad (37)$$

The curve 3 (black line) in Figure 4A comes from the model of Vieillard et al. [63] and is represented by the following equation:

$$\Delta \tilde{H}_{Hyd} = -23.0 * x_{hs} + x_{hs} * (1 - x_{hs}) * [8.0 * x_{hs} - 33.0 * (1 - x_{hs})] \quad (38)$$

It appears that integral enthalpy of hydration modelled by Vieillard et al. [63] (black line) based on experimental measurements of heat of adsorption from [15-17] encompasses nearly all experimental data. As the standard entropy of hydration is assumed constant in [66] and [68] models, the integral hydration enthalpies provided by these two previous models are nearly linear. Those obtained by [68] exhibit three sections of curves corresponding to the three states of hydration (1, 2 and 3 water layers).

In Figure 4B, a relationship between the standard state enthalpy of interlayer water with the nature of the interlayer cation located in the SWy-1 montmorillonite with a constant layer

charge of 0.38, characterised by its electronegativity ($\Delta_{\text{H}}\text{O}=\text{M}^{z+}$ (aq), Table 4) is proposed [63] and given as follows:

$$\Delta H_{f,298}^{\circ}(\text{H}_2\text{O})_i - \Delta H_{f,298}^{\circ}(\text{H}_2\text{O})_{(l)} = 0.02784 * \Delta_{\text{H}}\text{O}=\text{M}^{z+} - 6.275 \quad (39)$$

Lowering the electronegativity of cation in the interlayer sites stabilises the enthalpy of formation of the interlayer water. It should be kept in mind that Eq. (39) has been settled for the same support, *i.e.*, a constant layer charge. For natural montmorillonite-Na, most enthalpies of hydration of the interlayer water are consistent within a narrow range of interlayer charge, IC ($0.31 < \text{IC} < 0.38$) [63]. Due to the lack of calorimetric measurements of enthalpy of hydration for high charge ($\text{IC} > 0.5$) and low charge ($\text{IC} < 0.3$) montmorillonites, the variation of the standard hydration enthalpy as a function of the layer charge remains highly questionable. An important remaining matter of discussion is the extent to which the model is able to predict hydration properties of dioctahedral and trioctahedral smectites with different layer charges and compositions.

5.2. Entropy

Salts: Average values of the entropy of hydration water were obtained [39] and [35] within chlorides, sulphates and salts (table 2). These average values of salts appear very similar to the value of entropy for crystalline water, $S^{\circ} = 40.17 \text{ J/K}^{-1} \text{ Mol}^{-1}$ [70]. To improve the accuracy of prediction, statistical relationships between entropy and the molar volume of hydration should be investigated.

Zeolites: Initially, an average value of entropy of zeolitic water was proposed by Helgeson et al. [70] and was equal to $S^{\circ}\text{H}_2\text{O}_{(\text{zeol})} = 58.99 \text{ J/K}^{-1} \text{ Mol}^{-1}$. From very few available calorimetric measurements of anhydrous and hydrated zeolites [4, 6, 71], it has been shown that the entropy of hydration water, at saturation, remains constant at approximately $52.0 \text{ J/K}^{-1} \text{ Mol}^{-1}$ [72]. Some authors provide slight deviations of entropy of hydration depending of the nature of cations in clinoptilolite [22].

Clay minerals: Entropies of interlayer water in clay minerals have never been measured directly, but have been evaluated from indirect measurements such as a contribution of experimental enthalpies of immersion and adsorption-desorption isotherms [63] [34] or from the Clausius-Clapeyron rules with adsorption isotherms performed at different temperatures [31], [30]. A constant value $55.0 \text{ J/K}^{-1} \text{ Mol}^{-1}$ for the entropy of interlayer water has been chosen [67] and [68] regardless of the nature of the interlayer water and the numbers of interlayer waters layers. By considering the hydration of a smectite always as a symmetrical regular solid solution, the integral entropy is expressed as in [63]:

$$\begin{aligned} \Delta \tilde{S}_{\text{Hyd}} = & x_{hs} * \Delta S_{\text{Hyd}}^{\circ} - R \left[x_{hs} * \ln(x_{hs}) + (1 - x_{hs}) * \ln(1 - x_{hs}) \right] \\ & + x_{hs} * (1 - x_{hs}) * \left[W_{S_1} * x_{hs} + W_{S_2} * (1 - x_{hs}) \right] \end{aligned} \quad (40)$$

$$\text{with } \Delta S_{hyd,298}^0 = n_m * \left[S_{298}^0 (H_2O_{(i)}) - S_{298}^0 (H_2O_{liq}) \right] \quad (41)$$

where ΔS_{Hyd}° , W_{S_1} , and W_{S_2} represent the standard entropy of hydration and Margules parameters of the excess entropy of mixing, respectively. The integral entropy is expressed in J K⁻¹ mol⁻¹ of smectite based on O10(OH)2. The determination of these parameters is retrieved from values of ΔH_{Hyd}° , W_{H_1} , and W_{H_2} obtained previously in the minimisation procedure of integral hydration enthalpy and from the experimental adsorption-desorption isotherm interlayer water versus relative humidity. This minimisation procedure uses a least square method and provides ΔS_{Hyd}° , W_{S_1} and W_{S_2} (Table 8).

| | $S_{298}^{\circ} H_2O_{(i)}^1$ | $W_{S_1}^1$ | $W_{S_2}^1$ | $S_{Hyd}^{\circ} M^{z+}_{(aq)}^2$ |
|------------------|--------------------------------|-------------|-------------|-----------------------------------|
| | J/K/mole | J/K/mole | J/K/mole | J/K/mole |
| Cs ⁺ | 64.6 | 163.5 | -348.0 | -78. |
| Rb ⁺ | 63.8 | 142.0 | -355.0 | -84. |
| K ⁺ | 63.7 | 104.0 | -267.5 | -93. |
| Na ⁺ | 59.8 | 49.1 | -94.0 | -130. |
| Ba ²⁺ | 55.7 | -116.0 | -211.5 | -224. |
| Sr ²⁺ | 54.3 | -117.8 | -244.5 | -261. |
| Ca ²⁺ | 51.5 | -93.5 | -270.5 | -271. |
| Mg ²⁺ | 45.4 | -42.8 | -380.0 | -350. |

1 -[63]; 2 - [73].

Table 8. Standard thermodynamic enthalpy ΔS_{Hyd}° of interlayer water, Margules interactions parameters and hydration entropy of the ion under its hydrated aqueous state for the eight cations.

Figure 5A displays the comparison of the integral entropy of hydration of a smectite- Na computed from the three models [67] [68] and [63] developed previously with different experimental values.

As indicated in the enthalpy section, integral hydration entropies modelled by [66] (yellow dotted line, N°1) and [68] (green dotted line, N°2a, 2b and 2c corresponding to 1st, 2nd and 3rd layer) are linear and merge together. In the model proposed by Vieillard et al. [63], three calculated integral entropies of SWy1-Na –water system were plotted in Figure 5A and correspond to the adsorption (red line), the desorption (blue line) and the theoretical equilibrium water – Swy1-Na (black line, N° 3), whose equation is given:

$$\begin{aligned} \Delta \tilde{S}_{Hyd} = & -55.8 * x_{hs} - R \left[x_{hs} * \ln(x_{hs}) + (1 - x_{hs}) * \ln(1 - x_{hs}) \right] \\ & + x_{hs} * (1 - x_{hs}) * \left[49.05 * x_{hs} - 94.0 * (1 - x_{hs}) \right] \end{aligned} \quad (42)$$

The comparison of hydration-dehydration curves calculated by [63] with those provided by Fu et al. [34] show an opposite interpretation. The data from [34] show that integral entropies during adsorption are less negative than those during desorption. Data from our model show the opposite. This difference is explained by the fact that from experimental

works of [34], adsorption follows desorption, while with our data, desorption follows adsorption. Thus, a maximum entropy difference between hydration and dehydration functions can be depicted and is equal to 18 J/K/mole. These observations show the importance of movement of exchangeable cations from ditrigonal cavities and the rotation of tetrahedrals in the tetrahedral sheets when dry collapsed layers are progressively exposed to water vapour.

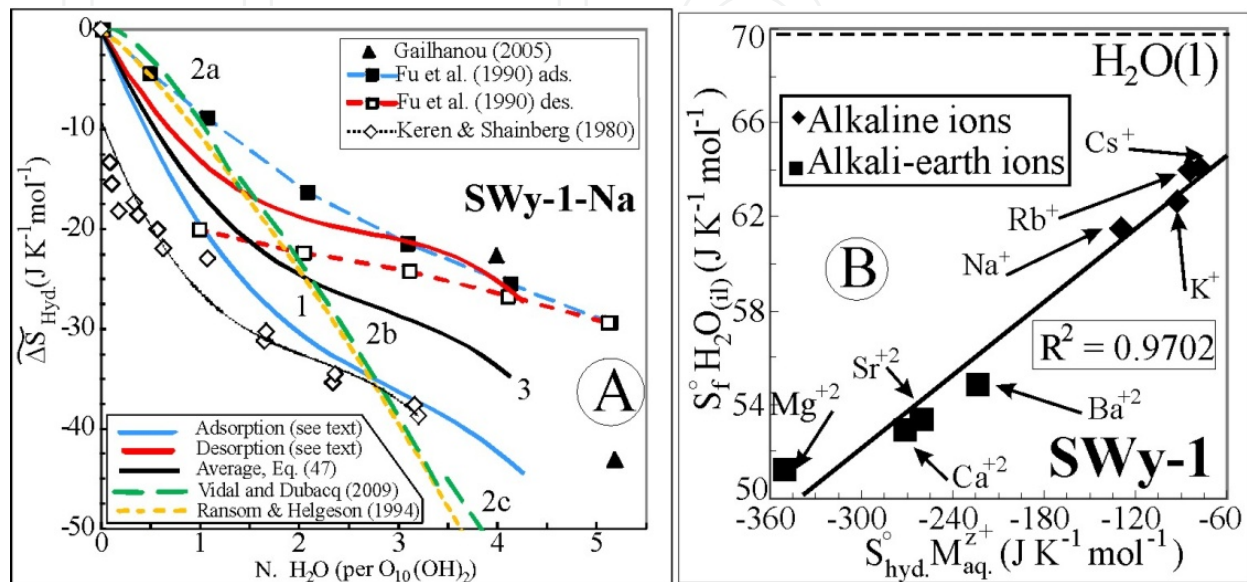


Figure 5. A – Integral entropy of hydration versus the number of interlayer cation; B – Standard entropy of formation of interlayer water versus the nature of the interlayer cation.

A correlation between the entropy of interlayer cation $S^{\circ}_{298}(H_2O)_i$ with the theoretical hydration entropy, $S^{\circ}_{hyd} M^{z+}$ [73] (Table 8), of the interlayer cation [63] is displayed in Figure 5B with the following equation:

$$S^{\circ}_{298}(H_2O)_i - S^{\circ}_{298}(H_2O)_{(l)} = 0.06542 * S^{\circ}_{hyd} M^{z+} - 0.413 \quad (43)$$

Negative values of the hydration entropy of the hydrated ion lower the hydration entropy of the interlayer water.

5.3. Heat capacity

Salts: An acceptable average heat capacity ranging from $39.0 \pm 5.3 J/K^{-1} mol^{-1}$ for sulphates and sulphites to $42.0 \pm 2.7 J/K^{-1} mol^{-1}$ for chlorates and chlorides has been proposed [35] and seems to be close to the average value of heat capacity for crystalline water $C_p = 40.04 J/K^{-1} mol^{-1}$ [70]. Only the average heat capacity function of crystalline water was proposed [70]:

$$C_p(H_2O)_{salts} = 29.75 - 3.448 * 10^{-2} * T \quad (44)$$

Zeolites: Three equations of heat capacities ([41], [74] [45]) were proposed for a set of silicate minerals, including analcime and natrolite, and are displayed in table 9.

| | Heat capacity function (298.15- 500 K) | |
|-------|---|------|
| Eq. A | $Cp(H_2O)_{sil} = 56.61 - 2.64 * 10^2 * T^{-0.5}$ | [41] |
| Eq. B | $Cp(H_2O)_{sil} = 87.62 + 7.58 * 10^2 * T^{-0.5} + 0.53 * 10^7 * T^{-3}$ | [74] |
| Eq. C | $Cp(H_2O)_{sil} = 39.65 + 32.5 * 10^{-3} * T - 4.694 * 10^5 * T^{-2}$ | [45] |
| Eq. D | $Cp(H_2O)_{zeol.} = 23.999 + 66.295 * 10^{-3} * T - 0.3948 * 10^5 * T^{-2}$ | [72] |

Table 9. Heat capacity functions for zeolites minerals

Heat capacities of the hydration in zeolites have been performed by Neuhoff & Wang [75] on three zeolites (analcime, natrolite and wairakite) and exhibit marked variations in the heat capacity of hydration with temperature. Four zeolites (mordenite, wairakite and two different values from different sources for analcime and natrolite) for which the heat capacity of zeolitic water can be obtained by a difference between the heat capacities measured on both the anhydrous and the hydrated phases [72] are represented in Figure 6A. Also displayed are the heat capacity values of water in all its states (ice, liquid and vapour) for comparison [35]. The heat capacity values of zeolitic water obtained by minimisation techniques (Eq. D of table 9, turquoise line) matches with the heat capacity function equations of [74] and [45].

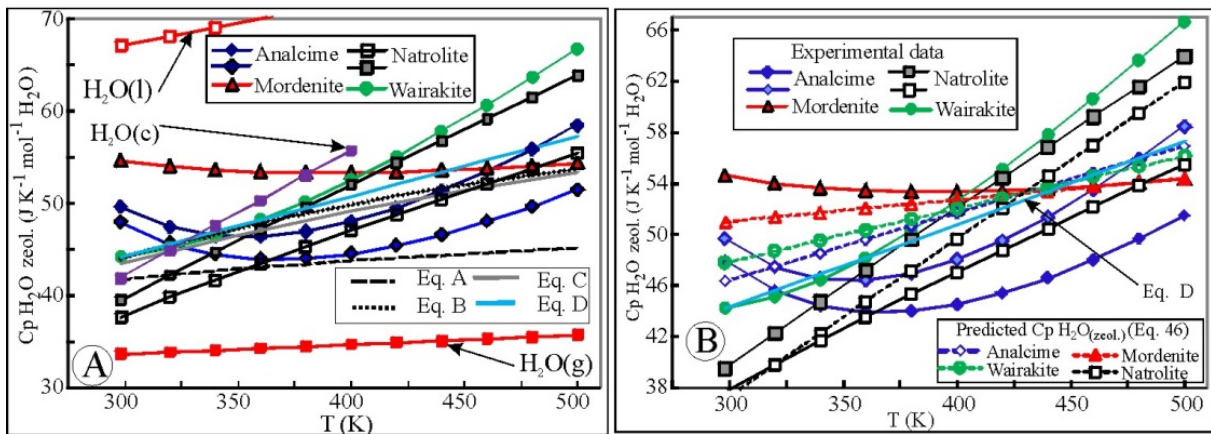


Figure 6. Heat capacity of zeolitic water versus temperature: A – Heat capacities of zeolitic water in zeolites, in different prediction models and of water in its various states (l for liquid, c for ice and g for vapour); B – Experimental heat capacities of zeolitic waters in natural zeolites and predicted heat capacities from Eq. (46).

Eq. D of table 9 provides a statistical error of 4.51%, 2.35% and 4.18% for hydrated zeolites at 298.15 K, 400 K and 500 K, respectively. To improve the accuracy of the prediction of the heat capacity of hydrated zeolites, one considers the normalised hydration volume, which is the difference of unit-cell volume ($V_{u.c.}$) between the hydrated and dehydrated forms for any zeolite per zeolitic water molecule [72]:

$$\Delta V_{Hy-Deh} = \frac{(V_{u.c.hydr.} - V_{u.c.dehyd.})}{n_{H_2O}} \quad (45)$$

$$Cp(H_2O)_{zeol.} = \left[55.85 - 13.073 * \sqrt{(\Delta V_{Hy-Deh})} \right] + \left[0.0062 + 0.0305 * \sqrt{(\Delta V_{Hy-Deh})} \right] * T + \left[0.008 + 0.0048 * \sqrt{(\Delta V_{Hy-Deh})} \right] * T^{-2} \quad (46)$$

The heat capacities of hydration water given in Figure 6B have been calculated for the four hydrated zeolites (mordenite, analcime, wairakite and natrolite) from the unit-cell volumes of their dehydrated and hydrated forms [72]. It can be observed that the heat capacities of hydration water calculated in this way are much better than those obtained by Eq. D of table 9 (indicated in Fig. 6B as a turquoise full line). With this improvement, the errors made on hydrated zeolites decrease to 3.5%, 2.35% and 3.89% at 298.15 K, 400 K and 500 K, respectively.

Clay minerals: The heat capacity function comes initially from [67] and is assumed to be independent of the nature of the interlayer cations:

$$Cp(H_2O)_{clays} = 37.84 + 51.631 * 10^{-3} * T - 4.0959 * 10^5 * T^{-2} \quad (47)$$

This heat capacity equation has also been used by [68] and by [63] in the behaviour of thermodynamic entities versus temperature.

5.4. Molar volume

Salts: Only [35] provided an average value for different salts: 14.5±1.2 cm³/mole for sulphates and sulphites and 14.1±2.3 cm³/mole for chlorides and chlorates. These average values appear to be similar to the molar volume of crystalline water (V(H₂O)_(salts)= 13.7 cm³/mole [76]).

Zeolites: No study on the variation of the molar volumes of the zeolitic water has been performed. Numerous values of molar volumes of hydrated and anhydrous zeolites have been provided and gathered in such calculations for enthalpy and entropy of hydration [77], [61], [72]. In the study of the relationship between entropy and molar volume within zeolites [72], an average value of the molar volume of hydration water has been calculated and is V(H₂O)_(zeol)=2.06 cm³/mole, which is not significantly different from those proposed by Helgeson (V(H₂O)_(zeol)= 8 cm³/mole) estimated from standard molal volumes of zeolites. The weak value of the molar volume of the hydration water is explained by the fact that the anhydrous zeolites exhibit a rigid (Si, Al) framework with different channels or cavities occupied by exchangeable cations. During the hydration process, the water molecules are bound to cations inside the cavities, do not affect the framework and have a weak impact on lattice parameters.

Clay minerals: The molar volume of the interlayer water was initially determined by Ransom [67] and also used by [68] and by [63] in thermochemical calculation. Its value is V(H₂O)_I = 17.22 cm³/mole. This value, greater than those of salts, is explained by the fact that, during hydration, the molar volume of clay minerals increases in one dimension characterised by basal spacing (Miller index 001).

6. Discussion of the Gibbs free energy of the formation behaviour of the hydration water in environmental conditions

The relationships among the free energy change, enthalpy of reaction and entropy for an isothermal process is:

$$\Delta G = \Delta H - T^* \Delta S \quad (48)$$

where ΔG stands for free energy change, ΔH for enthalpy of reaction, ΔS for the change in entropy and T for the absolute temperature. This relationship holds true for both the integral entities that are represented by $\Delta \tilde{G}$, $\Delta \tilde{H}$ and $\Delta \tilde{S}$ and for the partial quantities that are represented by $\Delta \bar{G}$, $\Delta \bar{H}$ and $\Delta \bar{S}$.

Salts: The free energy of formation of the hydration water of hydrated salts can be calculated from the enthalpy and entropy of hydration given previously. A relationship has been demonstrated by the statistical regressions [35] between the enthalpy and Gibbs free energy of crystalline water in the following relation:

$$\Delta G_{f,298}^{\circ} (H_2O_{salts}) = 1.008 * \Delta H_{f,298}^{\circ} (H_2O_{salts}) + 59.406 \quad (49)$$

The predicted values contribute to the variations of solubility products and the cation selectivity constants among the series of salts. An example is given in [78] for two series of hydrated salts of $MgCl_2$ and $SrCl_2$.

For zeolites and clays, the adsorbent (a single smectite or zeolite phase) is supposed to be inert so that the derived enthalpy and entropy functions formally represent the energy variations between the adsorbed and the bulk water.

The integral free energy of hydration $\Delta \tilde{G}_{hyd}$ may be determined from the gravimetric isotherms of adsorption of the water vapour by the following expression [79]:

$$\Delta \tilde{G}_{hyd} = R^* T^* \int_{n=0}^{n=n_w} \ln \left(\frac{P}{P_0} \right) * dn \quad (50)$$

where $R = 8.314 \text{ J.mol}^{-1}\text{K}^{-1}$ is the ideal gas constant, n is the amount of adsorbed water, P is the partial water vapour pressure, and P_0 is the saturated water vapour pressure at temperature T ($P/P_0 = \text{Relative Humidity}/100$). This value can be determined by plotting $R^* T^* \ln(P/P_0)$ versus the water content n (adsorbed or desorbed) and determining the area under the curve from 0 to n_w . When n_w approaches 0, $R^* T^* \ln(P/P_0)$ approaches infinity, making integration somewhat difficult.

Zeolites: Eq. (50) has been used on three clinoptilolites (-Na, -K and -Ca) [22] and show a good correlation between the Gibbs free energies calculated from the adsorption-desorption isotherms and from the contribution of the enthalpy of hydration and the entropy of hydration extracted from the equilibrium at high temperature. The model described by Carey & Bish [62] used a solution solid model between anhydrous and hydrated zeolite, and the variation of the

integral Gibbs free energies of hydration is expressed as a function of a parameter θ characterising the ratio of $H_2O/(\text{maximum } H_2O)$. The main difficulty in these calculations is the determination of the maximal amount of hydration water at the saturation state ($p/p^*=1$).

Clay minerals: Among the numerous measurements of adsorption-desorption isotherms on various clays, very few works provided a consistent Gibbs free energy of adsorption-desorption due to the difficulty of measurements in the low relative humidity domains. By choosing the system of water – SWy-1-Na, Figure 7 displays the adsorption-desorption isotherms (Figure 7A), the variation of the integral free energy of hydration versus the number of moles of the interlayer water (Figure 7B) and versus the relative humidity (Figure 7C) and the variation of the free energy of formation of the interlayer water versus the relative humidity (Figure 7D).

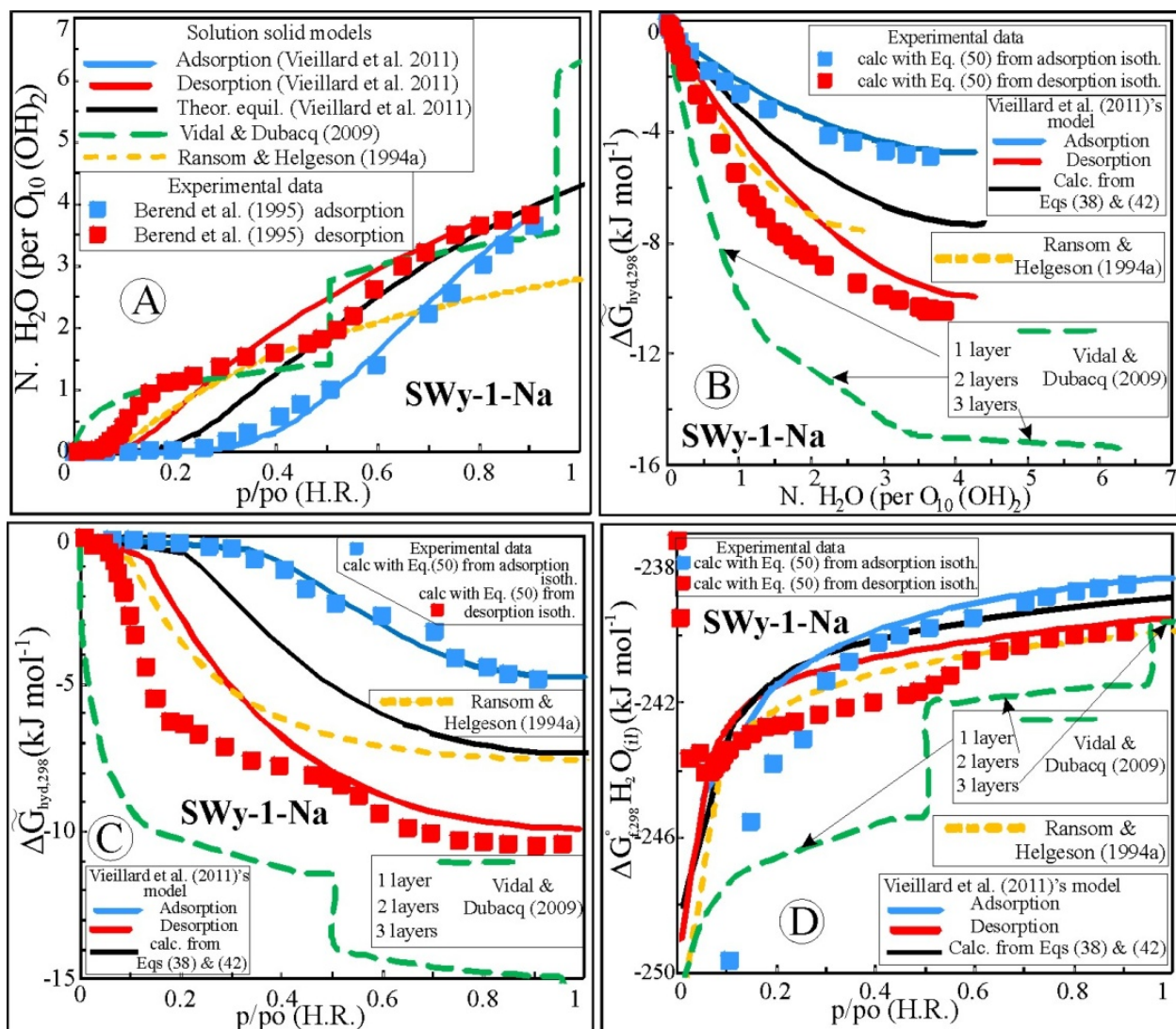


Figure 7. A - Adsorption-desorption isotherms; B - Integral free energy of hydration versus the number of moles of interlayer water; C - Integral free energy of hydration versus the relative humidity; D - Free energy of formation of the interlayer water versus the relative humidity.

In each figure, the data of the free energy of hydration (Eq. 50) from the experimental isotherms [15, 16] (blue square for adsorption and red square for desorption) and the free energy of hydration are computed and are reported for comparison of three different works: the Vieillard et al. model [63] (blue, red and black lines for adsorption, desorption and theoretical equilibrium, respectively), the Ransom & Helgeson model [66] (dotted yellow line), and the Vidal & Dubacq model [68] (dotted green line). For the adsorption and desorption reactions, the modelled isotherm calculated by the Vieillard et al. model [63] (blue and red lines, respectively) agrees well with the experimental data acquired by [15, 16] in high relative humidity.

At low relative humidity, the uncertainty appears very important between the experimental desorption data and the desorption curve from the model in [63] (3 kJ/mol for integral free energy, Fig C) due to the analytical limits and mathematical constraints.

The theoretical equilibrium (black line) suggests that the hydration of a Na-SWy-1 begins at only R.H.= 0.15 (Figure 7A), which correlates well with the experimental adsorption but not with the desorption. The integral Gibbs free energy of hydration (figure 7B and 7C) and the Gibbs free energy of the interlayer water (Figure 7D) of the theoretical equilibrium between the water and Na-Smectite (black line) are plotted and correspond to the average values of calculated adsorption-desorption isotherms. The theoretical curve of equilibrium between the water and Na-smectite provided by Ransom & Helgeson [66] displays a small number of moles of the interlayer water close to saturation, while those of Vidal & Dubacq [68] reproduce this stepwise behaviour fairly well because it assumes three solid solutions with 3 end-members (0.7 H₂O, 2 H₂O, 4.5 H₂O). However, it does not match the behaviour of water adsorption versus relative humidity, which is not a step function. The advantage of this approach is that it allows reproducing the observed stepwise evolution of the smectite volume and water content with varying T and relative humidity. At low relative humidity, as the hydration of a Na-SWy-1 begins at only R.H.= 0.15, the computations from [68] and [66] (green and yellow dotted lines) do not match the observed isotherms because there is a strong hydration in the RH= 0.0- 0.18 range. During the interval of R.H.=0.0-0.2, the adsorption of water molecules occurs predominantly on the external surface of tactoids (basal external faces and edges of tactoids). This explains why we observe a very negative integral free energy in the low relative humidity domain for these two models (green dotted line and in a less extent, yellow dotted lines). The necessity to take into account only the hydration water, *sensu-stricto*, is justified. This procedure has been incompletely performed by Ransom & Helgeson [66] with the external surface of a kaolinite to estimate the amount of surface covering water, while Vidal & Dubacq [68] made no correction on the gravimetric waters. At high relative humidity, Vidal & Dubacq [68] proposed a third step of hydration, with the number of water molecules increasing up to 7 moles per O10(OH)₂. All of the experimental isotherms performed by [15, 16] exhibit an increase in the water contents beyond RH = 0.9, identified as osmotic water. The osmotic swelling of the sodium montmorillonite corresponds to an

iso-enthalpic effect, with the heat of adsorption being constant. The theoretical equilibrium between water and Na-SWy-1 (black line) matches the experimental dehydration near saturation.

The cationic exchange and hydration reactions are intimately related, and the cationic exchange reactions not only modify the interlayer composition but also imply changes in the interlayer water content. These changes can be quite significant and can be evaluated using the Vieillard et al. model [63], which provides a theoretical number of moles of interlayer water and integral thermodynamic properties (H, S and G) for the SWy-1 montmorillonites. Thus, the cationic exchange reactions may depend on an external parameter, such as the relative humidity.

7. Conclusions and perspectives

This chapter demonstrated some useful relationships in the prediction of thermodynamic entities. Some important areas are still lacking and deserve further study.

Among the anhydrous and hydrated salts, the relationships between the entropy and molar volume may exist and will improve the prediction of the entropy of hydration. The function of the average heat capacities for the hydration water is lacking and will help in characterising the behaviour of the crystalline water versus temperature.

In the zeolite field, the relationships among the molar volume, water content and relative humidity may exist within zeolites families with a reversibility in the hydration-dehydration processes. These relationships will contribute to a better understanding of the behaviour of partial molar enthalpy versus the degree of saturation or versus the relative humidity.

In the clay Minerals, three following recommendations are needed: 1) to dissociate the hydration water from the gravimetric water; 2) to measure the heat of hydration among the dioctahedral and trioctahedral clays; and 3) to find a relationship between the hysteresis and the entropy of the hydration-dehydration by the molecular modellings. With these three aims, the knowledge of mechanisms of the hydration within clay minerals will advance our understanding of cationic exchange in soils under various physical and chemical constraints.

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