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ENTROPY OF ZEOLITIC WATER

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Abstract

Zeolite-water heat-pump system is suitable for effective use of low temperature heat sources such as solar energy and waste heats from factories, that is, for energy saving. The heat exchange function of zeolite owes obviously to the nature of the zeolitic water, the state of which can be described in terms of the entropy value as an independent component of H_2O. Most entropy values of zeolitic water have been given so far to be intermediate between those of liquid water (69.9 J mol^{-1} K^{-1} at 298 K) and ice (41.5 J mol^{-1} K^{-1} at 273 K). The present calorimetric measurements proved, however, that the entropy value for Mg-exchanged A-type zeolite is so small, even at the ambient temperature, as to be compared with the residual entropy of ice at 0 K.

Keywords: entropy, heat pump, hydration, zeolite, zeolitic water

Introduction

The zeolite-water heat-pump system was proposed by Tchernev to be useful for the solar refrigerator or the solar air conditioner without using electricity [1, 2]. The original heat pump system used natural zeolites as absorbers. Mizota *et al*. [3] suggested that the Mg-exchanged A-type of zeolite showed more than double ability to exchange heat in comparison with those of natural zeolites at the dehydration temperature of 373 K in vacuum. Their small scale test with only 350 g of zeolite showed that the heat pump system had the sufficient ability to make ice of the temperature as low as 255 K by using only two heat sources at 373 for dehydration and at 298 K for vapor-condensation [4].

Water in zeolites has been called ‘zeolitic water’, which is occluded in the small voids formed in the alumino-silicate framework of zeolite, and has been commonly recognized to have the physicochemical nature between those of liquid water and crystalline water. Many workers have been interested in energetic states of the zeolitic water in various zeolites and other micro-porous materials . Johnson and his group [5–8], and Hemingway and Robie [9], for example, gave entropy values of zeolitic water in various zeolites by measuring heat capacities from low temperature

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for both hydrated and dehydrated zeolite samples. The method is not always sufficient to evaluate the entropy of zeolitic water as an independent component, because it includes no interaction term for hydration or dehydration [10]. Van Reeuwijk measured precisely the dehydration enthalpies at high temperatures and gave the entropy values of zeolitic water [11]. Unfortunately, the values were given based on a rough estimation that the entropy of vapor at 373 K was equal to that at 298 K [10]. Most entropy values given so far have been in the intermediate value between those of water and ice [10]. This may indicate that these results have been influenced by the common sense on the zeolitic water that should have the characters in between those of water and ice.

In the process of clarifying the unique capability of the zeolite-water heat-pump system, we have been convinced, however, that the entropy of the zeolitic water is very low as the independent component of H_2O. Mizota *et al*. [10] made an attempt to estimate the entropy from the enthalpy data obtained from rehydration to dehydrated zeolites, and gave the very small entropy of 3 J mol^{-1} K^{-1} at 298 K. However, the method of derivation was also insufficient, as the equilibrium vapor pressure was not measured at the same time of the enthalpy-measurement but substituted with the value of the vapor pressure on liquid water equilibrated to supply vapor for the hydration in the calorimeter.

The main object of the present work is to fill up the above mentioned insufficiency and give the proper entropy of the zeolitic water to support the theoretical background of the zeolite-water heat-pump system, because the low entropy state of the water molecules in zeolites was considered as a key indicator to understand the proper function of the zeolite-water system.

Experimental

To evaluate the true entropy values of zeolitic water as an independent component of H_2O, it is necessary to determine the equilibrium water vapor pressure at the measurement of the vapor-hydration enthalpy. The well known Clausius–Clapeyron equation relates the differential molar hydration enthalpy to the equilibrated vapor pressure at the same temperature and at the same water content of the zeolite concerned. In order to measure the temperature dependence of equilibrium vapor pressure, we equipped a convenient apparatus (Fig. 1) [12], which is designed especially to decrease the volume of the dead space (25.60 cm^3) not to change the water content of the zeolite sample during temperature-change of the measurement. The sample amount is 1 g, and water content of the zeolite is about 26.7% at most. This shows that only 0.24% of the total water in zeolite or 0.06% of the zeolite sample-mass exists in the dead space at the maximum. The apparatus directly measures the vapor pressure of zeolite sample at various temperatures and at the same hydration level.

Another approach will be the direct measurement of the integrated molar hydration enthalpy of liquid water. We used the water hydration calorimeter (Fig. 2) [12] to measure directly the immersion heat evolved form the hydration, when the ampoule of sample-container is broken in water. The water content was determined

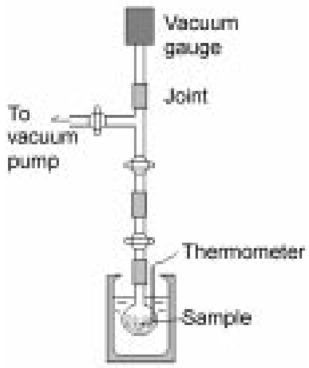

Fig. 1 Apparatus for measuring equilibrium vapor pressure of zeolite

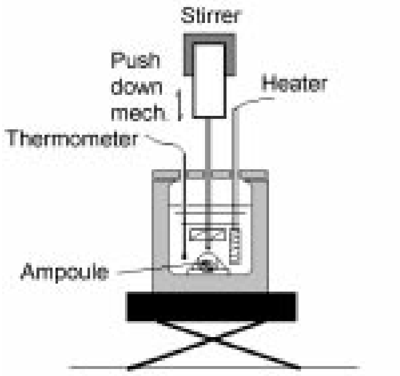

Fig. 2 Adiabatic water hydration calorimeter. Glass ampoule sealed with dehydrated zeolite sample is broken by pushing down the stirrer

by weighing the ampoule and the sealed off part after dehydration, considering the air weight evacuated out of the ampoule.

Results and discussion

The Clausius–Clapeyron method

The vapor pressure and the temperature relations are shown in Fig. 3 at three levels of the water content for Mg50-A, the expression of which indicates that the amount of Na^+ in the as synthesized Na-A type zeolite (LTA) is exchanged with corresponding amount of Mg^{2+} by 50%. The $\ln P$–$1/T$ plots can be simulated well with 2nd-order equations as shown in the figure with solid lines. Each equation determines the hydration enthalpy, ΔH, as the inclination at a temperature. This is obvious from the form of the Clausius–Clapeyron equation as follows:

$$\ln P = -\frac{\Delta H}{R}\left(\frac{1}{T}\right) + \text{const.} \qquad (1)$$

Relations between enthalpy and temperature are shown in Fig. 4. The equilibrium pressure is also specified from the process. The entropy value at 298.15 K is calculated as follows,

$$S_{\text{zw}} = 188.825 - R\ln\left(\frac{P}{P_0}\right) + \frac{\Delta H}{298.15} \qquad (2)$$

where P and P_0 are the equilibrium pressure of vapor and the standard pressure (101325 Pa), respectively. The value 188.825 J mol^{-1} K^{-1} is the standard entropy of vapor at 298.15 K and at 101325 Pa. Entropy values *vs*. dehydration level of the zeolite at 298 K are shown in Fig. 5. The figure does not include data in highly dehydrated state due to the limitation of pressure gauge used in the present work, but it shows clear tendency of the decrease of entropy values to the lower hydrated states.

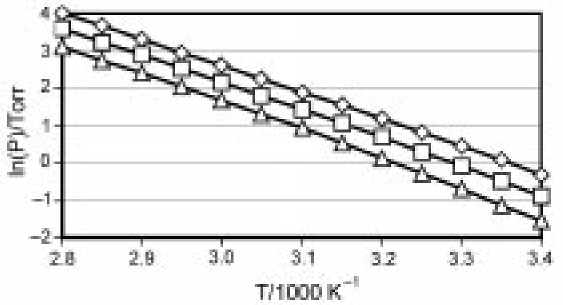

Fig. 3 ln$P$–1/T plot for zeolite dehydration. Dehydration levels are 0, 3.14 and 5.03% from upper to lower, respectively

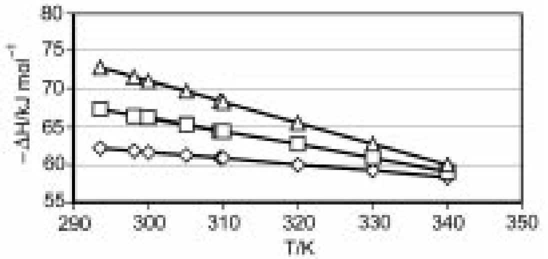

Fig. 4 ΔH–T plot for zeolite Mg50-A. Dehydration levels are 0, 3.14 and 5.03% from upper to lower, respectively

Direct hydration of liquid water

The enthalpy relations [13] among H_2O-phases we obtained were compiled in Fig. 6. The –20 kJ mol^{-1} for the liquid water hydration to the zeolite at 298 K derives the entropy of zeolitic water as follows,

$$S_{zw} = 69.9 - \frac{20\cdot 10^3}{298.15} = 3.0 \text{ J mol}^{-1}\text{ K}^{-1} \qquad (3)$$

Where, the 69.9 J mol^{-1} K^{-1} is the entropy value of liquid water at 298.15 K [14]. The value, 3.0 J mol^{-1} K^{-1}, corresponds to the derived form of the vapor hydration method by Mizota *et al.* who assumed that the equilibrium vapor pressure was equal to that of liquid water [10]. The coincidence is natural due to the relations in thermochemical consistency among H_2O-phases: vapor, water and zeolitic water as shown in Fig. 6.

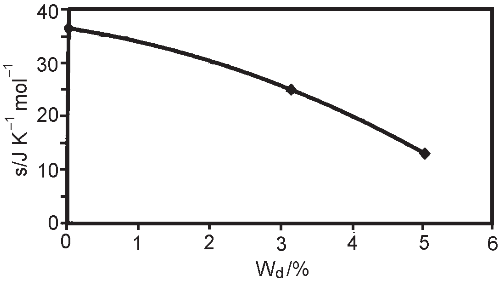

Fig. 5 Entropy *vs.* dehydration level. W_d: dehydration percent

Other examples for hydration enthalpy of zeolite from liquid water were given recently by Yang and Navrotsky for variously cation-exchanged types (HY, LaY, CaY, LiY, NaY, KY, RbY and CsY) of the zeolite Y [15]. The integral molar hydration enthalpies obtained from the drop calorimetry are ranging from –13 kJ mol^{-1} for KY to –23 kJ mol^{-1} for LiY in their figure and with a deviated value of –7.5 kJ mol^{-1} of HY. The former two enthalpies give the entropy values of the zeolitic water, followed by the Eq. (3), to be 26 and –7 J mol^{-1} K^{-1}, respectively. The negative value is not astonishing but coming from the limitation of the assumption as

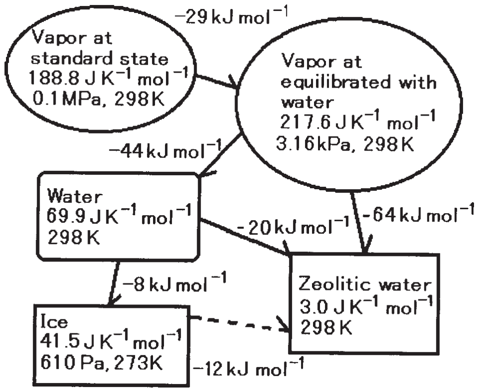

Fig. 6 Thermochemical relations among H_2O-phases. Entropy value of a phase is written in each frame with the equilibrium vapor pressure and temperature. The heat value necessary for the change between adjacent states is written with the arrow to show the direction

the independent component of H_2O in the zeolite. This shows only that the interaction of water molecules with cations or the framework of the zeolite is too strong to maintain the assumption of independency. The entropy for HY seems rather big to be 45 J mol^{-1} K^{-1} which is a little larger than 41.5 J mol^{-1} K^{-1} of ice at 273.15 K.

Relations with zeolite-water heat-pump system to improve Carnot efficiency

The very low vapor pressure of the dehydrated and cooled zeolite bed then induced strong vaporization of water in a reservoir, and resulted in freezing. The ice temperature reached 255 K even in the preliminary experiment [4].

The Carnot efficiency, $\eta=1-T_2/T_1$, determines the maximum and the ideal efficiency for any type of engines, which work between two heat sources of temperatures, T_1 and T_2. Most technologies have been concerned to improve the efficiency by adopting the higher temperature T_1 for an engine, because the available low temperature T_2 is restricted generally to the ambient temperature at around 298 K on the earth surface. The heat pump, however, has the ability of generating lower temperature heat sources which contribute to improve the Carnot efficiency by lowering T_2. The other important fact is that we can access the low entropy state of water molecules in the zeolite-void via vapor to extract energy.

Conclusions

Zeolitic water has been experimentally proved to be in a very low entropy state, based on the assumption of the independent component of H_2O in the zeolite. This provides the background for the operation of the zeolite-water heat-pump system, which is suitable for using relatively low temperature heat sources such as the solar heat and many waste heats from factories. The entropy value, 3 J mol^{-1} K^{-1}, of zeolitic water obtained for Mg50-A zeolite at 298 K is accidentally similar to the famous residual entropy of ice, 3.37 J mol^{-1} K^{-1}, at 0 K.

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