Kiselyova I.A.[1], Ogorodova L.P.[1], Mel'chakova L.V.[1], Belitskii I.A.[2]. Thermodynamic properties of zeolites of chabasite and phillipsite groups

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A wide utilization of zeolites of different composition owing to their high porosity, propensity to the cation exchange, and processes of hydration and re-hydration results in an increasing interest to the their study. Zeolites of the chabasite and phillipsite groups show the largest sizes of cavities in the net-work. Therefore, they are used more widely in diverse specific technological processes, such as catalysis, ion exchange, molecular screens, ecological problems, agriculture, etc.

Thermodynamic properties of zeolites are necessary for estimation of fields of their stability, in study of dehydration processes, and application of sorptive and catalytic properties of dehydrated zeolites. There are some data on low-temperature heat capacity of chabasite [1], erionite [2], and phillipsite [3] and data on enthalpies of formation and dehydration of synthetic calcic chabasites of diverse composition [4]. Thermodynamic data on gmelinite and harmotome are unknown so far. We studied natural samples of

*chabasite (*Trans-Baikalie, Russia)
$(Ca_{1.65}Na_{0.24}K_{0.10})[Al_{3.79}Si_{8.25}O_{24}]\cdot 12.47H_2O$,
erionite (Shurdo, Georgia)
$(K_{2.37}Na_{0.47}Ca_{2.06}Mg_{1.18})[Al_{8.50}Si_{27.30}O_{72}]\cdot 26.47H_2O$,
gmelinite (Antrim, Ireland)
$(Na_{7.67}K_{0.49}Ca_{0.14}Mg_{0.07})[Al_{8.26}Si_{5.66}O_{48}]\cdot 24.4H_2O$,
phillipsite (Khibiny, Russia)
$(K_{3.05}Na_{0.53}Ca_{1.26}Sr_{0.04}Ba_{0.03})[Al_{5.57}Si_{10.26}O_{32}]\cdot 11.67H_2O$,
and *harmotome* (Rodopy, Bulgaria)
$(Ba_{2.03}Na_{0.06}K_{0.07}Ca_{0.12}Sr_{0.02})[Al_{5.13}Si_{11.04}O_{32}]\cdot 12.05H_2O$.

Thermochemical investigation was performed with the high-temperature Tian-Kalve calorimeter and differential scanning calorimeter "Mettler TA-2000 B".

Enthalpies of formation from oxides were measured by the method of dissolution in the $2PbO\cdot B_2O_3$ melt at T = 973 K. In order to avoid the zeolite decomposition at high temperature, the method of "dropping-in" was applied. This method allows measuring simultaneously heat capacity and heat of dissolution $[(H^0_T-H^0_{298.15}) + \Delta H^0_{dissol.973}]$. The thermally static at 25^OC sample of 3-10 ($\pm 2\cdot 10^{-3}$) mg was dropped into the dissolving melt, which is kept in calorimeter at T = 973 K. Using the data on ΔH^0_f (298.15 K) for the corresponding oxides [5], the values of standard enthalpies of formation of the studied zeolites from elements were calculated: $-\Delta H^0_{f,\ el}$ (298.15 K) = -15716±34 kJ/mol (chabasite), -42874±106 kJ/mol (erionite), -31277±88 kJ/mol (gmelinite), -19717±33 kJ/mol (phillipsite), and -19589±42 kJ/mol (harmotome).

The measured values of enthalpies of formation of natural calcic chabasite are consistent with the results of previous study of synthetic cation-exchanged (Ca, Li, Na, K) zeolites with the chabasite-like net-work structure [4]. By the method of high-temperature calorimetry [4], enthalpies of formation of calcic, sodic, and potassic chabasites with different Si/Al ratio and cation and water contents. For the Ca-chabasite with close ratio Si/Al=1.95, the value $\Delta H^0_{f,\ ox}$ (298.15 K) = -349.9±10.3 kJ/mol, that is well consistent with our data (-347.2±32.8 kJ/mol).

Enthalpies of dehydration were measured by

(1) method of dropping-in of zeolite from room temperature into the Kalve calorimeter without melt; the total function including both enthalpy of the sample and its enthalpy of dehydration at T = 973 K $[(H^0_T-H^0_{298.15}) + \Delta H^0_{dehyd.973}]$;

(2) method of the differential scanning spectroscopy in the regime of heating with the rate 1-2 grad/min in the temperature interval corresponding to dehydration of zeolites. As a result, the following values of enthalpy of the complete dehydration were obtained: ΔH^0_{dehyd} = 1116 kJ/mol for harmotome in the interval 40-440^OC and ΔH^0_{dehyd} = 991 kJ/mol for phillipsite in the interval 50-500^OC. Enthalpies of dehydration of chabasite, gmelinite, and erionite were calculated from the experimental (microcalorimeter Kalve) data. The necessary values of $H^0_T-H^0_{298.15}$ for dehydrated zeolites is not possible to measure because of their rapid re-hydration after heating at 973 K. Therefore, the estimation of these values on the basis of the enthalpy increment for number of dehydrated zeolites, measured previously, is shown. For all dehydrated zeolites, we calculated the $H^0_T-H^0_{298.15}$ value per one oxygen atom in the formula. The values for different types of zeolites were found to be close to each other. An average value, 23±0.8 kJ/mol, was used for estimation of the enthalpy increment for dehydrated erionite, gmelinite, and chabasite. The following values of enthalpies of dehydration were obtained: ΔH^0_{dehyd} (298.15 K) = 534±136 kJ/mol (erionite), 671±75 kJ/mol (gmelinite), and 382±47 kJ/mol (chabasite). The values involve all thermal effects of all processes, which accompany the zeolite dehydration, including the compaction of the Al-Si net-work.

The values of Gibbs free energies of formation of the studied zeolites were calculated: $\Delta G^0_{f,\ el}$ (298.15 K) = -14366±34 kJ/mol (chabasite), -39492±106 kJ/mol (erionite), -28575±89 kJ/mol (gmelinite), -18200±34 kJ/mol (phillipsite), and -18082±42 kJ/mol (harmotome).

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