

## MEASUREMENTS OF HEAT OF ZEOLITE DEHYDRATION BY SCANNING HEATING

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### Abstract

A procedure for measurement of the heat of zeolite dehydration by scanning heating has been designed. Simultaneous data on heat flow (DSC) and mass loss (TG) are required for evaluation. The heating rate depends on the experimental conditions (point-spread function, sample mass, crucible design, and calorimetric reproducibility). Dehydration measurements have three advantages as compared with the sorption procedure: i) one can investigate samples with irreversible dehydration; ii) no approximation model is needed for calculation of the partial molar heat of dehydration; and iii) the procedure is not labor-consuming.

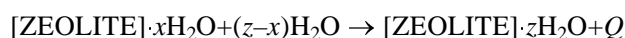
The procedure was tested on the natural zeolites heulandite, chabazite and mordenite. The results are close to those measured by the sorption procedure. The partial molar heat of dehydration was found to depend on the water content. It increases from 50 to 87 J mol<sup>-1</sup> K<sup>-1</sup> for heulandite, from 53 to 81 J mol<sup>-1</sup> K<sup>-1</sup> for chabazite, and from 51 to 71 J mol<sup>-1</sup> K<sup>-1</sup> for mordenite.

The approximation of the heat of sorption by linear regression was found to be wrong. Detection of a 'phase transition' after this approximation has no meaning.

**Keywords:** dehydration, DSC, TG, water, zeolites

### Introduction

The energy of the water-zeolite interaction is defined via the heats of immersion of outgassed zeolites [1]. The thermochemical equation for the reaction is



where  $x$  is the number of H<sub>2</sub>O molecules per unit cell (UC) of the zeolite. The final state of the zeolite here is full hydration ( $z$  molecules per UC). The result is the relationship  $Q=f(x)$ .

The sorption procedure has certain disadvantages. Firstly, the results of the measurements depend not only on the water content, but also on the procedure of sample preparation (temperature and duration of heating, gas phase). Secondly, the sorption procedure is labor-consuming. It takes vacuum operation, glass tube sealing, etc.

And finally, repeatability in the sorption procedure is not high. The differential heat sorption ( $dQ/dx$ ) from these measurements involves an approximation error, i.e. a systematic one. For example, while  $Q(x)$  is fitted to a polynomial of the 5th degree, the function  $dQ/dx(x)$  varies continuously within the limits 55 and 92 kJ mol<sup>-1</sup> for  $1.3 < x < 22.1$  [2]. An alternative evaluation yields  $dQ/dx = 90 \pm 4$  ( $0 < x < 6.5$ ) and  $dQ/dx = 76 \pm 5$  kJ mol<sup>-1</sup> ( $6.5 < x < 11.7$ ) [3].

The objective of this study was to design and test a desorption method for measurement of the energy of the water-zeolite interaction. The thermochemical equation for the reaction in question is



Both the heat sorption ( $\delta Q(k)$ ) and the mass loss ( $\delta k\text{H}_2\text{O}$ ) of the zeolite are to be measured while heating is continuing.

## Experimental

Natural zeolites were used in the experiments. The samples were described in [4].

The DSC-30 and TG-50 of the Mettler TA-3000 were used. The standard aluminum crucibles (40  $\mu\text{l}$ ) were from the tool kit of the DSC-30. Leads on crucibles were not sealed. All the calorimetric measurements were carried out with only one crucible. The temperature interval of the investigations was from 290 to 850 K, with a heating rate of 5 K min<sup>-1</sup>.

The mass of the empty crucible over 10 K intervals was reproduced within the limits of sensitivity of the balance:  $1 \cdot 10^{-6}$  g. There was no drift in the baseline. TG results were not corrected after blank measurements. The reproducibility of the mass loss over every 10 K interval was defined after five measurements for each zeolite. The error was found to be less than 1%. Calorimetric measurements were corrected on the blank run. The empty crucible was measured five times. The heat flow varied within the limits 0.1 and 0.3 mW for various temperature regions. TG and DSC measurements were carried out simultaneously. The sample masses are given in Table 1.

**Table 1** Data on samples

Zeolite	Composition	Sample mass/mg	
		TG	DSC
Heulandite	$\text{Na}_{1.46}\text{K}_{0.23}\text{Ca}_{3.44}\text{Al}_{8.55}\text{Si}_{27.44}\text{O}_{72} \cdot 24.0\text{H}_2\text{O}$	29.349	28.593
Chabazite	$\text{Na}_{0.24}\text{K}_{0.10}\text{Ca}_{1.65}\text{Al}_{3.79}\text{Si}_{8.25}\text{O}_{24} \cdot 11.9\text{H}_2\text{O}$	30.572	30.595
Mordenite	$\text{Na}_{4.08}\text{K}_{0.08}\text{Ca}_{1.92}\text{Al}_8\text{Si}_{40}\text{O}_{96} \cdot 26.7\text{H}_2\text{O}$	28.777	28.890

The point-spread function for calorimetric measurements on powdered zeolites was defined as follows. One grain of indium was placed on the bottom of the crucible. The powder of heulandite after heating was then added. Heulandite does not absorb water after heating up to 770 K and dehydration does not mask the melting peak of indium. Several grains of indium (total mass 1.1 mg) were placed uniformly inside the powder. On heating, the sample exhibits a set of peaks of In melting. The duration of heat absorption at melting was measured at heating rates of 1, 2.5, 5, 10, 20 and 40 K min<sup>-1</sup>. The time width of the point-spread function ( $\tau_L$ ) was found to be 22 s.

## Results

The results of the measurements are shown in Figs 1–3. Chabazite and mordenite have one peak of dehydration, while heulandite has two. The second peak is caused by the phase transition. The decrease in the DSC signal near 750 K is due to the partial decomposition [4].

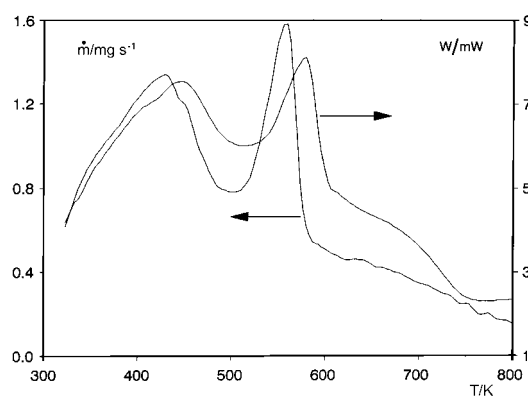


Fig. 1 Heat flow ( $W$ ) and mass loss ( $\dot{m}$ ) for heulandite

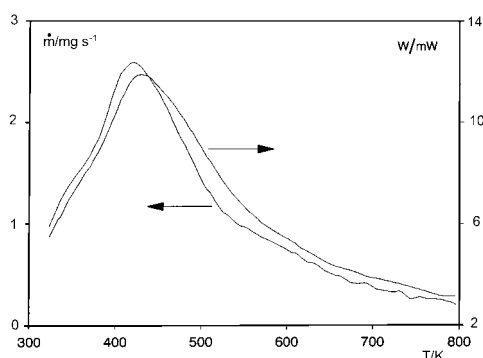


Fig. 2 Heat flow ( $W$ ) and mass loss ( $\dot{m}$ ) for chabazite

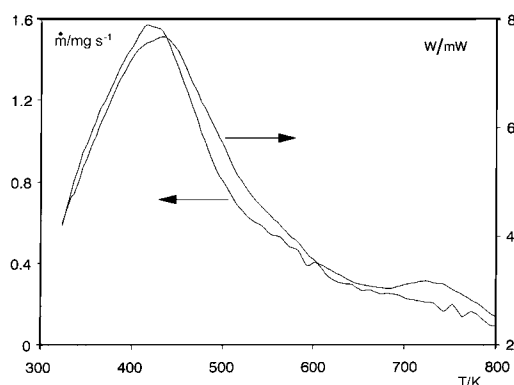


Fig. 3 Heat flow ( $W$ ) and mass loss ( $\dot{m}$ ) for mordenite

## Evaluation

### *Relationship between DTG and DSC*

The water content in the zeolite depends on the temperature and the pressure of  $H_2O$ . At constant pressure, the TG (and DTG) results can be approximated to by a smooth function [5]. In DTA and DTG experiments with scanning heating, the dehydration displays broad (about 100 K) peaks. With the absorption of heat, the zeolite is heated up and the water content is decreased:

$$dQ = \frac{\delta H}{\delta T}dT + \frac{\delta H}{\delta m}dm \quad (1)$$

Under scanning heating:

$$\dot{Q} = C\beta + q\dot{m} \quad (2)$$

where  $C$  is the heat capacity,  $\beta$  is the heating rate,  $q$  is the heat of dehydration per mass unit, and  $\dot{m}$  is the derivative of the mass with respect to time. The heat capacity varies slightly with temperature. Thermoanalytical peaks of dehydration are governed by the term  $q\dot{m}$ . One should measure  $Q$  by DTA or DSC, and  $\dot{m}$  by DTG. Investigations of zeolite dehydration by derivatography have shown a time lag between the peaks of DTA and DTG [6]. This holds for our results (Figs 1–3).

The heat flow measured in the experiment ( $W$ ) relates to the heat absorbed by the sample ( $Q$ ) by the point-spread function:

$$W(t) = \int_0^{\infty} \dot{Q}(t-\tau)f(\tau)d\tau \quad (3)$$

The function is normalized according to

$$\int_0^{\infty} f(\tau) d\tau = 1 \quad (4)$$

In an actual experiment, the duration of the point-spread function is limited by the noise level ( $\Delta W$ ):

$$\dot{Q}(t-\tau)f(\tau) \leq \Delta W \quad \text{at } \tau > \tau_L \quad (5)$$

Equation (4) changes to

$$\int_0^{\tau_L} f(\tau) d\tau = 1 \quad (6)$$

In the time interval from  $t_1$  to  $t_2$ , the calorimeter measures heat

$$\begin{aligned} H(t_1, t_2) &= \int_{t_1}^{t_2} dt \int_0^{\tau_L} \dot{Q}(t-\tau) f(\tau) d\tau = \\ &= \int_{t_1}^{t_2} \dot{Q}(t) dt + \int_0^{\tau_L} \dot{Q}(t_1-\tau) \int_{\tau}^{\tau_L} f(x) dx d\tau - \int_0^{\tau_L} \dot{Q}(t_2-\tau) \int_{\tau}^{\tau_L} f(x) dx d\tau = \\ &= \int_{t_1}^{t_2} \dot{Q}(t) dt + \int_0^{\tau_L} [\dot{Q}(t_1-\tau) - \dot{Q}(t_2-\tau)] \int_{\tau}^{\tau_L} f(x) dx d\tau \end{aligned} \quad (7)$$

$H(t_1, t_2)$  is not equal to the heat absorbed by the sample ( $Q(t_2) - Q(t_1)$ ). It includes the additional heat that was absorbed by the sample before  $t_1$ , but measured by the calorimeter after  $t_1$ , due to the point-spread function (or time lag). And vice versa, the part of the heat absorbed by the sample just before  $t_2$  ( $t > t_2 - \tau$ ) is not detected yet. Equation (7) allows one to define the systematic error by taking the heat measured by the calorimeter as the heat absorbed by the sample. This error is a negligibly small quantity on the evident condition

$$|\dot{Q}(t_1) - \dot{Q}(t_2)| \ll \dot{Q}(t) \quad (8)$$

One more condition exists that makes the evaluation valid. The contribution from the temperature boundaries to the heat is to be small. The systematic error will be negligible even at

$$|\dot{Q}(t_1) - \dot{Q}(t_2)| \sim \dot{Q}(t) \quad \text{if} \quad \tau_L \ll t_2 - t_1 \quad (9)$$

The smallest temperature interval for which the water content is decreased by one molecule per UC is about 10 K. In our experiments,  $\tau_L$  is 22 s. The temperature delay is 5 K for the heating rate  $14 \text{ K min}^{-1}$ . One should accept this value as an upper limit for an appropriate heating rate.

The lower limit is defined from the reproducibility of the baseline in calorimetric measurements. Over the time interval from  $t_1$  to  $t_2$ :

$$\int_{t_1}^{t_2} W(t) dt = (Q(t_2) - Q(t_1)) \pm \Delta W(T_1, T_2) \frac{T_2 - T_1}{\beta} \quad (10)$$

Here,  $\Delta W(T_1, T_2)$  is the standard deviation of the baseline over the temperature interval from  $T_1$  (at  $t_1$ ) to  $T_2$  ( $t_2$ ). Over the whole interval of measurements, it varies between 0.1 and 0.3 mW. The error can not be ignored, at least when it is equal to the contribution from the heat capacity of a sample. Taking the mass of the zeolite ( $m$ ) as 30 mg and the heat capacity ( $C$ ) as  $1 \text{ J g}^{-1} \text{ K}^{-1}$ , we have

$$\beta_{\min} = \frac{\Delta W}{Cm} = 0.6 \text{ K min}^{-1} \quad (11)$$

Finally, the equipment allows one to use the desorption method with a heating rate of from 1 to  $10 \text{ K min}^{-1}$ . To make the duration of the experiment tolerable, a heating rate of  $5 \text{ K min}^{-1}$  was accepted.

### Calculations

The water content in the zeolite is measured experimentally as mass loss vs. temperature. It is to be converted from mass units to number of  $\text{H}_2\text{O}$  molecules per UC,  $n(T)$ . Integer values  $n$  are matched one by one with a set of temperature  $T_n$ . The  $n$ -th molecule of water leaves the UC in the temperature range from  $T_n$  to  $T_{n-1}$ . The greater the temperature, the less the water content, and hence  $T_n < T_{n-1}$ . The sample absorbs heat  $Q(T_{n-1}) - q(T_n)$ . The initial mass of water in the sample ( $m_0$ ) corresponds to  $k$  molecules per UC. According to Eq. (2):

$$Q(T_{n-1}) - Q(T_n) = \int_{T_n}^{T_{n-1}} C(T, n) dT + q_n \frac{m_0}{k} \quad (12)$$

The heat capacity depends on the temperature and the water content. These data are not available. We use the approximation

$$C(T, k) = C(T, 0) + k C_{\text{H}_2\text{O}, z}(T) \quad (13)$$

where  $C_{\text{H}_2\text{O}, z}(T)$  is the partial molar heat capacity of the water in the zeolite. The values of  $C(T, k)$  and  $C(T, 0)$  are known for our samples [4], but these were measured over different temperature ranges:  $C(T, k)$  at  $T < 320 \text{ K}$ , and  $C(T, 0)$  at  $T > 290 \text{ K}$ . The values  $C_{\text{H}_2\text{O}, z}(298)$  were used:

$$q_n = \frac{k}{m_0} (Q(T_{n-1}) - Q(T_n)) - \int_{T_n}^{T_{n-1}} C(T, 0) dT - (n - \frac{1}{2}) C_{\text{H}_2\text{O}, z}(298) (T_{n-1} - T_n) \quad (14)$$

**Table 2** Heat of zeolite dehydration, ( $q_n/\text{kJ mol}^{-1}$ )

$n$	Heulandite	Chabazite	Mordenite
1			
2		72±7	
3	86±13	68.7±3.6	
4	87±7	80.6±3.0	42±18
5		78.0±2.5	49±9
6		71.9±2.3	56±6
7		66.7±2.4	61.2±4.7
8	(115)	62.7±2.3	65.7±3.9
9	(115)	57.8±2.4	68.9±3.5
10	(115)	54.9±3.4	70.7±3.1
11	83.0±3.4	52.5±4.1	69.3±2.9
12	87.0±3.5		66.5±2.8
13	84.6±3.4		64.7±2.9
14	76.6±3.2		63.5±3.0
15	70.2±3.2		61.8±2.9
16	64.9±3.2		59.0±2.9
17	63.3±3.3		57.2±2.8
18	63.1±3.7		53.9±2.9
19	62.0±4.1		55.3±2.9
20	60±5		53.6±3.7
21	56±6		53.1±4.0
22	50±8		53.9±4.3
23			51.3±4.5
24			51.5±4.8
25			49±6
26			51±7

The results at the very beginning of heating were rejected, as these do not satisfy condition (7). At low water content ( $n=1-3$ , depending on the zeolite), the desorption diminishes progressively. The error in  $q_n$  is too large. These data were rejected too. The values  $q_n$  ( $n=8-10$ ) for heulandite were calculated otherwise. This is the phase transition. The usual procedure is valid:  $q_n = \Delta H / \Delta m = 115 \text{ kJ mol}^{-1}$  [7]. The values  $q_n$  ( $n=3, 4$ ) were measured for the first time. Heulandite with low  $\text{H}_2\text{O}$  content does not absorb water. The results of the calculations are given in Table 2.

The standard deviation was estimated as follows.

- Thermogravimetric measurements: the errors are caused by imprecision in the mass loss in the temperature intervals. These are different for the various samples. The greatest value is less than 1%.
- Calorimetric measurements: the errors are caused by imprecision in the baseline. The values  $2\sigma$  were taken from blank measurements.
- The heat capacities of dehydrated zeolites were taken from [4].
- The partial molar heat capacity of water molecules was taken from [4].

## Discussion

The values  $q_n$  should be compared with those measured by the sorption procedure. This comparison, however, is not correct for two reasons. Firstly, the values of  $dQ/dx(x)$  after sorption measurements do depend on an approximation of  $Q(x)$ . Secondly, the scanning measurements yield the heats of desorption at different temperatures. The sorption measurements are carried out at constant temperature (at least room temperature). This will be discussed below.

The dehydration measurements in this work yield the energy of the water-zeolite interaction for the  $n$ -th molecule. It does not matter what the  $q$  value is for the  $(n-1)$ -th or  $(n+1)$ -th molecules. The procedure excludes the systematic error of a model approximation. This allows us to solve the problem in the thermochemistry of the zeolites.

The water content in a zeolite is counted in number of molecules per UC. On losing water, the zeolites are capable of undergoing phase transitions. By analogy with hydrated salts, the water loss is assumed to be stepwise, but in energy, not in temperature. A constant value of  $dQ/dx(x)$  is accepted for the water content over the intervals before and after the phase transition. The values are not equal. This concept was advanced as follows. If  $dQ/dx(x)$  evidently changes within an interval of  $x$ , then the phase transition exists. The transition point is attributed to the border between two intervals of constant values  $dQ/dx(x)$ . The border in turn is chosen in an arbitrary way. This procedure was used to treat the results of sorption experiments in [8].

The results in this work show that  $dQ/dx(x)$  is a function of  $x$ , not a constant. What relation is correct?

The 'constant' model is difficult to justify. This has been proposed by analogy. The background for the 'functional' model, in contrast, can be checked by crystallochemistry. The water molecules in the zeolite structure are localized at the fixed sites. Direct structural investigations show that the occupancy of the sites is not equal to 1. Let  $E_i$  be the bond strength of a water molecule at a site  $i$  ( $i=1, 2, \dots, k$ ), let  $w_i$  be the number of the identical sites in the UC, and let  $p_i$  be the occupancy. The number of water molecules per UC is

$$n = \sum_{i=1}^k w_i p_i \quad (15)$$



After change in the water content:

$$n' = \sum_{i=1}^k w_i' p_i' \quad (16)$$

For the heat of dehydration (or hydration if  $p_i' > p_i$ ):

$$q = \frac{\sum_{i=1}^k E_i w_i (p_i - p_i')}{\sum_{i=1}^k w_i (p_i - p_i')} \quad (17)$$

The  $q$  value can be constant over an interval of  $n$  only if  $E_i = E_j$  for all  $i$  and  $j$ . This is not the case. Structural data show that the  $p_i$  values are different. This is due to differences in  $E_i$ . Hence,  $q_n$  can not be a constant over any interval of water content.

Measurements of the heat of zeolite dehydration by scanning heating were reported in [9]. Their results (increasing values of heat) are in contradiction with this work (decreasing values) for low water content. The evaluation procedure was not described in [9] and we can only speculate. At low water content,  $\dot{m}$  tends to zero. According to Eq. (12), the contribution from the heat capacity to the measured heat is proportional to  $(T_{n-1} - T_n) \Delta Q / \Delta m$  must rise infinitely inasmuch as  $(T_{n-1} - T_n)$  tends to infinity for  $n \rightarrow 0$ .

On the other hand, the decrease in  $q_n$  for  $n \rightarrow 0$  in this work is not compatible with the explanation for Eq. (17). The greater  $E_i$ , the greater  $p_i$ . The energy of the water-zeolite interaction is to be the greatest for the last molecules. The reason for the discrepancy is changing temperature. According to Kirchhoff's rule, the heat of zeolite dehydration must change:

$$q_n(T_2) - q_n(T_1) = \int_{T_1}^{T_2} (C_{\text{H}_2\text{O}, \text{g}}(T) - C_{\text{H}_2\text{O}, \text{z}}(T)) dT \quad (18)$$

Here,  $C_{\text{H}_2\text{O}, \text{g}}$  is the heat capacity of the water molecules in the gas phase. It equals  $33.6 \text{ J mol}^{-1} \text{ K}^{-1}$ .  $C_{\text{H}_2\text{O}, \text{z}}(298)$  is equal to  $45.5 \pm 2.2$ ,  $60.6 \pm 1.9$  and  $57.3 \pm 2.6 \text{ J mol}^{-1} \text{ K}^{-1}$  for heulandite, chabazite, and mordenite, respectively [4]. As the heat capacity of the reactant ( $C_{\text{H}_2\text{O}, \text{z}}$ ) is evidently greater than that of the product ( $C_{\text{H}_2\text{O}, \text{g}}$ ),  $q_n$  decreases when the temperature rises. The difference can be as large as  $10 \text{ kJ mol}^{-1}$ . Thermodynamic evaluation must relate the heat of dehydration to the standard conditions, but this work deals with the process of thermal dehydration. The values in Table 2 characterize the process.

## Conclusions

1. An experimental procedure for measurement of the heat of zeolite dehydration by scanning heating was designed. It was tested by using the natural zeolites heulandite, chabazite and mordenite.
2. The results of the measurements characterize the process of thermal dehydration, not a thermodynamic function. The latter can be evaluated by bringing the data into the standard state.
3. The partial heat of zeolite dehydration is a function of the water content, not a constant. Approximation of the heat of sorption by linear regression is not correct.

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