Clays and Clay Minerals, Vol. 27, No. 6, 423–428, 1979.

THERMODYNAMIC AND STRUCTURAL FEATURES OF WATER SORPTION IN ZEOLITES

MARIE HÉLÈNE SIMONOT-GRANGE

Laboratoire de Recherches sur la Réactivité des Solides (L.A. 23)
Faculté des Sciences Mirande, B.P. 138, 21004 Dijon Cedex, France

Abstract—The water adsorption capacity of zeolites is a function of pressure and temperature. Desorption of zeolites may be of three types, wherein the crystal lattice undergoes (1) no or little change, (2) a reversible change, or (3) an irreversible change. In the first two cases, the divariance of the zeolite–water vapor equilibrium results in networks of isobars, isotherms, and isosteres which can be transformed into a "characteristic" curve following the Polanyi-Dubinin theory. Because the volume of the micropores of a zeolite structure is constant, the isotherms and "characteristic" curve can be transformed linearly. During desorption, if the volume of the micropores varies due to a change of structure, the curves show linearity breaks.

On the basis of X-ray diffraction, differential thermal, and thermal gravimetric analyses, the equilibrium curves and structural changes of heulandite and stilbite were determined, using specially designed equipment. In the reversible adsorption range, heulandite shows no linearity breaks in the transforms and no structural variation. Stilbite, however, shows a linearity break in the transforms corresponding to a structural change.

Key Words—Heulandite, Stilbite, Thermal stability, Water sorption, Zeolite.

INTRODUCTION

Divariance of the zeolite–water vapor system

Three intensive parameters, water vapor pressure (P), temperature (T), and water adsorption capacity (n) define the zeolite–water vapor system. Thermogravimetric data show that equilibrium points are obtained by fixing two of these three parameters. The exchanges between adsorbed water molecules and water vapor are therefore divariant. This divariance can be explained by the structure of the adsorbent. The zeolite framework consists of AlO_4 and SiO_4 tetrahedra surrounding numerous cavities and constitutes a rigid, practically undeformable structure in which water molecules can be housed. The zeolite crystalline framework remains unchanged during water sorption, and at no time does a new phase form. From a thermodynamic point of view, only exchanges between the water molecules in the zeolite and those in the vapor state must be considered. Equilibrium may therefore be expressed as follows:

$$H_2O_{(zeolite)} \rightleftarrows H_2O_{(gas)}$$

The arbitrary choice of two of the three intensive parameters that define the zeolite–water vapor system leads to a series of continuous equilibrium curves that are isobaric $(n,T)_P$, isothermic $(n,P)_T$, or isosteric $(P,T)_n$. Two sets of curves can be expressed as series of straight lines. On the one hand, the isosteres may be represented by:

$$\text{Log } P = f(1/T)_n$$

which is a linear function over a relatively restricted temperature range. These straight lines lead to the determination of the isosteric enthalpies and entropies. On the other hand, for temperatures well below the critical temperature of water (374°C), the adsorbed water molecules are in a state comparable to that of liquid water. The volume available for adsorbed water in a rigid zeolite framework is a constant, independent of P and T. Thus, it is possible to define a filling coefficient θ for a zeolite at temperature T, by the ratio of the actual amount of adsorbed water, $W = nv$ (under a pressure P), to the maximum amount of adsorbed water, $W_0 = n_0v$ (under the saturating vapor pressure, P_0), as follows:

$$\theta = W/W_0 = n/n_0$$

where v is the molar volume of water at temperature T.

By analogy with the Langmuir theory (1918) and the work of Peterson *et al.* (1965), the isotherms may then be represented on the linear diagram by

$$\text{Log}(1 - \theta)/\theta = f(\text{Log } P)_T$$

except where P is close to P_0. Obviously, if for any reason the zeolitic framework were changed, i.e., if the intracrystalline volume available for water molecules is no longer constant (W_0 is not constant along an isotherm), breaks in linearity of these curves would be seen. It is obvious that these breaks will also be found on the isobars and isotherms; but as these curves are not linear they are often difficult to detect, and it is preferable to perform linear transforms. Therefore, such linear curves can be particularly valuable in detecting structural changes in the zeolite framework.

Adsorption potential theory

Because zeolites are microporous, the adsorption potential theory of Polanyi (1914, 1916), experimentally

Copyright © 1979, The Clay Minerals Society

https://doi.org/10.1346/CCMN.1979.0270605 Published online by Cambridge University Press

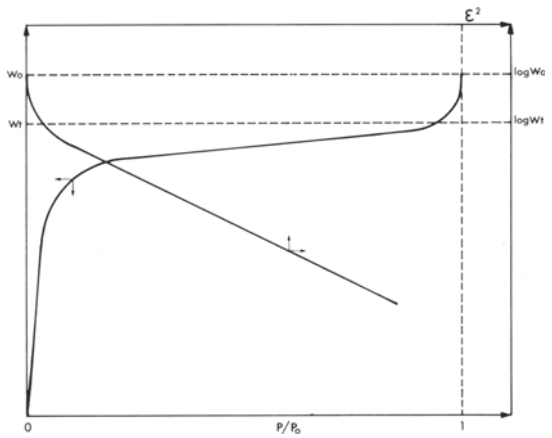


Figure 1. Theoretical forms of the isotherms and the characteristic curve.

developed by Dubinin (1966), may be applied to the zeolite–water vapor system. This theory leads to a characteristic curve $\epsilon = f(W)$, relating the adsorption potential ϵ to the adsorbed quantity W. Such a curve is specific for each adsorbent–adsorbate pair. Where temperature is less than the critical temperature of the adsorbate, i.e., where the adsorbate may be regarded as a liquid, the adsorption potential ϵ expresses the free enthalpy variation accompanying the isothermic, reversible transformation of a mole of adsorbate on the adsorbent phase into a mole of adsorbate in the liquid state, i.e., where $\epsilon = RT \text{ Log } P_0/P$. It can be predicted by this theory that if the adsorbed volume is held constant, ϵ is independent of temperature.

The great importance of this curve is that for a given adsorbent, the adsorption isotherms of any gas can be predicted. Indeed, for a given gas, it is possible to calculate the whole series of curves if the characteristic curve can be plotted from an adequately selected isotherm. In addition, it is possible to pass from the characteristic curve of a given gas to that of any gas by means of affinity coefficients.

Assuming the adsorbed volume to be a Gaussian function of the adsorption potential, Dubinin (1966) expressed the relationship $\epsilon = f(W)$ as $W = W_t e^{-A\epsilon^2}$, where A is a constant characteristic of the gas and of the distribution of pores in the adsorbent, and W_t is the total volume available to the adsorbate. When W_t is constant this relationship, written as $\text{Log } W = \text{Log } W_t - A\epsilon^2$, can be plotted as a straight line $\text{Log } W = f(\epsilon)^2$, which is the linear transform of the characteristic curve. Its intercept on the ordinate gives the total volume available for the adsorbate. W_t differs from W_0 by the fact that it does not take into account the amount adsorbed under conditions close to saturation, but only that adsorbed at the end of the stage of the adsorption isotherm (Figure 1). In the literature W_t and W_0 are, however, often mistaken.

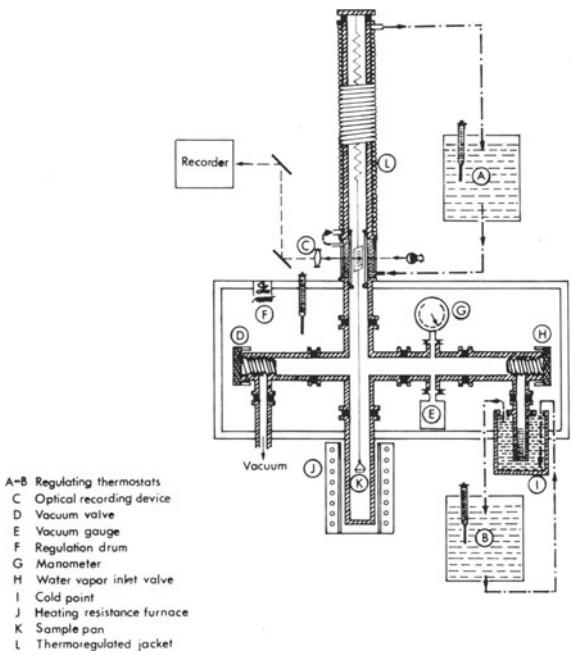


Figure 2. McBain-type thermobalance with automatic water-vapor pressure regulator designated "cold point."

If the total volume available for the adsorbate varies because of a change in the zeolite framework, it is obvious that breaks in the linear transform will result. The characteristic curve is therefore of particular interest because it summarizes the isobars, isotherms, and isosteres, and it allows possible structural changes to be noted.

EXPERIMENTAL

To acquire a precise knowledge of P, T, n, and the zeolite structure, thermal gravimetric (TGA), differential thermal (DTA), and X-ray powder diffraction (XRD) methods were used to study the solid–water vapor systems investigated by Simonot (1970). Experiments were devised such that for each technique, the water vapor pressure over the sample was known and controlled. The "cold point" process described by Tiselius and Brohult (1934) and used by Lavanant (1963) was employed. The "cold point" method utilizes a trough of distilled and degassed water, thermoregulated at T_0 by means of an external water flow. A water vapor pressure is created which corresponds to the vapor pressure of the water at T_0; thus, the water in the trough constitutes the coldest point in the system, thereby fixing the water vapor pressure. This device is also an automatic pressure regulator; indeed, any pressure increases resulting from sample dehydration bring about a condensation in the trough, and any pressure decreases resulting from sample rehydration bring about water evaporation.

https://doi.org/10.1346/CCMN.1979.0270605 Published online by Cambridge University Press

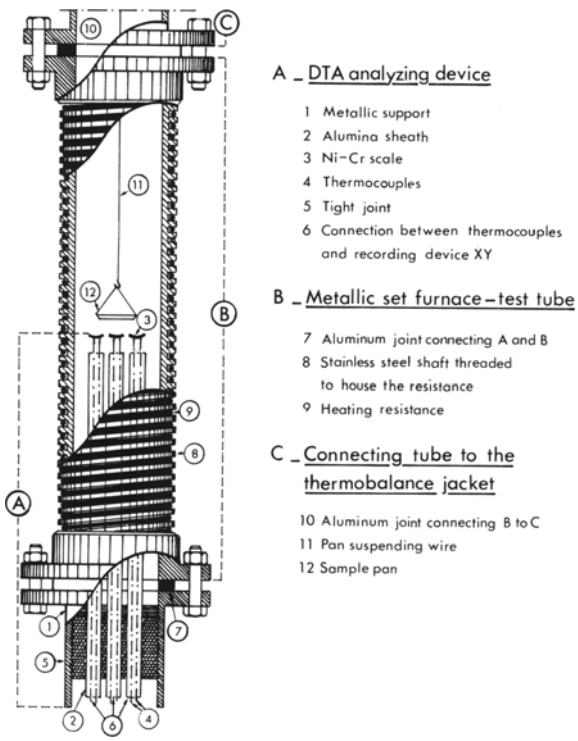


Figure 3. DTA analyzing device coupled to the thermobalance under controlled water-vapor pressure.

TGA was performed in a McBain-type balance (McBain and Bakr, 1926) (Figure 2). The material to be analyzed was placed in a pan at the end of a silica spring and heated by means of a thermoregulated bath or furnace. The system for regulating the water vapor pressure was placed as close to the sample as possible. Weight variations were recorded as a function of time by means of a spot tracer which detected the displacements of a luminous aperture articulated to the spring (Barret, 1957).

DTA was coupled with TGA to locate accurately the temperatures of the thermal effects and weight losses (Figure 3) relative to one another. For this purpose, the analyzing device (Mazières, 1959) consisted of three chromel-alumel thermocouples (one for temperature, the other two mounted in opposition to form the differential device) placed at the bottom of the testtube of the balance, less than 2 cm from the sample holder.

XRD analyses were performed in a heating cell (Barret and Gérard, 1964) constructed so that the sample, placed at the core of the furnace under controlled water vapor pressure, was simultaneously exposed to CuKα radiation, oscillated through a small, angular domain, and heated at a constant rate. This method allowed a structural change to be detected by means of shifts in d spacings and intensities of a small group of reflections at known P and T. To locate the temperatures of structural changes relative to thermal effects, DTA was coupled with XRD by dividing the sample holder of the heating cell into halves, corresponding to the two differential thermocouples of the DTA (Gérard, 1967). Thus, through DTA, coupled on the one hand with TGA, and on the other with XRD, it was possible to locate accurately weight variations relative to structural changes.

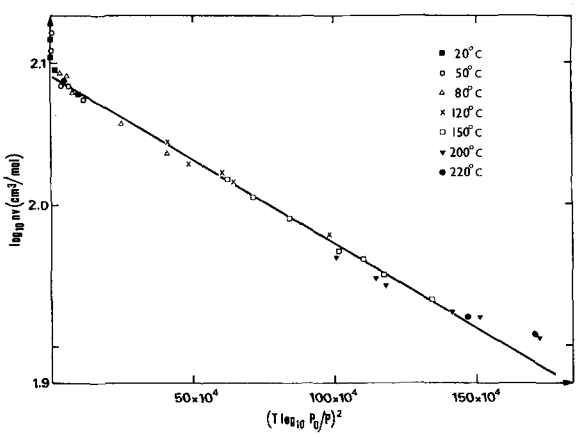


Figure 4. Heulandite characteristic curve in linear form.

Static experiments were carried out at constant T and P to obtain data for equilibrium point plots, and linear temperature-rise experiments were made to detect thermal effects associated with structure changes and weight variations.

EXAMPLES

Heulandite

The locatality of the natural heulandite sample used is not known; however its chemical composition is:

$$Ca_{1.00}Na_{0.12}Mg_{0.06}K_{0.08}[Al_{2.20}Si_{6.79}O_{18}]\cdot 6.51\ H_2O$$

$$Z = 4 \quad \text{(Simonot, 1970).}$$

As noted by Merkle and Slaughter (1968), although the framework of heulandite is monoclinic, a pseudo-orthorhombic unit cell can be developed.

The study of the water sorption of heulandite relative to P and T shows a divariant domain between the hydration states, 6.51 H_2O and 3.20 H_2O. Networks of isobars, isotherms, and isosteres are summarized in Figure 4 by the linear transform resulting from the characteristic curve. By means of experimental techniques described previously, no change was observed in the X-ray powder diffraction pattern during the removal of 3.31 H_2O, and a slight continuous depression relative to the base line suggested only a weak thermal effect (Simonot-Grange *et al.*, 1968; Simonot-Grange and Cointot, 1969). In this region, H_2O molecules do not seem to contribute to the stability of the zeolite framework. The linear transform of the characteristic curve

https://doi.org/10.1346/CCMN.1979.0270605 Published online by Cambridge University Press

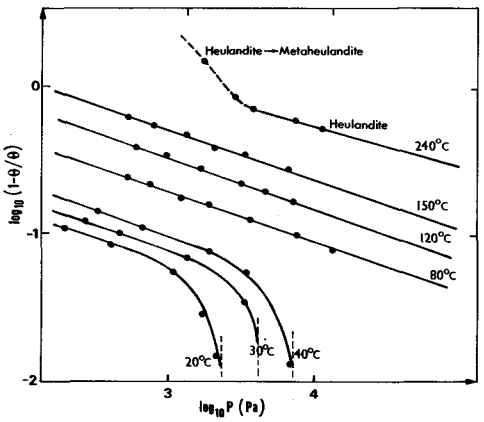


Figure 5. Heulandite isotherms in linear form: --- irreversibility; — reversibility.

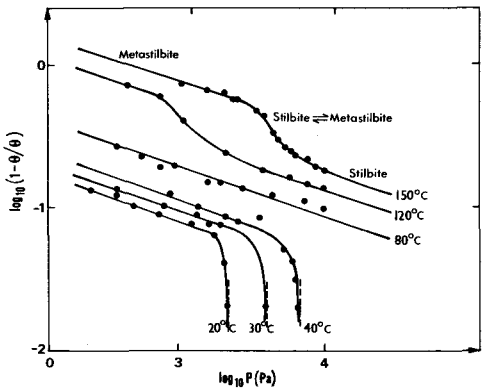


Figure 7. Stilbite isotherms in linear form showing up a break owing to a structural transformation.

yields a bulk volume available for water of W_t = 114 cm³/mole, a value which is comparable to that calculated by the geometrical method of Kiselev and Lopatkin (1963), i.e., 115 cm³/mole, but differs by about 7%, from W_0, a saturation value determined from the adsorption isotherms. If dehydration is carried on beyond 3.20 H_2O, heulandite is irreversibly converted into metaheulandite (Simonot, 1970; Alberti, 1973). No equilibrium point can be obtained, and it is no longer logical to refer to zeolitic water but to structural H_2O molecules. Because the zeolite framework has been changed, the linear transforms, Log $(1-\theta)/\theta$ = $f(\text{Log P})_T$ (Figure 5), show sharp changes in their slopes in the vicinity of the transformation.

Stilbite

The chemical formula of the natural stilbite sample used from Dauphiné, France, is:

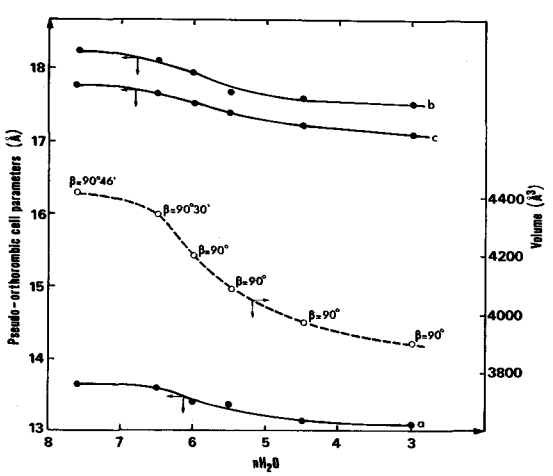


Figure 6. Evolution of the stilbite cell parameters during water sorption.

$$Ca_{1.08}Na_{0.12}Mg_{0.02}K_{0.08}[Al_{2.18}Si_{6.76}O_{18}]\cdot 7.64\ H_2O$$

Z = 8 (Simonot, 1970).

The framework of stilbite is monoclinic, but a pseudo-orthorhombic unit cell can be found (Galli and Gottardi, 1966; Slaughter, 1970).

The study of water sorption by stilbite relative to P and T shows a divariant domain between the hydration states, 7.64 H_2O and 3.00 H_2O. Unlike heulandite, however, removal of water between the 6.70 H_2O state and the 5.00 H_2O state gives rise to a continuous and reversible contraction of the lattice involving a significant DTA effect (Grange, 1964) which corresponds to the reversible transformation of stilbite to metastilbite. Unlike reversible crystal water which is associated with monovariant equilibrium and discontinuous structural changes between two limiting hydration states, every hydration state located between 6.70 H_2O and 5.00 H_2O can be found. The conversion analysis (Simonot-Grange *et al.*, 1970) followed *in situ* by X-ray powder diffractometry relative to P and T shows that, between these two hydration states, the amount of water adsorbed fixes the dimensions of the unit cell (Figure 6) (cf. Abbona and Franchini Angela, 1970, similar; Aumento, 1966, different results; Van Reeuwijk, 1974). Contrary to the present results and to those of Abbona and Franchini Angela (1970), Aumento (1966) noted an increase in the *a* and *b* parameters during desorption. The Ca/Na and Si/Al ratios of the samples examined by Abbona and Franchini Angela and in the present study (both from Dauphiné, France) are larger than those of the samples studied by Aumento (from a different locality) and approach the theoretical formula of stellerite, rather than stilbite proper. Such compositional differences may explain the differences in cell-dimension behavior.

In this range there is a continuous decrease in the volume available for water, and the transforms of the isotherms and the characteristic curve show a contin-

https://doi.org/10.1346/CCMN.1979.0270605 Published online by Cambridge University Press

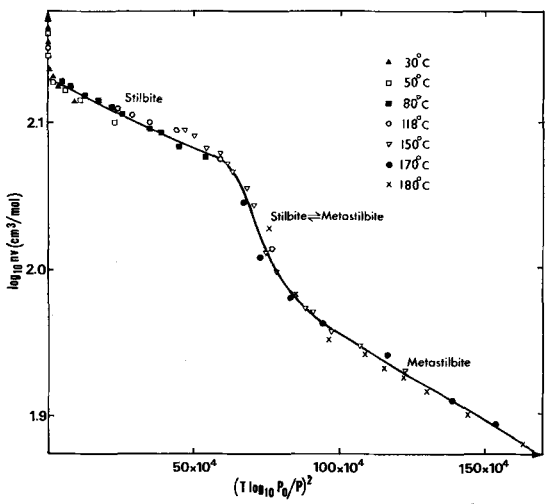


Figure 8. Stilbite characteristic curve in linear form showing a break owing to a structural transformation.

uous break in linearity (Figures 7 and 8). The linear parts of these curves correspond to the stability domains of stilbite and metastilbite, i.e., those in which a zeolite framework is stable. The intersections of the linear parts of the curves on the ordinate give as a total volume available for water, W_t = 134 cm³/mole for stilbite and W_t = 117 cm³/mole for metastilbite. The stilbite value is comparable with that calculated from the geometrical method of Kiselev and Lopatkin (1963), i.e., 136 cm³/mole, but differs by about 8% from W_0, a value determined at saturation from adsorption isotherms. If dehydration is carried beyond 3.00 H_2O, the product cannot be rehydrated to the initial stilbite phase.

CONCLUSIONS

The studies of heulandite and stilbite clearly show that sorption is closely related to the total volume available for the adsorbate in the zeolite framework, and that the shape of the water sorption curves corresponds to the structural changes occurring during dehydration or rehydration. Therefore, it is possible to speak of "typical" zeolitic water (Van Reeuwijk, 1974) in the range 6.51 H_2O–3.20 H_2O of heulandite and of both structural and divariant water in range 7.64 H_2O–3.00 H_2O of stilbite. The sorption curves required for the accurate knowledge of adsorption capacity can also be used to detect structural changes that may occur during sorption.

REFERENCES

Abbona, F. and Franchini Angela, M. (1970) Sulla disidratazione della stilbite. Nota I. Ricerche termiche e roentgenografiche: *Atti. Accad. Sci. di Torino* **104,** 309–321.

Alberti, A. (1973) The structure type of heulandite B (heat-collapsed phase): *Tschermak's Mineral. Petrog. Mitt.* **19,** 173–184.

Aumento, F. (1966) Thermal transformations of stilbite: *Can. J. Earth Sci.* **3,** 351–366.

Barret, P. (1957) Dispositif de projection et d'enregistrement optique des élongations d'une balance à hélice de quartz: *Bull. Soc. Chim. Fr.* **165,** 912–914.

Barret, P. and Gérard, N. (1964) Enceinte à température et atmosphères contrôlées utilisable pour la diffractométrie des rayons X: Brevet d'invention français no. 1352990.

Dubinin, M. M. (1966) Modern state of theory of gas vapour adsorption by microporous adsorbents: *Pure Appl. Chem.* **10,** 309–321.

Galli, E. and Gottardi, G. (1966) The crystal structure of stilbite: *Mineral. Petrogr. Acta* **12,** 1–10.

Gérard, N. (1967) Contribution à l'étude de la dégradation thermique de l'acide oxalique et des oxalates alcalino-terreux. Thèse doctorat d'état, Dijon, France, 143 pp.

Grange, M. H. (1964) Critère pour l'identification d'eau zéolitique dans les hydrates en analyse thermique différentielle et en thermogravimétrie: *C. R. Acad. Sci. Paris* **259,** 3277–3280.

Kiselev, A. V. and Lopatkin, A. A. (1963) Geometric structure of zeolite cavities of the A and X types: *Kinet. Katal.* **4,** 786–791.

Langmuir, I. (1918) The adsorption of gases on plane surfaces of glass, mica and platinium: *J. Amer. Chem. Soc.* **40,** 1361–1403.

Lavanant, F. (1963) Contribution à l'étude de quelques aluminates de calcium hydratés: Thèse ingénieur-docteur, Dijon, France, 137 pp.

Mazières, C. (1959) Appareil pour microanalyse thermique différentielle: *C. R. Sci. Paris* **248,** 2990–2992.

McBain, J. W. and Bakr, A. M. (1926) A new sorption balance: *J. Amer. Chem. Soc.* **48,** 690–695.

Merkle, A. B. and Slaughter, M. (1968) Determination and refinement of the structure of heulandite: *Amer. Mineral.* **53,** 1120–1138.

Peterson, D. L., Helfferich, F., and Blytas, G. C. (1965) Sorption and ion exchange in sedimentary zeolites: *Phys. Chem. Solids* **26,** 835–848.

Polanyi, M. (1914) Über die Adsorption vom Standpunkt des dritten Wärmesatzes: *Verh. Dtsch. Phys. Ges.* **16,** 1012–1016.

Polanyi, M. (1916) Adsorption von Gasen (Dämpfen) durch ein festes nichtflüchtiges Adsorberis: *Verh. Dtsch. Phys. Ges.* **18,** 55–80.

Simonot, M. H. (1970) Contribution à l'étude des systèmes divariants zéolite-eau. Cas de la heulandite et de la stilbite: Thèse doctorat d'état, Dijon, France, 165 pp.

Simonot-Grange, M. H. and Cointot, A. (1969) Evolution des propriétés d'adsorption de l'eau par la heulandite en relation avec la structure cristalline: *Bull. Soc. Chim. Fr.* 421–427.

Simonot-Grange, M. H., Cointot, A., and Thrierr-Sorel, A. (1970) Etude des systèmes divariants zéolite-eau. Cas de la stilbite. Comparaison avec la heulandite: *Bull. Soc. Chim. Fr.* 4286–4297.

Simonot-Grange, M. H., Watelle-Marion, G., and Cointot, A. (1968) Caractères physico-chimiques de l'eau dans la heulandite. Etude diffractométrique des phases observées au cours de la déshydratation et de la réhydratation: *Bull. Soc. Chim. Fr.* 2747–2754.

Slaughter, M. (1970) Crystal structure of stilbite: *Amer. Mineral.* **55,** 387–397.

Tiselius, A. and Brohult, S. (1934) Sorption von Wasserdampf an Chabasit bei verschiedenen Temperaturen: *Z. Phys. Chem. Abt. A* **168,** 248–256.

Van Reeuwijk, L. P. (1974) The thermal dehydration of natural zeolites: *Mededelingen Landbouwhogeschool* **74-9,** Wageningen, Netherlands, 88 pp.

(Received 13 February 1979; accepted 10 July 1979)

https://doi.org/10.1346/CCMN.1979.0270605 Published online by Cambridge University Press

Резюме—Способность цеолитов адсорбировать воду является функцией давления и температуры. Десорбция цеолитов может быть трех типов, в соответствии с которыми кристаллическая решетка подвергается (1) небольшому изменению или оно отсутствует, (2) обратимому изменению, или (3) необратимому изменению. В первых двух случаях флуктуация равновесия цеолит–водяной пар характеризуется изобарами, изотермами и изостерами, которые могут быть превращены в «характерную» кривую согласно теории Поляного-Дубинина. В виду того, что объем микропор цеолитовой структуры постоянен, изотермы и «характерная» кривая могут быть линейно преобразованы. Во время дисорбции, если объем микропор изменяется из-за изменения структуры, кривые показывают нарушения линейности.

На основе дифракционно-рентгеновских, дифференционно-термальных, и термально-гравиметрических анализов с использованием специально сконструированного оборудования были определены кривые равновесия и структурные изменения гейландита и стильбита. При обратимой адсорбции гейландит не проявляет никаких нарушений линейности в превращениях и никаких структурных изменений. Стильбит, однако, показывает нарушение линейности в превращениях, соответствующих структурному изменению.

Resümee—Das Wasseraufnahmevermögen der Zeolithe ist eine Funktion von Druck und Temperatur. Die Wasserabgabe der Zeolithe kann auf drei verschiedene Arten erfolgen, wobei die Kristallstruktur (1) nicht oder kaum, (2) reversibel, oder (3) irreversibel verändert wird. In den ersten beiden Fällen führt die Divarianz des Gleichgewichtes des Zeolithwasserdampfes zu einem Netzwerk von Isobaren, Isothermen, und Isosteren, das in eine "charakteristische" Kurve nach der Polanyi-Dubinin Theorie umgeformt werden kann. Da das Volumen der Mikroporen einer Zeolithstruktur konstant ist, können die Isothermen und die "charakteristische" Kurve linear umgeformt werden. Während der Wasserabgabe zeigen die Kurven Linearitätsbrüche, wenn sich das Volumen der Mikroporen infolge einer Strukturänderung verändert.

Aufgrund von Röntgendiffraktometrie, Differentialthermoanalyse, und Thermogravimetrie wurden die Gleichgewichtskurven und strukturellen Veränderungen von Heulandit und Stilbit bestimmt, wobei eine speziell entwickelte apparative Ausrüstung verwendet wurde. Im Bereich der reversiblen Adsorption zeigt Heulandit keine Linearitätsbrüche in den umgeformten Kurven und keine strukturelle Veränderung. Stilbit zeigt dagegen einen Linearitätsbruch in den umgeformten Kurven, der einer Strukturänderung entspricht.

Résumé—La capacité d'adsorption de l'eau par les zéolites est une fonction de la pression et de la température. Lors de la désorption des zéolites trois cas peuvent se présenter; le réseau cristallin subit (1) pas ou peu de modification, (2) une transformation réversible, ou (3) une transformation irréversible. Dans les deux premiers cas la divariance de l'équilibre zéolite–vapeur d'eau conduit aux tracés de réseaux d'isobares, d'isothermes, et d'isostères se transformant en une courbe "caractéristique" d'après la théorie de Polanyi-Dubinin. Le volume géométrique des micropores étant constant, les isothermes et la courbe "caractéristique" se transforment linéairement. Si au cours de la désorption le volume géométrique des micropores varie par suite d'un changement de structure, ces courbes présentent des accidents de linéarité.

Les courbes d'équilibre et les changements de structure de la heulandite et de la stilbite sont déterminés au moyen d'un équipement spécialement adapté mettant en oeuvre l'analyse thermogravimétrique, l'analyse thermique différentielle, et la diffraction des rayons X. Dans le domaine d'adsorption réversible, la heulandite ne montre aucun accident dans la linéarité des transformées, alors que la stilbite en accuse un correspondant à une modification structurale.

https://doi.org/10.1346/CCMN.1979.0270605 Published online by Cambridge University Press