Thermochemical Study of the Relative Stability of Dense and Microporous Aluminophosphate Frameworks

Yatao Hu*,[†] and Alexandra Navrotsky

Princeton Materials Institute and Department of Geological and Geophysical Sciences,
Princeton University, Princeton, New Jersey 08544

Cong-Yan Chen and Mark E. Davis

Department of Chemical Engineering, California Institute of Technology,
Pasadena, California 91125

Received January 13, 1995. Revised Manuscript Received July 13, 1995[®]

To understand why $AlPO_4$ exhibits the structural diversity observed, the relative stability of a series of dense and microporous $AlPO_4$ frameworks, e.g., berlinite, tridymite, cristobalite, $AlPO_4$-5, -8, -11, -42, and VPI-5, has been examined by the combination of DSC and high-temperature calorimetric experiments with molten lead borate ($2PbO{\cdot}B_2O_3$) solvent at 979 K. The enthalpies of formation at 298 K, relative to berlinite (quartz structure), are the following (in kJ/mol): tridymite, 5.1 (1.4); cristobalite, 6.1 (1.2); $AlPO_4$-5, 14.0 (2.2); $AlPO_4$-8, 11.5 (1.4); $AlPO_4$-11, 12.4 (1.2); $AlPO_4$-42, 15.6 (1.9); and VPI-5, 16.7 (2.3). All microporous $AlPO_4$ frameworks are only 11–17 kJ/mol less stable in enthalpy than berlinite. The calcined and then fully rehydrated microporous $AlPO_4$'s, $AlPO_4{\cdot}nH_2O$, show a linear correlation between the degree of hydration (n) and their molar volume. The enthalpy of interaction of adsorbed water with the framework ranges from −11 to −30 kJ/mol of $AlPO_4$, or −10 to −13 kJ normalized per mole of water. Taking the enthalpy of interaction into account, many of these microporous frameworks are energetically comparable to or more stable than berlinite in an aqueous environment. This may imply that there is little or no energy barrier to the formation of microporous $AlPO_4$ frameworks and explain the structural diversity observed for $AlPO_4$. These results are compared to those of a previous study on microporous high-silica zeolites.

Introduction

Like silica (SiO_2), aluminophosphate, $AlPO_4$, exhibits rich structural diversity. Besides three dense polymorphs, berlinite, tridymite, and cristobalite which are isostructural to quartz, tridymite, and cristobalite forms of SiO_2, a class of crystalline, microporous aluminophosphates has been discovered.[1,2] This family of aluminophosphates ($AlPO_4$'s) includes more than two dozen structures, of which some are isostructural to zeolites, some are novel.[3] $AlPO_4$'s are synthesized hydrothermally at 373–523 K from reaction mixtures containing structure-directing organic templates. The discovery of $AlPO_4$'s has triggered the synthesis of various new molecular sieves such as silicoaluminophosphates (SAPO's), metal-substituted aluminophosphates (MeAPO's) and silicoaluminophosphates (MeAPSO's), beryllophosphates, zincophosphates, molybdenum phosphates, aluminoarsenates, galloarsenates, etc.[4,5] However, despite great advances in the synthesis of molecular sieves, the discovery of novel phases is still a practice of serendipity and the method of synthesis remains largely empirical.

To understand why SiO_2, $AlPO_4$, and other systems mentioned above exhibit such rich structural diversity, a thorough understanding of framework stability and the relation between framework stability and framework topology is essential. Also knowledge about framework stability will provide support to fundamental studies of molecular sieve synthesis toward the ultimate goal: synthesizing new materials through rational design. For these reasons, we have launched a systematic investigation of the stability of microporous frameworks.

The first study was on the framework stability of a series of high silica zeolites, ZSM-5, ZSM-11, ZSM-12, SSZ-24, and cubic and hexagonal faujasite.[6] Results from high-temperature calorimetric experiments indicate that all these microporous frameworks are metastable energetically with respect to quartz by only 8–14 kJ/mol, despite a factor of 2 variation in the molar volume. The destabilization of the microporous framework may be associated with small Si–O–Si angles (<140°). These results are supported by ab initio calculations on various silicate molecules[7] and by a

---

[†] Present address: W. R. Grace & Co.-Conn., Washington Research Center, 7500 Grace Drive, Columbia, MD 21044-4098.

[®] Abstract published in *Advance ACS Abstracts,* September 1, 1995.

(1) Wilson, S. T.; Lok, B. M.; Messina, C. A.; Cannan, T. A.; Flanigen, E. M. *J. Am. Chem. Soc.* **1982**, *104*, 1146.

(2) Wilson, S. T.; Lok, B. M.; Messina, C. A.; Cannan, T. A.; Flanigen, E. M. *Intrazeolite Chemistry,* Stucky, G. D., Dwyer, F. G., Eds.; ACS Symp. Ser. 218; American Chemical Society: Washington, DC, 1983; p 79.

(3) Meier, W. M.; Olson, D. H. *Atlas of Zeolite Structure Types,* 3rd ed.; Butterworth-Heinemann: London, 1992.

(4) Kessler, H. *Proc. of the 9th Int. Zeol. Conf.*; von Ballmoos, R., et al., Eds.; Butterworth-Heinemann: Montreal, 1993; p 73.

(5) Haushalter, R. C.; Mundi, L. A. *Chem. Mater.* **1992**, *4*, 31.

(6) Petrovic, I.; Navrotsky, A.; Davis, M. E.; Zones, S. I. *Chem. Mater.* **1993**, *5*, 1805.

(7) Gibbs, G. V. *Am. Miner.* **1982**, *67*, 421.

0897-4756/95/2807-1816$09.00/0

recent theoretical calculation by Henson et al., in which symmetry-constrained lattice energy minimization has been performed on a series of pure silica polymorphs using the shell model for silicates.[8] The next calorimetric study was on a family of mesoporous silica phases, with pore diameters in the 2–5 nm range, which was synthesized using self-assembling aggregates of surfactants as structure-directing agents. All these mesoporous frameworks were found to be only 14–15 kJ/mol less stable than quartz,[9,10] with the pores behaving energetically like an inert second phase. These results imply that there is little energy barrier to the formation of microporous and mesoporous silica.

As a continuation of this work, we examined the stability of several $AlPO_4$ frameworks. Using high-temperature solution calorimetry with molten lead borate as solvent and differential scanning calorimetry, we have determined the relative enthalpies of formation of a series of $AlPO_4$ frameworks, tridymite, cristobalite, $AlPO_4$-5, -8, -11, -42, and VPI-5, along with the enthalpy of interaction of water with microporous $AlPO_4$ frameworks. In this paper, we report the results and discuss their implications for the synthesis of microporous materials.

Experimental Section

Sample Preparation. Berlinite was synthesized following Cohen and Klement's procedure.[11] Poorly crystalline $AlPO_4$-tridymite (99.9%, Alfa) was moistened with 4 M H_3PO_4 solution and then converted to the berlinite structure by hydrothermal treatment at 553 K and 5000 psi for 1 day in a sealed Pt capsule. Tridymite was prepared by treating $AlPO_4$ (99.9%, Alfa) at 1273 K for 1 day in air. Cristobalite was obtained by heating berlinite at 1573 K for 1 day in air. Microporous $AlPO_4$'s were all prepared hydrothermally from gels containing organic templates. $AlPO_4$-5 sample was synthesized, by modifying the procedure outlined in example 3 of the Union Carbide patent,[12] from a gel with composition $1.5Pr_3N{:}Al_2O_3{:}P_2O_5{:}40H_2O$ at 423 K for 48 h under autogenous pressure in a Teflon-lined autoclave (Pr_3N:tripropylamine). This as-synthesized $AlPO_4$-5 sample was then calcined at 823 K in air for 10 h. $AlPO_4$-11 was prepared, following the procedure outlined in example 32 of the Union Carbide patent,[12] from a gel with composition $Pr_2NH{:}Al_2O_3{:}P_2O_5{:}40H_2O$ at 473 K for 24 h under autogenous pressure (Pr_2NH:dipropylamine). This as-synthesized sample was then calcined at 873 K in O_2 for 10 h. VPI-5 was obtained from a gel with composition $0.025TMAOH{:}TIPOA{:}Al_2O_3{:}P_2O_5{:}40H_2O$ at 415 K for 8 h under autogenous pressure (TMAOH, tetramethylammonium hydroxide; TIPOA, triisopropanolamine).[13] The obtained solid product was then boiled in water under reflux for 12 h. $AlPO_4$-8 was made by calcining VPI-5 at 673 K in air for 12 h. $AlPO_4$-42 sample, synthesized using TMA and $(EtOH)_2NH$ as templates and in the presence of F^-,[14] was kindly provided by Dr. Henri Kessler of Laboratoire de Matériaux Minéraux, France (TMA, tetramethylammonium ion; $(EtOH)_2NH$, diethanolamine). The as-synthesized sample was then calcined at 923 K for 10 h in air. Berlinite, tridymite, and cristobalite were stored in a desiccator, whereas $AlPO_4$-5, -8, -11, -42, and VPI-5 were stored in air and were in equilibrium with the atmospheric humidity for the reason explained later in this paper.

Characterization. The physicochemical properties of $AlPO_4$ samples were characterized by various techniques described below. The chemical composition (Al:P) was determined from electron microprobe analysis using a CAMECA SX-50 microprobe. X-ray powder diffraction (XRD) patterns were collected on a Scintag PAD V diffractometer with Cu Kα radiation. For the determination of lattice parameters, XRD patterns were collected from 2θ 5–60° in steps 0.03° and a scan rate 1°/min, with Si as the external standard. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed using a SETARAM TG-DSC 111 apparatus. TGA scans were carried out in static air at a heating rate of 10 K/min. For DSC experiments, about 50 mg of the sample was encapsulated in an aluminum volatile-sample pan that has a tightly fitting lid. The lid was pierced with a small hole through which the water vapor escapes. All scans were run in a flowing Ar atmosphere from 298 to 523 K at a heating rate of 1 K/min. The heat flux sensitivity of the SETARAM 111 calorimeter, as opposed to temperature, was calibrated with α-Al_2O_3 prior to DSC experiments.

High-Temperature Calorimetry. All high-temperature calorimetric experiments were performed using a Tian-Calvet twin calorimeter, which was described in detail by Navrotsky.[15] The following three types of calorimetric experiments were performed: (1) Drop solution calorimetry that involves experiments in which sample pellets weighing from 10 to 20 mg were dropped from room temperature into molten lead borate ($2PbO{\cdot}B_2O_3$) solvent in the calorimeter maintained at 979 K. The heat of drop solution contains the heat content of the sample ($H°_{979} - H°_{298}$) plus the heat of solution of the sample at 979 K ($\Delta H_{soln,979}$). Difference in heats of drop solution of two samples gives the enthalpy difference of these two samples at room temperature. (2) Transposed temperature drop calorimetry that involves experiments in which sample pellets were dropped from room temperature into calorimeters at 979 K, without the presence of solvent. If the structure persists at 979 K during the experiment, the heat of transposed temperature drop $\Delta H_{t.t.d,979}$ measures the heat content of the sample ($H°_{979} - H°_{298}$). If chemical changes such as decomposition or dehydration occur, their energetics are included in this measurement. (3) Solution calorimetry, in which about 15 mg of sample in loose powder form was equilibrated in the calorimeter, about 5 mm above lead borate solvent, and then dissolved in solvent. All high-temperature calorimetric experiments were performed under flowing dry air atmosphere at a flow rate 1 cm^3/s. The difference in enthalpy of solution of various structures gives their relative stability at 979 K.

Results

Characterization. Figure 1 shows X-ray diffraction (XRD) patterns of various $AlPO_4$ polymorphs. All samples have good crystallinity. For the three dense polymorphs of $AlPO_4$, XRD patterns of berlinite and cristobalite agree very well with those of the corresponding low-temperature forms (α-form) in literature. Tridymite is more complex, as is its SiO_2 counterpart. The SiO_2-tridymite was found to exhibit several structural modifications at ambient temperature, and its XRD pattern varies considerably from sample to sample, due to texture effects, stacking faults, intergrowths of different modifications, etc.[16] No such detailed structural studies on $AlPO_4$–tridymite are available. The XRD pattern of our $AlPO_4$–tridymite sample resembles that of the pseudoorthorhombic L2-T$_D$ modification of SiO_2–tridymite (disordered low-tridymite $PO_{5/10}$).[16]

For microporous $AlPO_4$'s, XRD patterns are collected on their wet forms (calcined and then fully rehydrated

---

(8) Henson, N. J.; Cheetham, A. K.; Gale, J. D. *Chem. Mater.* **1994**, *6*, 1647.

(9) Petrovic, I.; Navrotsky, A.; Chen, C.-Y.; Davis, M. E. *Zeolites and Related Microporous Materials: State of the Art 1994*; Weitkamp, J., et al., Eds.; Studies in Surface Science and Catalysis, 1994; Vol. 84, p 677.

(10) Navrotsky, A.; Petrovic, I.; Hu, Y.; Chen, C.-Y.; Davis, M. E. *Microporous Mater.*, in press.

(11) Cohen, L. H.; Klement, W. *Am. Miner.* **1973**, *58*, 796.

(12) Wilson, S. T.; Lok, B. M.; Flanigen, E. M. U.S. Patent 4,310, 440, 1982.

(13) Davis, M. E.; Young, D. *Chemistry of Microporous crystals: Proc. of the Int. Symp. on Chem. of Microporous Crystals*; Inul, T., et al., Eds.; Kodunsha and Elsevier: 1991, p 53.

(14) Sierra, L.; Deroche, C.; Gies, H.; Guth, J. L. *Microporous Mater.* **1994**, *3*, 2923.

(15) Navrotsky, A. *Phys. Chem. Miner.* **1977**, *2*, 89.

(16) Graetsch, H.; Florke, O. W. *Z. Kristalogr.* **1991**, *195*, 31.

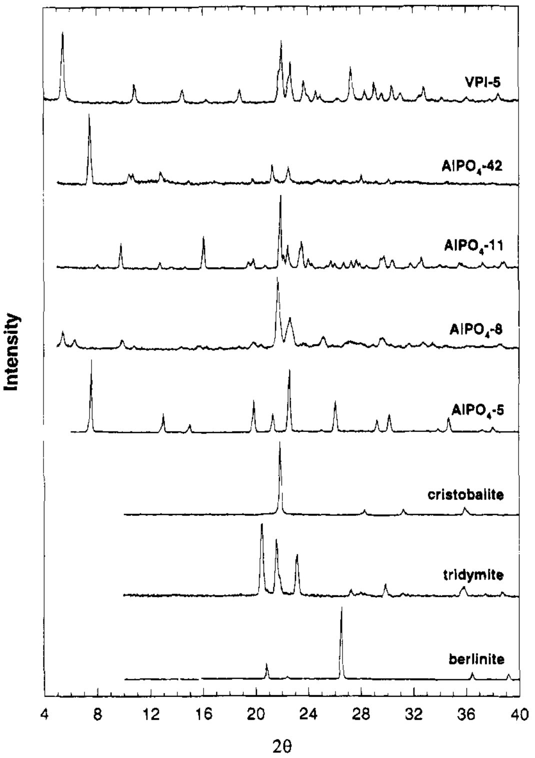

Figure 1. XRD patterns of various $AlPO_4$ polymorphs. All microporous polymorphs are in their wet forms.

Table 1. Crystallographic Data of Dense and Microporous $AlPO_4$ Phases

$AlPO_4$	space group	lattice parameters	ref
berlinite	$P3_12_1$	$a = 4.9423(3)$, $c = 10.9446(10)$	25
tridymite	F1	$a = 9.99(1)$, $b = 17.39(1)$, $c = 82.55(5)$, $\alpha = \beta = \gamma \approx 90°$	this work
cristobalite	$C222_1$	$a \approx b = 7.099(3)$, $c = 7.006(3)$	26
$AlPO_{4\text{-}5}$[a]	$P6cc$	$a = 13.700(3)$, $c = 8.404(4)$	this work
$AlPO_{4\text{-}8}$[b]	$Cmc2_1$	$a = 33.290(4)$, $b = 14.704(2)$, $c = 8.3863(6)$	21
$AlPO_{4\text{-}11}$[a]	$Pbn2_1$	$a = 13.844(2)$, $b = 17.994(4)$, $c = 8.120(2)$	this work
$AlPO_{4\text{-}42}$[c]	$Fm\bar{3}c$	$a = 23.782(6)$	this work
VPI-5[a]	$P6_3$	$a = 18.9752(1)$, $c = 8.1044(1)$	27

[a] Data for wet samples. [b] Data for dry $AlPO_4$-8. [c] Data for as-synthesized $AlPO_4$-42 with composition $[Al_{12}P_{12}O_{48}]\cdot(CH_3)_4NF\cdot 2(NH_2(CH_2CH_2OH)_2F)\cdot NH(CH_2CH_2OH)_2\cdot 8H_2O$.

samples). The reason we worked with wet samples is explained later in this paper. The XRD pattern of wet $AlPO_4$-5 agrees well with that of the as-synthesized $AlPO_4$-5,[17] although a difference in relative peak intensity due to removal of the organic template is observed. The XRD pattern of wet $AlPO_4$-11 is very different from those of as-synthesized and dry $AlPO_4$-11. As pointed out by Tapp et al.,[18] dry $AlPO_4$-11 adsorbs water at ambient temperature, resulting in a reversible but significant structural change from a body-centered orthorhombic unit cell (*Icmm*) to a primitive orthorhombic cell ($Pbn2_1$). The XRD pattern of our $AlPO_4$-11 is identical to that of wet $AlPO_4$-11 in Tapp et al.'s paper, and all peaks can be indexed on a $Pbn2_1$ cell. The pattern of VPI-5 agrees well with the literature.[19] $AlPO_4$-8 was obtained by calcining VPI-5 in air at 673 K for 12 h. There have been several studies on the transformation of VPI-5 to $AlPO_4$-8 upon calcination under various conditions.[20-22] Although under certain conditions the transformation from VPI-5 to $AlPO_4$-8 can be reversible or partially reversible, Akporiaye and Stocker[20] have shown by means of solid state MAS NMR, which is a much more sensitive technique than XRD to study this transformation, that calcining VPI-5 for 12 h at 673 K in air results in irreversible transformation to $AlPO_4$-8 and the structure of $AlPO_4$-8 persists upon hydration. Therefore, although the XRD pattern of our wet $AlPO_4$-8 is different from that of dry $AlPO_4$-8 reported in the literature,[23,24] mostly in relative peak intensity, we believe that the difference is due to the adsorption of water in our sample. The as-synthesized $AlPO_4$-42 contains a minor amount of $AlPO_4$-5.[14] Upon calcination, there seems to be a small lattice distortion, as manifested by the occurrence of double peaks at $2\theta \approx 10.5°$ compared to a single peak in the XRD pattern of the as-synthesized $AlPO_4$-42. However, peak overlap as well as the presence of minor amounts of $AlPO_4$-5 prevent a quantitative analysis.

In Table 1 lattice parameters of $AlPO_4$ polymorphs, which are used to calculate the molar volume (volume per mole of $AlPO_4$), are summarized. Whenever accurate literature data are available, we use those data, otherwise lattice parameters were obtained by least-squares refinement of Bragg peak positions of our XRD pattern, using Si as the external standard. Although berlinite, tridymite, and cristobalite undergo $\alpha \rightarrow \beta$ transformation at $473 < T < 873$ K and microporous $AlPO_4$'s undergo dehydration at $T \approx 373$ K, only one set of lattice parameters is used for each polymorph over all the temperatures concerned. Specifically, for dense polymorphs, unit-cell parameters of their low-temperature forms (α-forms) are used, and for microporous $AlPO_4$'s, lattice parameters of the wet form are used for $AlPO_4$-5, −11, and VPI-5, but parameters of the dry form are used for $AlPO_4$-8, and parameter of the as-synthesized form is used for $AlPO_4$-42 for reasons mentioned above.

Electron microprobe analyses indicate that within experimental error, the Al:P ratios of all samples are 1:1. Since the as-synthesized $AlPO_4$-42 contains 1.7−3.6 wt % F^-,[14] we have analyzed F for our calcined $AlPO_4$-42 sample. No F was detected, suggesting that all F has been removed upon calcination.

Microporous $AlPO_4$'s are very hygroscopic and calcined, dry $AlPO_4$'s adsorb water rapidly when they are exposed to air. For example, Tapp et al.[18] have reported that the adsorption of water on dry $AlPO_4$-11 at 54% relative humidity is extremely fast and a 12.7% weight gain within 20 min was observed. Due to rapid water

---

(17) Bennett, J. M.; Cohen, J. P.; Flanigen, E. M.; Pluth, J. J.; Smith, J. V. *Intrazeolite Chemistry*, Stucky, G. D., Dwyer, F. G., Eds.; ACS Symp. Ser. 218; American Chemical Society: Washington, DC, 1983; p 109.

(18) Tapp, N. J.; Milestone, N. B.; Bowden, M. E.; Meinhold, R. H. *Zeolites* **1990**, *10*, 105.

(19) Davis, M. E.; Saldarriage, C.; Montes, C.; Garces, J.; Crowder, C. *Zeolites* **1988**, *8*, 362.

(20) Akporiaye, D. E.; Stocker, M. *Proc. of the 9th Int. Zeol. Conf.*; Von Ballmoons, R., et al., Eds.; Butterworth-Heinemann: Montreal, 1993; p 563.

(21) Akporiaye, D. E.; Stocker, M. *Microporous Mater.* **1993**, *1*, 423.

(22) Maistriau, L.; Gabelica, Z.; Derouane, E. G.; Vogt, E. T. C.; van Oene, J. *Zeolites* **1991**, *11*, 583.

(23) Richardson, J. W.; Vogt, E. T. C. *Zeolites* **1992**, *12*, 13.

(24) Dessau, R. E.; Schlenker, J. L.; Higgins, J. B. *Zeolites* **1990**, *10*, 522.

(25) Thong, N.; Schwarzenbach, D. *Acta Crystallogr.* **1979**, *A35*, 658.

(26) Mooney, R. C. L. *Acta Crystallogr.* **1956**, *9*, 728.

(27) McCusker, L. B.; Baerlocher, Ch.; Jahn, E.; Bulow, M. *Zeolites* **1991**, *11*, 308.

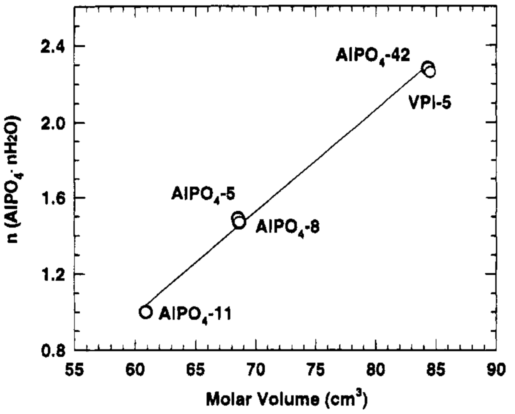

Figure 2. Correlation between the degree of hydration (n) and the molar volume of wet, microporous $AlPO_4$s, $AlPO_4{\cdot}nH_2O$.

Table 2. Water Content of Wet, Microporous $AlPO_4$'s

sample	mol vol (cm^3)	H_2O content (wt %)	n^a ($AlPO_4{\cdot}nH_2O$)
$AlPO_4$-5	68.54	18.02	1.488
$AlPO_4$-8	68.64	17.82	1.468
$AlPO_4$-11	60.88	12.88	1.000
$AlPO_4$-42	84.34	25.20	2.281
VPI-5	84.52	24.99	2.256

[a] On molar basis.

adsorption of $AlPO_4$'s in air, it is extremely difficult to work with dry samples or to control the degree of hydration of partially hydrated samples. Since the heat content of water ($H°_{979} - H°_{298}$), on a per gram basis, is more than 4 times as large as that of $AlPO_4$-berlinite,[28] a small variation in the degree of hydration will result in large variation in calorimetric data. Therefore, controlling the degree of hydration is essential to obtain accurate calorimetric data. For this reason, we worked with fully hydrated samples—samples which were exposed to the controlled temperature and humidity of the laboratory and thus were in equilibrium with the atmospheric humidity. The water content of fully hydrated $AlPO_4$ samples was measured by TGA, and the results are listed in Table 2. A linear relation is observed between molar volume and water content for wet $AlPO_4$'s (see Figure 2).

Enthalpy of Interaction of Adsorbed Water with $AlPO_4$ Framework. In as-synthesized microporous materials, species such as organic or inorganic charge-compensating cations, ion pairs (organic or inorganic), and solvent molecules (e.g., water) are occluded in the channels and cavities. Microporous materials free of occluded guest species cannot be directly prepared. The presence of these guest species is important. It lowers the enthalpy of the as-synthesized microporous materials through the interaction with the framework. As an initial effort to understand this host–guest interaction and its effect on the crystallization of microporous materials, we studied the enthalpy of interaction of adsorbed water with the $AlPO_4$ framework. Also, since wet $AlPO_4$ samples have been used in this study, it is essential to know the strength of this interaction in order to separate the energetics of the framework from that of the interaction.

In microporous $AlPO_4$'s, the adsorbed water interacts with framework through hydrogen bonding with a framework O atom, or bonding with a framework Al atom which expands the coordination sphere of Al. In this study, DSC experiments were performed to estimate the enthalpy of interaction of water with the $AlPO_4$ framework, which is defined as the enthalpy of the following reaction:

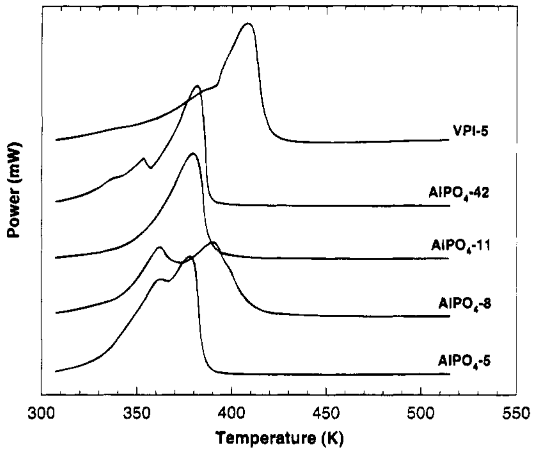

Figure 3. DSC scans of wet, microporous $AlPO_4$s. All scans are run at a heating rate of 1 K/min and under flowing Ar atmosphere.

$$\mathrm{AlPo_4(s,\ 298\ K)} + n\mathit{H}_2\mathrm{O(l,\ 298\ K)} \rightarrow \mathrm{AlPO_4}{\cdot}n\mathrm{H_2O(s,\ 298\ K)} \qquad \Delta H_{\mathrm{inter}} \quad (1)$$

where liquid water is used as the reference state. Figure 3 shows the DSC scans of $AlPO_4$-5, -8, -11, -42, and VPI-5. Three scans were performed for each sample.

The enthalpy of interaction of water with framework was estimated according to the following thermochemical cycle:

$$\mathrm{AlPO_4}{\cdot}n\mathrm{H_2O(s,\ T)} \rightarrow \mathrm{AlPO_4(s,\ T)} + n\mathrm{H_2O(g,\ T)} \qquad \Delta H_{\mathrm{DSC}} \quad (2)$$

$$n\mathrm{H_2O(g,\ T)} \rightarrow n\mathrm{H_2O(l,\ T)} \qquad -\Delta H_{\mathrm{evap}} \quad (3)$$

$$\mathrm{AlPO_4}{\cdot}n\mathrm{H_2O(s,\ T)} \rightarrow \mathrm{AlPO_4(s,\ T)} + n\mathrm{H_2O(l,\ T)} \qquad -\Delta H'_{\mathrm{inter}} \quad (4)$$

where

$$\Delta H'_{\mathrm{inter}} = \Delta H_{\mathrm{evap}} - \Delta H_{\mathrm{DSC}} \quad (5)$$

Equation 2 represents the reaction that occurred during the DSC scan, and ΔH_{DSC} is the corresponding enthalpy change obtained by peak integration. ΔH_{evap} is the enthalpy of evaporation of water at temperature T. $\Delta H'_{\mathrm{inter}}$ corresponds to the enthalpy of interaction of water with framework at T. As shown in Figure 2, all DSC peaks are broad and encompass temperatures ranging from 298 to 400 K. But except for VPI-5, peak positions of wet $AlPO_4$'s are all around 373 K; therefore, enthalpy of evaporation of water at 373 K (40.866 kJ/mol[28]) is a good estimation for ΔH_{evap} and the above thermochemical cycle gives the enthalpy of interaction of water with the framework at 373 K, which we used as an estimation for the enthalpy of interaction at 298 K. Results from DSC experiments are summarized in Table 3.

---

(28) Knacke, O.; Kubaschewski, O.; Hesselmann, K. *Thermochemical Properties of Inorganic Substances*, 2nd ed.; Springer-Verlag: Berlin, 1991.

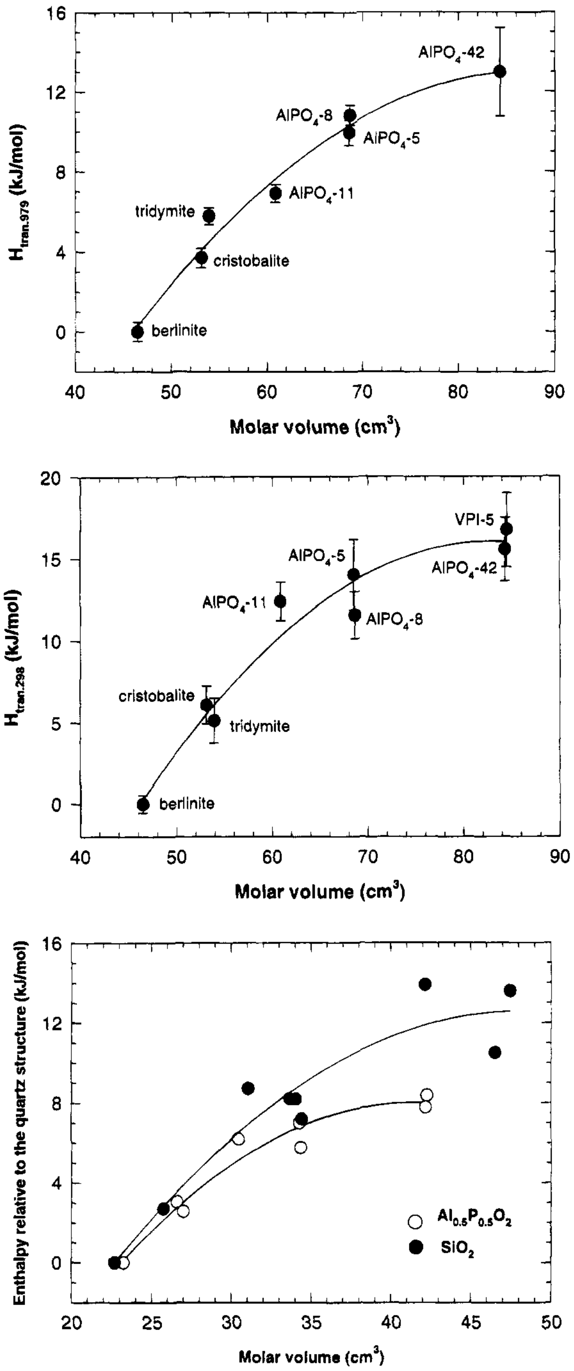

Figure 4. (a, top) Relative instability of $AlPO_4$ framework at 979 K as a function of molar volume. (b, middle) Relative instability of $AlPO_4$ framework at 298 K as a function of molar volume. (c, bottom) Comparison of relative stability of SiO_2 and $Al_{0.5}P_{0.5}O_2$ microporous frameworks at 298 K. SiO_2 data from Petrovic et al.[6]

Since VPI-5 can transform to $AlPO_4$-8 upon heating, we examined the VPI-5 sample after DSC experiment by XRD and found that VPI-5 has partially transformed to $AlPO_4$-8. Therefore, data from $\Delta H_{evap} - \Delta H_{DSC}$ (−20.74 kJ/mol) do not give a good estimation of the enthalpy of interaction for VPI-5. Fortunately, Janchen et al.[29] have reported the calorimetric measurement of the adsorption heat of water on VPI-5 using a Calvet-type microcalorimeter at 303 K. The measured heat of adsorption is −64 kJ/mol. With the heat of condensation of −40.61 kJ/mol, an enthalpy of interaction of −23.39 kJ/mol is obtained for VPI-5. This is 2.6 kJ/mol more exothermic than the value obtained from $\Delta H_{evap} - \Delta H_{DSC}$ (−20.74 kJ/mol), consistent with the observation that during DSC experiments, VPI-5 has partially transformed to $AlPO_4$-8, which is energetically more stable (see Table 5). Janchen et al.'s result is also listed in Table 3.

The enthalpy of interaction, per mole of $AlPO_4$, varies considerably from sample to sample, from −11.12 kJ for $AlPO_4$-11 to −29.36 kJ for $AlPO_4$-42. However, if the enthalpy of interaction is normalized for per mole of H_2O, the values for all samples are similar, about −10 to −13 kJ/mol. As expected, these values are between those of hydrophilic zeolites such as NaX or analcime (−61 to −84 kJ/mol)[30−32] and those of hydrophobic high-silica zeolites (≈−1 to −2 kJ/mol).[29]

Framework Stability. To elucidate the relative stability of various $AlPO_4$ frameworks, three types of high-temperature calorimetric experiments were performed: (1) solution calorimetry (soln), (2) drop solution calorimetry (d.s.), and (3) transposed temperature drop calorimetry (t.t.d.). According to Navrotsky et al.,[33] high-temperature solution calorimetry with molten lead borate ($2PbO{\cdot}B_2O_3$) as solvent can be used for determining enthalpies of formation of hydrous compounds. Under flowing gas atmosphere, all H_2O is expelled with no interaction with solvent, leading to a reproducible final state. Since microporous $AlPO_4$ samples contain up to 25 wt % water, all high-temperature calorimetric experiments were performed under a flowing dry air atmosphere at a flow rate of 1 cm^3/s. For solution and transposed temperature drop calorimetric experiments, there are certain requirements on the high-temperature metastability of $AlPO_4$ samples. Specifically, samples must persist at 979 K for at least 1 h for transposed temperature drop calorimetry, and persist at 979 K under the presence of lead borate vapor for about 10 h for solution calorimetry. So before solution and transposed temperature drop calorimetric experiments, the apparent stabilities of $AlPO_4$ samples treated under corresponding conditions were examined by powder XRD, and results are summarized in Table 4.

Berlinite, tridymite, and cristobalite are known to undergo $\alpha-\beta$ transition at 473−873 K. The enthalpy of $\alpha-\beta$ transition is 1.69 kJ/mol for berlinite[34] and 2.46 kJ/mol for cristobalite.[35] Therefore, it is worthwhile to examine the framework stability of $AlPO_4$'s at both high temperature (979 K) and room temperature (298 K).

Framework Stability at 979 K. Two thermochemical cycles are used to calculate the enthalpy of the following transition, i.e., the energy difference between the metastable phases and the stable quartz structure (berlinite) at 979 K:

$$\text{berlinite(s, 979 K)} \rightarrow AlPO_4\text{(s, 979 K)} \qquad (6)$$

---

(29) Janchen, J.; Stach, H.; Grobet, P. J.; Martens, J. A.; Jacobs, P. A. *Proc. of the 9th Int. Zeol. Conf.*; Von Ballmoons, R., et al., Eds.; Butterworth-Heinemann: Montreal, 1993; p 21.

(30) Barrer, R. M.; Cram, P. J. *Molecular Sieve Zeolites. II. Advances in Chemistry Series No. 102*, **1971**, 105.

(31) Johnson, G. K.; Flotow, H. E.; O'Hare, P. A. G.; Wise, W. S. *Am. Miner.* **1982**, *67*, 736.

(32) Johnson, G. K.; Tasker, I. R.; Jurgens, R.; O'Hare, P. A. G. *J. Chem. Thermodyn.* **1991**, *23*, 475.

(33) Navrotsky, A.; Rapp, R. P.; Smelik, E.; Burnley, P.; Circone, S.; Chai, L.; Bose, K.; Westrich, H. R. *Am. Miner.* **1994**, *79*, 1099.

(34) Hemingway, B. S.; Robie, R. A.; Krupka, K. M. *U. S. Geo. Survey, Open-file Report* 92-510, **1992**.

(35) Leaderbetter, A. J.; Smith, T. W. *Philos. Mag.* **1976**, *33*, 113.

Table 3. Enthalpies of Interaction of Adsorbed H_2O with $AlPO_4$ Framework (Estimated from DSC Experiments[a])

sample	n ($AlPO_4 \cdot nH_2O$)	ΔH_{DSC}[b] (kJ/mol of $AlPO_4$)	ΔH_{evap}[c] (kJ/mol of $AlPO_4$)	$\Delta H_{inter}(AlPO_4)$[d] (kJ/mol of $AlPO_4$)	$\Delta H_{inter}(H_2O)$[e] (kJ/mol of H_2O)
$AlPO_4$-5	1.488	80.35(1.70)	60.81	−19.54(1.70)	−13.13(1.14)
$AlPO_4$-8	1.468	78.70(0.74)	59.99	−18.71(0.74)	−12.74(0.52)
$AlPO_4$-11	1.000	51.99(0.44)	40.87	−11.12(0.44)	−11.12(0.44)
$AlPO_4$-42	2.281	122.58(1.38)	93.22	−29.36(1.38)	−12.87(0.60)
VPI-5	2.256	112.93(0.66)[f]	92.19	−23.39[g]	−10.35

[a] Uncertainties are reported as two standard deviations of the mean. [b] Data obtained from integrating DSC peaks. [c] $\Delta H_{evap} = 40.866n$ kJ, enthalpy of evaporation of H_2O. [d] $\Delta H_{inter}(AlPO_4) = \Delta H_{evap} - \Delta H_{DSC}$, enthalpy of interaction of adsorbed water with framework, on molar $AlPO_4$ base. [e] $\Delta H_{inter}(H_2O) = \Delta H_{inter}(AlPO_4)/n$, enthalpy of interaction normalized per mole of H_2O. [f] Partial transformation of VPI-5 to $AlPO_4$-8 was observed after DSC experiment. [g] Data from Janchen et al.[29]

Table 4. High-Temperature Persistence of $AlPO_4$'s under Solution Calorimetry (soln) and Transposed Temperature Calorimetry (t.t.d.) Conditions

sample	soln conditions[a]	t.t.d. conditions[b]
berlinite	yes	yes
tridymite	yes	yes
cristobalite	yes	yes
$AlPO_4$-5	yes	yes
$AlPO_4$-8	yes	yes
$AlPO_4$-11	yes	yes
$AlPO_4$-42	no (part. transf to tridymite)	yes
VPI-5	no (transf to $AlPO_4$-8)	no (part. transf to $AlPO_4$-8)

[a] Samples were heated for 10 h at 979 K in the presence of lead borate ($2PbO \cdot B_2O_3$) vapor (samples were positioned 5 mm above the lead borate melt). [b] Samples were dropped from 298 to 979 K and stayed at 979 K for 1 h.

The first cycle uses solution calorimetry data, according to

$$\text{berlinite(s, 979 K)} \rightarrow \text{AlPO}_4\text{(soln, 979 K)} \qquad \Delta H_{\text{soln},979}(\text{berlinite}) \tag{7}$$

$$\text{AlPO}_4\text{(soln, 979 K)} \rightarrow \text{AlPO}_4\text{(s, 979 K)} \qquad -\Delta H_{\text{soln},979}(\text{AlPO}_4) \tag{8}$$

$$\text{berlinite(s, 979 K)} \rightarrow \text{AlPO}_4\text{(s, 979 K)} \qquad \Delta H_{\text{tran},979} \tag{9}$$

where

$$\Delta H_{\text{tran},979} = \Delta H_{\text{soln},979}(\text{berlinite}) - \Delta H_{\text{soln},979}(\text{AlPO}_4) \tag{10}$$

$\Delta H_{\text{soln},979}$ represents enthalpy of solution at 979 K.

For the second cycle, enthalpies of solution at 979 K were obtained by the combination of drop solution and transposed temperature drop calorimetry, according to

$$\text{AlPO}_4\text{(s, 979 K)} + n\text{H}_2\text{O(g, 979 K)} \rightarrow \text{AlPO}_4 \cdot n\text{H}_2\text{O(s, 298 K)} \qquad -\Delta H_{\text{t.t.d.},979}(\text{AlPO}_4) \tag{11}$$

$$\text{AlPO}_4 \cdot n\text{H}_2\text{O(s, 298 K)} \rightarrow \text{AlPO}_4\text{(soln, 979 K)} + n\text{H}_2\text{O(g, 979 K)} \qquad \Delta H_{\text{d.s.},979}(\text{AlPO}_4) \tag{12}$$

$$\text{AlPO}_4\text{(s, 979 K)} \rightarrow \text{AlPO}_4\text{(soln, 979 K)} \qquad \Delta H_{\text{soln},979} \tag{13}$$

where

$$\Delta H_{\text{soln},979}(\text{AlPO}_4) = \Delta H_{\text{d.s.},979}(\text{AlPO}_4) - \Delta H_{\text{t.t.d.},979}(\text{AlPO}_4) \tag{14}$$

The validity of eq 12 is supported by Navrotsky et al.'s study,[33] which shows that for hydrous materials, there is no interaction between water and lead borate solvent when calorimetric experiments are performed under flowing gas atmosphere. Calorimetry data and calculated enthalpies of transition, $\Delta H_{\text{tran},979}$, are summarized in Table 5. Since data from solution calorimetry are more accurate than those from the combination of drop solution and transposed temperature drop calorimetry, only solution calorimetry data are used to calculate $\Delta H_{\text{tran},979}$. Data from the combination of drop solution and transposed temperature drop calorimetry, however, are used to check the reliability of solution calorimetry data. As indicated in Table 5, these two sets of data agree very well.

In Figure 4a the enthalpies of transition (or the relative instabilities of $AlPO_4$ frameworks) at 979 K, $\Delta H_{\text{tran},979}$, are plotted as a function of the molar volume. Enthalpies of transition are calculated from solution calorimetry data except for $AlPO_4$-42, whose enthalpy of transition is calculated from the combination of drop solution and transposed temperature drop calorimetry because $AlPO_4$-42 framework does not persist under solution calorimetry conditions. No $\Delta H_{\text{tran},979}$ is available for VPI-5, due to its facile transformation to $AlPO_4$-8 upon heating. Compared to berlinite, the most stable form, all other $AlPO_4$ frameworks are only 3−13 kJ/mol less stable, and all microporous frameworks are only 7−13 kJ/mol less stable. These small instabilities are comparable to the thermal energy, RT, at 979 K (8.1 kJ/mol).

Framework Stability at 298 K. The following thermochemical cycle is used to calculate the enthalpy of transition, berlinite → $AlPO_4$ at 298 K:

$$\text{berlinite(s, 298 K)} \rightarrow \text{AlPO}_4\text{(soln, 979 K)} \qquad \Delta H_{\text{d.s.},979}(\text{berlinite}) \tag{15}$$

$$\text{AlPO}_4\text{(soln, 979 K)} + n\text{H}_2\text{O(g, 979 K)} \rightarrow \text{AlPO}_4 \cdot n\text{H}_2\text{O(s, 298 K)} \qquad -\Delta H_{\text{d.s.},979}(\text{AlPO}_4) \tag{16}$$

$$\text{AlPO}_4 \cdot n\text{H}_2\text{O(s, 298 K)} \rightarrow \text{AlPO}_4\text{(s, 298 K)} + n\text{H}_2\text{O(l, 298 K)} \qquad -\Delta H_{\text{inter}}(\text{AlPO}_4) \tag{17}$$

$$n\text{H}_2\text{O(l, 298 K)} \rightarrow n\text{H}_2\text{O(g, 979 K)} \qquad \Delta H_{\text{c}}\,(\text{H}_2\text{O}) \tag{18}$$

$$\text{berlinite(s, 298 K)} \rightarrow \text{AlPO}_4\text{(s, 298 K)} \qquad \Delta H_{\text{tran},298} \tag{19}$$

where

Table 5. Calorimetry Data and Calculated Relative Instability of Various $AlPO_4$ Frameworks at 979 K[a]

sample	molar vol (cm^3)	$\Delta H_{soln,979}$[b] (kJ/mol)	$\Delta H_{tran,979}$ (kJ/mol)	$\Delta H_{d.s.,979}$[c] (kJ/mol)	$\Delta H_{t.t.d.,979}$[d] (kJ/mol)	$\Delta H_{soln,979}$[e] (kJ / mol)
berlinite	46.46	−41.03(0.48)	0.00(0.48)	50.58(0.56)		
tridymite	53.96	−46.84(0.42)	5.81(0.42)	45.66(1.38)		
cristobalite	53.14	−44.74(0.50)	3.71(0.50)	44.95(1.30)		
$AlPO_4$-5	68.54	−51.00(0.64)	9.97(0.64)	158.94(1.06)	210.01(2.34)	−51.07(2.57)
$AlPO_4$-8	68.64	−51.88(0.50)	10.85(0.50)	159.95(1.48)	210.40(1.84)	−50.45(2.36)
$AlPO_4$-11	60.88	−47.97(0.44)	6.94(0.44)	118.63(0.98)	166.28(1.88)	−47.65(2.12)
$AlPO_4$-42	84.34	N/A	13.00(2.22)[f]	222.09(1.36)	276.12(1.76)	−54.03(2.22)
VPI-5	84.52	N/A	N/A	213.20(2.26)	N/A	N/A

[a] Uncertainties are reported as 2 standard deviations of the mean. [b] Enthalpies of solution at 979 K from solution calorimetry, per mole of $AlPO_4$. [c] Enthalpies of drop solution at 979 K, per mole of $AlPO_4{\cdot}nH_2O$. [d] Heat content from transposed temperature drop at 979 K, per mole of $AlPO_4{\cdot}nH_2O$. [e] Enthalpies of solution at 979 K, calculated from $\Delta H_{d.s.,979} - \Delta H_{t.t.d.,979}$. [f] Calculated from the combination of drop solution and transposed temperature drop calorimetry.

Table 6. Calorimetry Data and Calculated Relative Instability of Various $AlPO_4$ Frameworks at 298 K[a]

sample	molar vol (cm^3)	$\Delta H_{d.s.,979}$[b] (kJ/mol)	$\Delta H_{d.s.,979}$[c] (kJ/mol)	$\Delta H_{d.s.,979}$[d] (kJ/mol)	$\Delta H_c(H_2O)$[e] (kJ/mol)	$\Delta H_{inter}(AlPO_4)$[f] (kJ/mol)	$\Delta H'_{d.s.,979}(AlPO_4)$[g] (kJ/mol)	$\Delta H_{tran,298}$[h] (kJ/mol)
berlinite	46.46	50.58(0.56)		50.58(0.56)	0	0	50.58(0.56)	0(0.54)
tridymite	53.96	45.66(1.38)		45.66(1.38)	0	0	45.66(1.38)	5.12(1.38)
cristobalite	53.14	44.95(1.30)		44.95(1.30)	0	0	44.95(1.30)	6.09(1.16)
$AlPO_4$-5	68.54	158.94(1.06)	159.01(2.42)	158.98 (1.32)	102.87	−19.54(1.70)	36.57(2.15)	14.01(2.15)
$AlPO_4$-8	68.64	159.95(1.48)	158.52(1.91)	159.24(1.21)	101.49	−18.71(0.74)	39.04(1.42)	11.54(1.42)
$AlPO_4$-11	60.88	118.63(0.98)	118.30(1.93)	118.46(1.08)	69.14	−11.12(0.44)	38.20(1.17)	12.38(1.17)
$AlPO_4$-42	84.34	222.09(1.36)	N/A	222.09(1.36)	157.70	−29.36(1.38)	35.03(1.94)	15.55(1.94)
VPI-5	84.52	213.20(2.26)	N/A	213.20(2.26)	155.97	−23.39 [i]	33.84(2.26)	16.74(2.26)

[a] Uncertainties are reported as 2 standard deviations of the mean. [b] Enthalpies of drop solution at 979 K from drop solution calorimetry, per mole of $AlPO_4{\cdot}nH_2O$. [c] Enthalpies of drop solution calculated from transposed temperature drop and solution calorimetry data. [d] Recommended data for $\Delta H_{d.s.,979}$ (average of *c* and *d* for $AlPO_4$-5, −8, and −11). [e] Calculated enthalpy change for the reaction $nH_2O(l, 298\ K) \rightarrow nH_2O(g, 979\ K)$, which is 69.135*n* kJ. [f] Enthalpy of interaction of adsorbed water with $AlPO_4$ framework, obtained by integrating DSC peak and then subtracting the enthalpy of evaporation of H_2O (see Table 2). [g] $\Delta H'_{d.s.,979} = \Delta H_{d.s.,979} - \Delta H_{inter}$, corresponding to enthalpies of drop solution of $AlPO_4$ framework, $AlPO_4(s, 298\ K) \rightarrow AlPO_4$ (soln, 797 K). [h] Enthalpy of transition at 298 K, calculated from $\Delta H'_{d.s.,979}(\text{berlinite}) - \Delta H'_{d.s.,979}(AlPO_4)$. [i] Data from Janchen et al.[29]

$$\Delta H_{tran,298} = \Delta H_{d.s.,979}(\text{berlinite}) - \{\Delta H_{d.s.,979}(AlPO_4) - \Delta H_c(H_2O) + \Delta H_{inter}(AlPO_4)\} \quad (20)$$

$\Delta H_{inter}(AlPO_4)$ represents enthalpy of interaction of adsorbed water with $AlPO_4$ framework, which was estimated from DSC experiments (see Table 3). $\Delta H_c(H_2O)$ represents the heat content of water, which is 69.135 k/mol of H_2O according to the literature.[27]

$\Delta H_{d.s.,979}(AlPO_4)$ was obtained in two ways: (1) directly from drop solution calorimetry; (2) from the combination of solution and transposed temperature drop calorimetry according to

$$AlPO_4{\cdot}nH_2O(s, 298\ K) \rightarrow AlPO_4(s, 979\ K) + nH_2O(g, 979\ K) \qquad \Delta H_{t.t.d.,979} \quad (21)$$

$$AlPO_4(s, 979\ K) \rightarrow AlPO_4(soln, 979\ K) \qquad \Delta H_{soln.979} \quad (22)$$

$$AlPO_4{\cdot}nH_2O(s, 298\ K) \rightarrow AlPO_4(soln, 979\ K) + nH_2O(g, 979\ K) \qquad \Delta H_{d.s.,979} \quad (23)$$

where

$$\Delta H_{d.s.,979} = \Delta H_{t.t.d.,979} + \Delta H_{soln,979} \quad (24)$$

These two sets of data have similar accuracy and the average of these two, whenever possible, was used for subsequent calculations.

For wet, microporous $AlPO_4$'s, the enthalpy of drop solution contains contributions from (1) $AlPO_4$ framework ($\Delta H'_{d.s.,979}(AlPO_4)$), (2) adsorbed water ($\Delta H_c(H_2O)$), and (3) interaction of adsorbed water with $AlPO_4$ framework ($\Delta H_{inter}(AlPO_4)$). With $\Delta H_{inter}(AlPO_4)$ estimated from DSC experiments and $\Delta H_c(H_2O)$ calculated from literature data, we are able to separate out the enthalpy of drop solution of $AlPO_4$ framework, according to

$$\Delta H'_{d.s.,979}(AlPO_4) = \Delta H_{d.s.,979}(AlPO_4) - \Delta H_c(H_2O) + \Delta H_{inter}(AlPO_4) \quad (25)$$

Experimental data and calculated enthalpies of transition $\Delta H_{tran,298}$ for reaction, berlinite → $AlPO_4$ at 298 K are summarized in Table 6. In Figure 4b the relative instabilities of various $AlPO_4$ frameworks are plotted as a function of molar volume. Again, the microporous $AlPO_4$ frameworks are less stable than berlinite by only 11−17 kJ/mol.

Discussion

The relative stability of various $AlPO_4$ frameworks at 298 and 979 K has been examined, and a similar trend has been found: microporous frameworks are not particularly unstable with respect to their corresponding stable quartz structure (berlinite). Compared to berlinite, microporous $AlPO_4$ frameworks are less stable by only 11−17 kJ/mol at 298 K and by only 7−13 kJ/mol at 979 K. These small energetic differences may explain the structural diversity of the large family of microporous $AlPO_4$ materials that has been synthesized, as well as imply that there is little driving force for the transformation of microporous frameworks to dense structures.

The interaction of adsorbed water with $AlPO_4$ framework may result in expansion of the coordination sphere of some framework Al atoms from tetrahedral to octahedral, such as in VPI-5,[27] as well as change in framework symmetry, such as in $AlPO_4$-11.[18] The enthalpy of interaction of water with the framework ranges from −11 to −30 kJ/mol. Since microporous

Table 7. Enthalpy of Reaction for $AlPO_4 \cdot nH_2O$ (s, 298 K) → Berlinite (s, 298 K) + nH_2O(l, 298 K)

microporous $AlPO_{4}$s	$\Delta H_{react,298}$ (kJ/mol)
$AlPO_4$-5	+5.5 (1.4)
$AlPO_4$-8	+7.0 (1.4)
$AlPO_4$-11	−1.3 (1.2)
$AlPO_4$-42	+13.8 (1.5)
VPI-5	+6.6 (2.3)

$AlPO_4$ frameworks are destabilized at 298 K, with respect to berlinite, by only 11−17 kJ/mol, this small destabilization energy can be compensated by this water−framework interaction. Considering the reaction

$$AlPO_4 \cdot nH_2O(s, 298\ K) \rightarrow berlinite(s, 298\ K) + nH_2O(l, 298\ K) \quad (26)$$

the enthalpy of this reaction $\Delta H_{react,298}$ can be calculated according to the following thermochemical cycle:

$$AlPO_4 \cdot nH_2O(s, 298\ K) \rightarrow AlPO_4(soln, 979\ K) + nH_2O(g, 979\ K) \qquad \Delta H_{d.s.,979} \quad (27)$$

$$AlPO_4(soln, 979\ K) \rightarrow berlinite(s, 298\ K) \qquad -\Delta H_{d.s.,979}(berlinite) \quad (28)$$

$$nH_2O(g, 979\ K) \rightarrow nH_2O(l, 298\ K) \qquad -\Delta H_c(H_2O) \quad (29)$$

$$AlPO_4 \cdot nH_2O(s, 298\ K) \rightarrow berlinite(s, 298\ K) + nH_2O(l, 298\ K) \qquad \Delta H_{react,298} \quad (30)$$

where

$$\Delta H_{react,298} = \Delta H_{d.s.,979} - \Delta H_{d.s.,979}(berlinite) - \Delta H_c(H_2O) \quad (31)$$

Values of $\Delta H_{react,298}$ are listed in Table 7. Except for $AlPO_4$-11, the decomposition of wet microporous $AlPO_4$'s to berlinite and liquid water are endothermic, indicating that with the interaction between water and framework taken into account, the microporous frameworks are not unstable at all. It is safe to assume that organic templates also stabilize microporous $AlPO_4$ frameworks through guest−host interaction. As a result, there is little or no energetic barrier to the formation of microporous $AlPO_4$ frameworks under the typical hydrothermal synthesis conditions, in which both organic and water are present. The very small energetic difference implies that the role of templates in $AlPO_4$ molecular sieve synthesis is not to stabilize a very unstable structure; rather, it plays a kinetic or entropic role by directing the path of the reaction.

The correlation between framework instability and molar volume found for $AlPO_4$'s is very similar to that of SiO_2.[6] For both systems, the dependence of framework instability on molar volume is small, with instability leveling off, on a two oxygen base, at about 14 kJ/mol for SiO_2 and about 9 kJ/mol for $AlPO_4$ (see Figure 4c). The dependence of framework instability on molar volume for $AlPO_4$'s is even smaller than that for SiO_2. This implies that it may be possible to synthesize mesoporous $AlPO_4$ materials considering that mesoporous structures have been synthesized for SiO_2. However, we must point out that energetic analysis alone cannot provide any information concerning the pathways of the hydrothermal reaction or about mechanistic differences in silica and aluminophosphate.

Petrovic et al.[6] have demonstrated that the instability of the SiO_2 framework maybe associated with small Si−O−Si angles (<140°). We attempted to establish a similar correlation between framework stability and structural features for $AlPO_4$ frameworks. Unfortunately, for microporous $AlPO_4$'s structural data with desirable accuracy are not all available. Although Al and P atoms strictly alternate in $AlPO_4$ frameworks, it is rather difficult to refine $AlPO_4$ frameworks in this ordered fashion; instead many calcined, microporous $AlPO_4$ frameworks are refined in disordered space groups, such as in $AlPO_4$-5[36] and $AlPO_4$-8.[22] The bond lengths d_{Al-O} and d_{P-O}, when Al and P are tetrahedrally coordinated, are about 1.73 and 1.52 Å, respectively. Therefore, the accuracy of bond lengths and bond angles calculated from a disordered structural model is very poor, and no correlation between framework instability and framework structure is established. More accurate structural data based on ordered model are highly desired and will surely provide more insights into the polymorphism of $AlPO_4$ materials.

Conclusions

Like high-silica zeolites, aluminophosphate molecular sieves ($AlPO_4$'s) show only a very small dependence of framework stability on molar volume (or framework density). Despite a factor of 2 variation in the molar volume, microporous $AlPO_4$ frameworks are energetically less stable, with respect to the stable quartz structure (berlinite), by only 11−17 kJ/mol. This very small dependence of framework stability on framework structure may explain the structural diversity of the large family of $AlPO_4$ materials which has been synthesized and implies that more new microporous and even mesoporous $AlPO_4$ materials are likely to come.

Enthalpies of interaction of adsorbed water with the framework in wet $AlPO_4$'s are −11 to −13 kJ/mol of water, which are between those of the hydrophilic zeolites and those of the hydrophobic high-silica zeolites. The interaction of water with framework provides some −11 to −30 kJ of stabilizing energy/mol of $AlPO_4$. As a consequence, microporous frameworks energetically comparable to or even more favorable than berlinite are possible. Therefore, there is little or no energetic barrier to the formation of microporous frameworks under normal hydrothermal synthetic conditions. Results from the $AlPO_4$ system strongly support our previous conclusion from study of the SiO_2 system that the role of templates in molecular sieve synthesis is not to stabilize a very unstable structure; rather it plays a kinetic and/or entropic role by directing the path of the reaction.

Acknowledgment. This work was supported by the State of New Jersey through its Innovative Partnership Grants Program. We thank Dr. H. Kessler of Laboratoire de Matériaux Minéraux, France, for providing the sample of $AlPO_4$-42, Dr. J. B. Higgins of Mobil Research and Development Co. for many discussions and comments, Dr. E. Vicenzi of Princeton University for help in electron microprobe analysis.

CM9500263

---

(36) Richardson, J. W.; Pluth, J. J.; Smith, J. V. *Acta Crystallogr.* **1987**, *C43*, 1469.