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Note

THERMOGRAVIMETRIC INVESTIGATION OF THE PHASE TRANSITION IN THE ZEOLITE HEULANDITE AT DEHYDRATION

V.A. DREBUSHCHAK

Institute of Geology and Geophysics, Siberian Branch of the U.S.S.R. Academy of Sciences, Novosibirsk 90 (U.S.S.R.)

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A common natural zeolite, heulandite contracts to a B-phase on dehydration. There have been many thermoanalytical and thermogravimetric investigations of this phase transition because it forms the basis of the classification of the heulandite–clinoptilolite minerals. Zeolites are usually investigated using temperature-scanning DTA and DTG.

The thermodynamic features of the phase transition have not been studied. The order, enthalpy and necessary conditions of the transition are still unknown.

The temperature values of the phase transition published in the literature are contradictory: 255–330 °C [1], $> 202 \pm 3$ °C [2], 200–250 °C and 350–450 °C (for different heulandite groups) [3], and 110 °C [4]. The temperature of the phase transition changes not only for different samples, but also for the same sample with different dehydration conditions: 110 °C, in a vacuum [4]; 175 °C [5]; and, by heating in air at a heating rate of 9 °C min^{-1}, 290 °C [6].

The aim of this work was to investigate the thermodynamic features of the heulandite–B-heulandite phase transition using thermogravimetry.

EXPERIMENTAL

The heulandite used in the present study is from the Nidym River, East Siberia. The composition of the unit cell is $Na_{1.46}K_{0.23}Ca_{3.44}Al_{8.55}Si_{27.44}O_{72} \cdot 23.99H_2O$. The water content was determined by weight loss after heating to 820 °C.

The weight-loss measurements were carried out on the thermogravimetric analyser TG-50 of the Mettler TA-3000 system at set temperatures, using the TC10A processor. Powder of the crushed sample (30–50 mg) was placed in a furnace and heated up to the necessary temperature. The weight was continuously registered till the end of the dehydration. The dehydration was considered to be over when the rate of weight loss was near 1 μg per 5 min.

The sample was then either heated up to the next temperature value or cooled down. Once cooled, a sample was never heated again. The investigations were carried out without purge gas in normal air. Air-dried samples were used in the measurements.

RESULTS

The weight of the heulandite decreases with increasing temperature (see Fig. 1). The weight values decrease from room temperature to 240 ° C, and from 250 ° C to the maximum temperature of the measurements. The equilibrium water content in the sample decreases step-wise in the temperature range 240–250 ° C. By adding Δm to the weight in the temperature range $250 \leqslant T \leqslant 310$ ° C, the value of the step was determined as a quadratic regression coefficient in the temperature range $200 \leqslant T \leqslant 310$ ° C by the least squares method ($\Delta m = 1.62\%$). This is the weight step that is connected with the phase transition from heulandite to B-heulandite.

According to the literature [7], the thermal dehydration of heulandite is first-type, although this is is not strictly correct: the dehydration temperature ranges from room temperature up to nearly 600 ° C, and within a narrow temperature range at the phase transition, under normal conditions, only about 0.1 of the total water content of the heulandite has been lost.

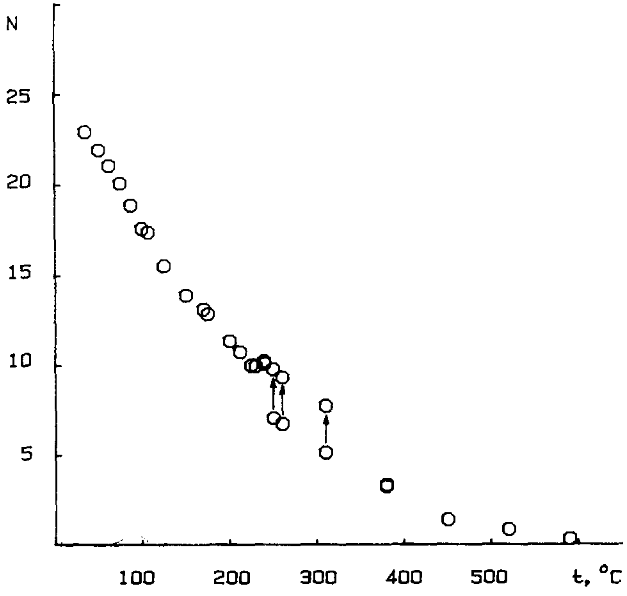

Fig. 1. The number of water molecules N in the unit cell of the heulandite versus temperature T. The arrows show addition of Δm.

Before the phase transition, heulandite–B-heulandite, there are 9.7 ± 0.5 H_2O molecules per unit cell. After the phase transition 7.2 ± 0.5 H_2O molecules remain, 2.5 ± 0.2 H_2O molecules having left the unit cell.

Kinetic measurements were carried out at 250 °C and 260 °C. During the final stage, the sample was dehydrated at 260 °C for 160 ± 15 min and at 250 °C for 575 ± 30 min when the concentrations of A- and B-phases changed from 100% to 0% and from 0% to 100%, respectively. The dehydration was believed to be over if the error in the determination of sample mass exceeded the mass change following complete desorption. If ΔM is the error in the experimental mass determination, dehydration is complete when

$$M \exp\left(-\frac{t}{\tau}\right) \leqslant \Delta M \tag{1}$$

where M is the mass of water lost during dehydration. For the phase transition, M is the weight-loss step (1.62%). The kinetic equation describes the isothermal desorption and phase transition

$$-\frac{\mathrm{d}m}{\mathrm{d}t} = km \tag{2}$$

$$k_i \sim \frac{1}{\tau_i} \tag{3}$$

One may use

$$k_i \sim \frac{n}{t_i} \tag{4}$$

According to the Arrhenius equation

$$k_i = k_0 \exp\left(-\frac{H}{RT}\right) \tag{5}$$

$$\ln\frac{t_2}{t_1} = -\frac{H}{R}\frac{\Delta T}{T_1T_2} \tag{6}$$

$$H = R\frac{T_1T_2}{\Delta T}\ln\frac{t_2}{t_1} \tag{7}$$

For these measurements, $T_1 = 523$ K, $T_2 = 533$ K and $\Delta H_1 = 296 \pm 37$ kJ mol^{-1}.

DISCUSSION

Because there is a jump-like change in the sample mass over the temperature range 240–250 °C, the heulandite–B-heulandite phase transition can be considered to be first order. This phase transition is connected with H_2O molecules leaving the structure and, because of the kinetic character of this process, some time is necessary for the structure to equilibrate with the environmental conditions (T and H_2O-vapour pressure). Usually when investigating the dehydration by scanning heating, the H_2O molecules usually leave the unit cell simultaneously with T increase, which masks the step nature of the phase transition.

According to ref. 4, there are 10.5 H_2O molecules in the unit cell at the beginning of the phase transition. Unfortunately, the precision of this measurement was not reported. In the present work, the phase transition began with 9.7 ± 0.5 H_2O molecules per unit cell, whereas ref. 6 suggests approximately 10.9 molecules per unit cell: unfortunately, it is difficult to estimate the precision of this value, one may put it at ± 1.0.

As can be seen from the above, despite variations in the dehydration conditions, the number of H_2O molecules per unit cell at the start of the phase transition is unchanged, within experimental error.

The number of H_2O molecules in the unit cell of heulandite changes during the phase transition. According to ref. 4, the number of molecules lost was 3, whereas in this work, as mentioned above, 2.5 ± 0.2 H_2O molecules left the unit cell during the phase transition.

It is more difficult to determine the weight-loss step using the data of ref. 6. Estimating from the total weight loss in the temperature range from 290 °C to 410 °C (4.12%), the weight loss at transition is $1.4 \leqslant \Delta m \leqslant 2.1\%$ or 2.6 ± 0.5 H_2O molecules per unit cell.

The differential heats of adsorption of water by dehydrated heulandite are given in ref. 4. For the water content at which phase transition occurs, $\Delta H_{\text{diff}} = 102 \pm 10$ kJ mol^{-1} (H_2O). The phase transition of a single heulandite mole is accompanied by desorption of three H_2O moles. The complete enthalpy of the phase transition calculated using differential heats of adsorption of water, ΔH_2, is 306 kJ mol^{-1}. It is impossible to calculate the precision of this value because the precision of the weight-loss value at phase transition is not known, see ref. 4.

TABLE 1

The parameters of the phase transition heulandite–B-heulandite

	M (H_2O per unit cell)	Δm (H_2O per unit cell)	ΔH (kJ mol^{-1})	Temperature range (°C)
This work	9.7 ± 0.5	2.5 ± 0.2	296 ± 37	$240 \leqslant T \leqslant 250$
Valueva et al. [4]	10.5	3	306 [a]	$100 \leqslant T \leqslant 170$
Belitsky et al. [6]	10.9 ± 1.0 [a]	2.6 ± 0.5 [a]	–	$290 \leqslant T \leqslant 410$
Drebushchak [5]	–	–	299 ± 30	$135 \leqslant T \leqslant 210$

[a] Author calculations.

The excess heat capacity ΔC of the phase transition was measured on the same sample by heating in a vacuum [5]. The enthalpy of the transition was 108 ± 11 kJ g^{-1} (of initial non-dehydrated sample weight). The molecular weight of non-dehydrated heulandite (see above chemical formula) is 2766 g mol^{-1}, and $\Delta H_3 = 299 \pm 30$ kJ mol^{-1}.

All the parameters of the phase transition are given in Table 1. One can see that the values of the phase transition enthalpy, measured at different temperatures (20, 175 and 250 °C) by different methods (the heats of H_2O adsorption, the excess heat capacities, the temperature–rate relation of the phase transition) coincide within experimental error. The constant values, characterising the phase transition of heulandite, are the values of the H_2O content in the unit cell at the beginning of the phase transition and the change in the H_2O content at the phase transition. The large differences observed in the temperature ranges of the phase transition are a reflection of different experimental conditions.

CONCLUSIONS

The main results of this work can be summarised as follows: the heulandite–B-heulandite phase transition is first order; the phase transition in the investigated heulandite starts with 10.0 ± 0.4 H_2O molecules per unit cell and loses 2.6 ± 0.2 H_2O molecules; and the enthalpy of the phase transition is 299 ± 21 kJ mol^{-1} (the unit cell composition is assumed to be the molecular formula).

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