

# Thermodynamics of Pure-Silica Molecular Sieve Synthesis

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The thermodynamics of pure-silica molecular sieves (denoted by their structural codes \*BEA, MFI, MTW, and STF) are investigated by solution calorimetry at 323.15 K using 25% aqueous HF as solvent. The enthalpies of solution are determined for both calcined (silica frameworks) and organic structure-directing agent (SDA) occluded samples (SDAs: tetraethylammonium (TEA), tetrapropylammonium (TPA), trimethylenebis(*N*-methyl,*N*-benzylpiperidinium) (BISPIP), and 2,6-dimethyl-1-aza-spiro[5.4]decane (SPIRO)). These measurements provide data that enable the determination of the following interaction enthalpies between the molecular sieve frameworks and SDAs at 323.15 K: \*BEA/TEA,  $-3.1 \pm 1.4$  kJ/mol SiO<sub>2</sub> ( $-32 \pm 15$  kJ/mol SDA); \*BEA/BISPIP,  $-5.9 \pm 0.7$  kJ/mol SiO<sub>2</sub> ( $-181 \pm 21$  kJ/mol SDA); MFI/TEA,  $-1.1 \pm 1.4$  kJ/mol SiO<sub>2</sub> ( $-27 \pm 33$  kJ/mol SDA); MFI/TPA,  $-3.2 \pm 1.4$  kJ/mol SiO<sub>2</sub> ( $-81 \pm 34$  kJ/mol SDA); MTW/BISPIP,  $-1.6 \pm 1.3$  kJ/mol SiO<sub>2</sub> ( $-124 \pm 97$  kJ/mol SDA); and STF/SPIRO,  $-4.9 \pm 0.9$  kJ/mol SiO<sub>2</sub> ( $-83 \pm 16$  kJ/mol SDA). Interaction entropies are estimated, and when used in combination with the measured interaction enthalpies, provide the following Gibbs free energies of interaction between the SDAs and the molecular sieve frameworks: \*BEA/TEA,  $-5.4 \pm 1.5$  kJ/mol SiO<sub>2</sub>; MFI/TEA,  $-2.0 \pm 1.4$  kJ/mol SiO<sub>2</sub>; and MFI/TPA,  $-4.9 \pm 1.4$  kJ/mol SiO<sub>2</sub>. The energetics of the synthesis of molecular sieves (considering all components present in the synthesis mixture) are examined and reveal small differences between various molecular sieve/SDA combinations. Assuming complete transformation of the starting amorphous silica into a molecular sieve, the Gibbs free energy changes for the crystallization are \*BEA/TEA,  $-8.5 \pm 2.9$  kJ/mol SiO<sub>2</sub>; MFI/TEA,  $-4.9 \pm 2.8$  kJ/mol SiO<sub>2</sub>; and MFI/TPA,  $-8.1 \pm 2.8$  kJ/mol SiO<sub>2</sub>. No single factor (enthalpy, entropy, etc.) dominates the overall Gibbs free energies, and these small energetic differences suggest that kinetic factors are of major importance in molecular sieve preparation.

## Introduction

Despite the industrial importance of zeolites and other molecular sieves,<sup>1–3</sup> their syntheses are still not well understood at the fundamental level. Extensive screening of different organic structure-directing agents (SDAs) and conditions are the normal method of producing new framework structures.<sup>4–6</sup>

In our earlier work, the enthalpies<sup>7,8</sup> and entropies<sup>9,10</sup> of pure-SiO<sub>2</sub> molecular sieves were determined relative to the thermodynamically stable polymorph of SiO<sub>2</sub>,  $\alpha$ -quartz. The silica molecular sieves were found to be only moderately metastable (5.4–12.6 kJ/mol). Therefore, there are no strong thermodynamic barriers to transformations between silica polymorphs. The role of the SDA in molecular sieve syntheses is thus not the stabilization of otherwise highly unstable frameworks. To better understand how SDAs select one structure over others, a quantitative characterization of molecular sieve/SDA interactions is required.

Patarin et al.<sup>11,12</sup> studied the interaction between different SDAs and pure-silica MFI<sup>13</sup> by HF calorimetry and found tetrapropylammonium ions (TPA<sup>+</sup>) to stabilize MFI considerably more than either di- or tri-propylammonium cations. The authors linked this difference to the high specificity of the TPA<sup>+</sup> cation toward the formation of MFI.<sup>12</sup> Helmkamp and Davis used the Patarin et al. data to estimate the Gibbs free energy of

formation of MFI/TPA from aqueous TPA<sup>+</sup>F<sup>−</sup> and silica glass to be  $-10.9$  kJ/mol SiO<sub>2</sub>.<sup>14</sup> They concluded that there is a moderate thermodynamic driving force for the formation of MFI/TPA from amorphous silica precursors and aqueous TPA<sup>+</sup>.<sup>14</sup>

Solution calorimetry using 25% aqueous HF solvent at 323.15 K is employed here to measure the enthalpies of interaction between six pure-SiO<sub>2</sub> molecular sieve/organic SDA pairs. First, the interaction enthalpies of the commonly synthesized molecular sieve ZSM-5 (MFI) and two SDAs, tetraethylammonium (TEA<sup>+</sup>) and TPA<sup>+</sup>, were compared to examine the difference between a highly specific SDA (TPA) and a less specific SDA (TEA can also make other frameworks). Second, the interactions between zeolite beta (\*BEA) and the two organics, TEA and trimethylenebis(*N*-methyl,*N*-benzylpiperidinium) (BISPIP), were investigated to determine the effect of variable cation sizes. Third, the interaction enthalpy between the one-dimensional (1-D) ZSM-12 (MTW) framework and the BISPIP SDA was determined to probe how the dimensionality of the inorganic framework affects the molecular sieve/SDA energetics (compared to the 3-D, \*BEA). Finally, the interaction between the SSZ-35 (STF) framework and the 2,6-dimethyl-1-aza-spiro[5.4]-decane (SPIRO) cation was investigated as a model for syntheses using rigid, bicyclic SDAs. All molecular sieves studied here were prepared using fluoride as the mineralizing agent<sup>15</sup> in order to minimize the formation of silanol (Si–O–H) defect groups.<sup>16,17</sup> The entropies of interaction are estimated and the Gibbs free energies of interaction are calculated for \*BEA/TEA, MFI/TEA,

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TABLE 1: Reaction Conditions for Molecular-Sieve Syntheses

Hydrothermal Syntheses			
sample	synthesis mixture composition	synthesis temperature (K)	synthesis time (d)
*BEA/TEA	1 SiO <sub>2</sub> /0.5 TEAF/7.25 H <sub>2</sub> O	413	14
*BEA/BISPIP	1 SiO <sub>2</sub> /0.27 BISPIP(OH) <sub>2</sub> /0.54 HF/7 H <sub>2</sub> O/0.002 *BEA/BISPIP seed	423	14
MFI/TEA	1 SiO <sub>2</sub> /0.5 TEAF/15 H <sub>2</sub> O/0.05 MFI/calc seed	448	55
MFI/TPA	1 SiO <sub>2</sub> /0.11 TPABr/0.56 NH <sub>4</sub> F/21 H <sub>2</sub> O	469	5
MTW/BISPIP	1 SiO <sub>2</sub> /0.27 BISPIP(OH) <sub>2</sub> /0.54 HF/40 H <sub>2</sub> O	448	23
STF/SPIRO	1 SiO <sub>2</sub> /0.5 SPIRO(OH)/0.5 HF/15 H <sub>2</sub> O	423	22
Air Calcination Procedures			
calcined sample	sample used for calcination	calcination temperature (K)	
*BEA/calc	*BEA/TEA	823	
MFI/calc	MFI/TPA	823	
MTW/calc	MTW/BISPIP	1173	
STF/calc	STF/SPIRO	1073	

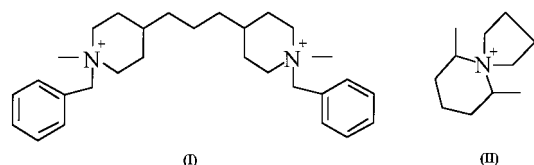
and MFI/TPA. With these samples, estimates of the Gibbs free energy changes for the molecular-sieve crystallization are also calculated.

### Experimental Section

**Molecular-Sieve Samples.** Each molecular sieve sample is denoted by MS/SDA where MS is the structural code of the framework and SDA is the occluded structure-directing agent (or MS/calc for calcined materials—organic SDA removed by combustion). Table 1 summarizes the reaction conditions for the molecular sieve syntheses. In each case, the hydrothermal synthesis was performed at autogenous pressure in a Teflon-lined stainless steel reactor. The product was collected by cooling the mixture to room temperature, filtering and washing the solids with water and acetone. For \*BEA/TEA,<sup>18</sup> \*BEA/BISPIP,<sup>19</sup> MTW/BISPIP,<sup>19</sup> and STF/SPIRO,<sup>20</sup> the SiO<sub>2</sub> source was tetraethoxysilane (TEOS) and the reaction mixture was hydrolyzed before starting the hydrothermal synthesis. For MFI/TEA and MFI/TPA<sup>21</sup> the SiO<sub>2</sub> source was Cab-O-Sil M-5 amorphous silica.

**Organic Structure-Directing Agents.** Solutions of tetrapropylammonium fluoride and tetraethylammonium fluoride were prepared by reacting stoichiometric amounts of TPAOH (40%, Alfa) and TEOH (40%, Alfa), respectively, with HF (48%, Mallinckrodt). The exact concentrations of the tetraalkylammonium hydroxide and HF solutions were determined by standard titration techniques.

BISPIP (**I**) dibromide was prepared by the reaction of trimethylenebis(*N*-methylpiperidine) with benzyl bromide in ethyl acetate,<sup>19</sup> and recrystallized from a mixture of ethyl acetate and ethanol. An aqueous solution of the hydroxide was prepared by ion exchanging twice the BISPIP bromide over a BioRad Ag1-X8 hydroxide ion-exchange resin. The fluoride salt was prepared by reacting the hydroxide solution with the stoichiometric amount of aqueous HF.



The SDA, SPIRO (**II**) appears as entry 21 in Table 3 of ref 20. The SDA was made in its iodide form by a 1-step reaction between 2,6-dimethylpiperidine and 1,4-diiodobutane using methanol as the solvent and 1 equiv of KHCO<sub>3</sub> as the base acceptor for the HI generated as a side product. SPIRO hydroxide was prepared by ion exchange of an aqueous solution

of SPIRO iodide over a BioRad Ag1-X8 hydroxide ion-exchange resin. The fluoride salt was prepared by reacting this hydroxide solution with the stoichiometric amount of aqueous HF.

**Characterizations.** Room temperature, powder X-ray diffraction (XRD) patterns of the molecular sieves were collected on a Scintag XDS 2000 diffractometer operating in a Bragg–Bretano geometry (liquid nitrogen cooled Ge detector, Cu K $\alpha$  radiation,  $\lambda = 1.54184$  Å). The data were collected in a stepwise mode with  $2\theta$  ranging from 2 to 51° (step size = 0.01°, count time = 4 s) in order to identify the crystalline phases synthesized.

Thermogravimetric analyses (TGA) were performed on approximately 15 mg sample using a TA Instruments 2100 Analyzer to measure the mass fraction of water and organics present in the samples introduced into the calorimeter. The heating rate was 10 K/min to 1173 K, and buoyancy corrections were performed for all runs. Alternatively, the measurement was performed on approximately 10 mg sample using a Netzsch STA449C system. The heating rate for those cases was 10 K/min to 1573 K.

The molecular sieve specimens were also analyzed by Galbraith Laboratories, Inc., Knoxville, TN for their carbon contents in order to confirm the organic SDA contents determined by TGA.

Solid-state <sup>29</sup>Si NMR spectra for all molecular sieve samples were collected on a Bruker DSX-200 spectrometer equipped with a Bruker cross-polarization, magic angle spinning (MAS) accessory. The samples were packed into a 7 mm ZrO<sub>2</sub> rotor and spun in air at 4 kHz. Proton-decoupled <sup>29</sup>Si NMR spectra (operating frequency 39.761 MHz, pulse angle 90°, pulse width 4  $\mu$ s) referenced to tetrakis(trimethylsilyl)silane) (downfield peak at  $\delta = -10.053$  ppm) were collected using MAS.

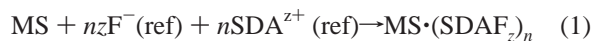
Solid-state <sup>13</sup>C NMR spectra for the as-made molecular-sieve samples were collected on the same Bruker DSX-200 spectrometer. The samples were packed into a 7 mm ZrO<sub>2</sub> rotor and spun in air at 4 kHz. Proton-decoupled <sup>13</sup>C NMR spectra (operating frequency 50.328 MHz, pulse angle 90°, pulse width 4  $\mu$ s) referenced to adamantane (upfield peak at  $\delta = 38.47$  ppm) were collected using MAS.

Solid-state <sup>1</sup>H NMR spectra for all molecular-sieve samples were collected on a Bruker DSX-500 spectrometer equipped with a Bruker cross-polarization, magic angle spinning (MAS) accessory. The samples were packed into 4 mm ZrO<sub>2</sub> rotors and spun in air at 10–14 kHz. <sup>1</sup>H NMR spectra (operating frequency 500.248 MHz, pulse angle 90°, pulse width 4  $\mu$ s) were collected using MAS and referenced to tetrakis(trimethylsilyl)silane) (upfield peak at  $\delta = 0.247$  ppm).

**Calorimetry.** Solution calorimetry was employed to obtain the heats of solution of the molecular sieves. The thermochemical measurements were performed using a Setaram C-80 twin microcalorimeter equipped with HF-resistant cells developed jointly at California Institute of Technology and at the Thermochemistry Facility of the University of California at Davis. The enthalpy of solution of a commercial quartz sample (Fluka, purum,  $\leq 0.3\%$  loss on ignition,  $\geq 230$  mesh) was determined in addition to those of the molecular sieves in order to calculate the enthalpies of transition from quartz to the other silica polymorphs. These values allowed for comparison to the *quartz*  $\rightarrow$  *molecular-sieve* enthalpies of transition calculated from high-temperature, oxide melt, solution calorimetry data.<sup>7,8</sup>

The solvent was 25 wt % aqueous HF at 323.15 K. The appropriate SDA fluoride solutions in 25% aqueous HF were added to the HF solvent for the dissolution of the calcined materials (see below). An amount of substance corresponding to approximately 0.18 mmol SiO<sub>2</sub> molecular sieves (10.8–13.7 mg) was contacted with 5.4 g HF solvent by the downward push of a retractable rod. This rod dropped a small plug into the HF solution, exposing the molecular sieve or quartz crystals to the solvent. While it was not possible to stir the reaction mixture, the completion of the dissolution reaction was easily identified by the return of the calorimeter heat flow signal to a stable constant value. The dissolution times ranged from two (\*BEA, MTW, STF) to 3 h (MFI) for the molecular sieves; 4 h were necessary for the complete dissolution of quartz. Blank runs were also performed to determine the heat effect of pushing the rod. Three to four measurements were performed on each molecular sieve sample in order to obtain acceptable uncertainty statistics. The calorimeter was calibrated by determining the enthalpy of solution of KCl in water at 300.15 K.<sup>22</sup>

**Thermodynamic Cycles.** The interaction enthalpy refers here to the enthalpy of the following reaction:

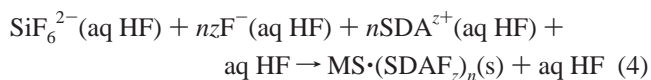
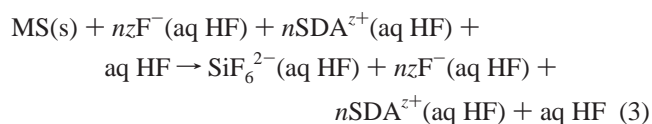


where MS is a generic designation for one mole of SiO<sub>2</sub> of any of the molecular sieve frameworks,  $n$  is the number of organic groups present per mole SiO<sub>2</sub>,  $z$  is the charge on the organic SDA, and (ref) is an appropriate reference state for the fluoride and SDA ions. To avoid the experimental difficulties associated with the solid organic fluorides that are extremely hygroscopic,<sup>23,24</sup> the dilute ions in 25% HF were chosen as the reference states for the SDA fluorides. At the low SDA fluoride molalities present in the solution calorimetry experiments of this work, the concentration dependence of the energetics of the SDA<sup>z+</sup> and F<sup>−</sup> ions can be neglected<sup>25</sup> and the SDA fluoride reference state is well-defined.

The idealized enthalpy of interaction at 323.15 K,  $\Delta H_{\text{int}}^{323}$ , between the inorganic framework, MS, and its SDA, present in the dilute ion reference state, can then be described by the reaction 2:



The enthalpy for reaction 2 can be obtained by adding the enthalpies from reactions 3 and 4:



according to  $\Delta H_2 = \Delta H_3 + \Delta H_4$ . The enthalpies  $\Delta H_3$  and  $-\Delta H_4$  are the experimentally measured heats of solution for the calcined and as-made molecular sieves,  $\Delta H_{\text{soln}}^{323}(\text{MS/calc})$  and  $\Delta H_{\text{soln}}^{323}(\text{MS/SDA})$ , respectively. For this thermodynamic cycle to be exact, the final state after dissolution of the molecular sieves into the HF solutions must be the same for the as-made and calcined materials. This is the reason for the addition of  $n$  moles SDAF<sub>*z*</sub> to the HF solution into which the calcined material is dissolved. An additional contribution to the overall transition enthalpy is due to the difference in the levels of hydration between the as-made and calcined materials. This step contributes no more than 0.03 kJ/mol SiO<sub>2</sub> to the interaction enthalpies<sup>26</sup> and is omitted in the thermodynamic cycle above.

## Results and Discussion

**Molecular Sieve Characterizations.** The X-ray powder diffraction patterns indicate the presence of a single molecular sieve phase for each sample, and the crystal sizes are larger than 1  $\mu\text{m}$  (from microscopy). For particles larger than 1  $\mu\text{m}$ , surface energy effects can be neglected in the measurement of energetics via calorimetry.<sup>7</sup> The X-ray powder diffraction patterns after the calcination treatment show that there is no degradation of the structures.

Table 2 lists the TGA data collected from the molecular sieve and quartz specimens, along with the calculated unit cell compositions. For the as-made materials, TGA mass losses below 423 K were attributed to water, while the remainder of the mass losses were assigned to enclathrated organic SDA fluoride. The low water contents ( $< 1.5\%$  for all samples) are consistent with the hydrophobic nature of pure-silica molecular sieves prepared in fluoride media. For the samples where the SDA/uc amounts have been previously reported in the literature (MFI/TPA<sup>21,27</sup> and \*BEA/TEA<sup>28</sup>), there is good agreement with the values in Table 2. For example, MFI has four channel intersections per unit cell<sup>13</sup> that can be occupied by the SDA. The SDA/uc value near 4 for MFI/TEA and MFI/TPA are within experimental error of that expected value. The carbon contents determined by elemental analysis (not shown) are consistent with the SDA/uc ratios calculated from the TGA data. They also confirm that complete removal of the organic SDA is achieved for each of the calcined materials.

All molecular sieve materials were prepared in fluoride-containing media so the Q<sup>3</sup> concentrations will be lower than those achieved in the presence of hydroxide.<sup>16,21</sup> The <sup>1</sup>H and <sup>29</sup>Si solid-state NMR spectra of all samples (in Supporting Information) quantitatively confirmed the absence of significant concentrations of Q<sup>3</sup> (defect) Si sites for all the calcined materials, as well as for the MFI/TEA and MTW/BISPIP specimens. For the other samples, small amounts of Q<sup>3</sup> sites are observed. For MFI/TPA, the use of NH<sub>4</sub>F in the synthesis mixture results in a lower density of defect sites than MFI/TPA prepared in its absence. Elemental analyses on MFI/TPA materials made in the presence and absence of NH<sub>4</sub>F showed identical C/N ratios, proving that no NH<sub>4</sub><sup>+</sup> is incorporated in TPA/MFI when synthesized in the presence of NH<sub>4</sub>F. The \*BEA samples contain somewhat higher defect concentrations. No thermodynamic data are available for defects in as-made molecular sieves. Since there are no significant amounts of Q<sup>3</sup> sites in all the specimens studied here, no attempt was made to assess the effects of the defect energetics in the thermodynamic



**TABLE 2: Sample Compositions by TGA Analyses**

sample	% water loss	% organic loss	Si/uc <sup>a</sup>	SDA/uc	H <sub>2</sub> O/uc	SDA/SiO <sub>2</sub>	H <sub>2</sub> O/SiO <sub>2</sub>	MW (g/mol SiO <sub>2</sub> )
MFI/calc	1.32		96		4.29		0.045	60.89
MFI/TEA	0.08	9.24	96	3.94	0.29	0.041	0.003	66.26
MFI/TPA	0.00	11.85	96	3.78	0.00	0.039	0.000	68.64
*BEA/calc	1.32		64		2.85		0.044	60.89
*BEA/TEA	1.31	19.30	64	6.26	3.51	0.098	0.055	75.68
*BEA/BISPIP	1.45	19.56	64	2.08	3.92	0.032	0.061	76.06
MTW/calc	1.20		56		2.27		0.041	60.89
MTW/BISPIP	0.27	9.06	56	0.73	0.56	0.013	0.010	66.27
STF/calc	1.35		16		0.73		0.046	60.89
STF/SPIRO	0.07	15.58	16	0.95	0.04	0.059	0.003	71.23
Quartz	0.00		3		0.00		0.000	60.08

<sup>a</sup> Values from structures listed in ref 13.**TABLE 3: Measured Enthalpies of Solution (Mass Basis)**

framework	organic SDA	$\Delta H_{\text{soln}}^{323}$ (MS/calc) (kJ/g)	uncertainty (kJ/g)	$\Delta H_{\text{soln}}^{323}$ (MS/SDA) (kJ/g)	uncertainty (kJ/g)
MFI	TPA	-2.407	0.012	-2.103	0.017
MFI	TEA	-2.428	0.021	-2.214	0.006
*BEA	TEA	-2.438	0.016	-1.920	0.014
*BEA	BISPIP	-2.437	0.011	-1.874	0.003
MTW	BISPIP	-2.391	0.020	-2.170	0.005
STF	SPIRO	-2.426	0.015	-2.005	0.003
Quartz		-2.334	0.018		

**TABLE 4: Measured Enthalpies of Solution (Molar Basis)**

framework	organic SDA	$\Delta H_{\text{soln}}^{323}$ (MS/calc) (kJ/mol SiO <sub>2</sub> )	uncertainty (kJ/mol SiO <sub>2</sub> )	$\Delta H_{\text{soln}}^{323}$ (MS/SDA) (kJ/mol SiO <sub>2</sub> )	uncertainty (kJ/mol SiO <sub>2</sub> )
MFI	TPA	-146.56	0.70	-143.35	1.16
MFI	TEA	-147.84	1.30	-146.73	0.39
*BEA	TEA	-148.43	0.98	-145.30	1.07
*BEA	BISPIP	-148.41	0.64	-142.55	0.20
MTW	BISPIP	-145.44	1.23	-143.80	0.32
STF	SPIRO	-147.74	0.89	-142.80	0.23
Quartz		-140.23	1.09		

cycles for the interaction enthalpies. These effects are expected to be small and are thus implicitly included in the interaction enthalpies.

The <sup>13</sup>C solid-state NMR spectra for the as-made materials (in Supporting Information) were compared to liquid-state <sup>13</sup>C NMR spectra for the corresponding SDAs and in each case it was confirmed that the organic molecules had been occluded intact.

**Calorimetry.** *Enthalpies of Solution in Aqueous HF,  $\Delta H_{\text{soln}}^{323}$ .* The typical heat effects for the HF solution experiments ranged from -25 to -27 J. The magnitude of the heat effect due to pushing the rod was approximately -0.06 J, i.e., less than 0.3% of the total heat of solution.

The measured enthalpies of solution of the molecular sieves and of quartz on a mass and mole basis are shown in Tables 3 and 4, respectively. The uncertainties (2 standard deviations from the mean) in  $\Delta H_{\text{soln}}^{323}$  are 0.2–1.3 kJ/mol SiO<sub>2</sub>, and never exceed 0.9% of the enthalpy of solution. Such errors compare favorably to the study of Patarin et al.<sup>11,12</sup>

**Quartz.** The enthalpy of solution of quartz in HF solutions at various HF concentrations and temperatures has been studied by several groups.<sup>11,12,29–33</sup> While the values reported for dissolution in 25% HF between 348 and 353 K are all in good agreement, larger discrepancies are observed at lower temperatures (possible causes for these differences are discussed in refs 29 and 30). Kilday and Prosen performed a systematic study of the changes in  $\Delta H_{\text{soln}}^T$  (quartz) with concentration (18–30 wt % HF) and temperature (298–358 K).<sup>30</sup> These correlations enable the  $\Delta H_{\text{soln}}^T$  (quartz) values from other investigators to be compared on the same basis by correcting for the concentration and temperature variations. The  $\Delta H_{\text{soln}}^{323}$  values from the most

recent studies corrected to 25% HF and 323.15 K using Kilday and Prosen's regressions are shown in Table 5. The  $\Delta H_{\text{soln}}^{323}$  values range from  $-137.1 \pm 0.2$ <sup>29</sup> to  $-142.3 \pm 0.4$ <sup>31</sup> kJ/mol SiO<sub>2</sub>. The value determined here of  $-140.2 \pm 1.1$  kJ/mol SiO<sub>2</sub> falls well within the range determined by previous workers and confirms that the calorimeter used here had been well-calibrated.

**MFI.** The measured solution enthalpy for MFI is in very good agreement with the data of Johnson et al.<sup>33</sup> but not with those of Patarin et al. (4.8% discrepancy, see Table 5).<sup>11,12</sup> The average  $\Delta H_{\text{soln}}^{323}$  (MFI/calc) value from solution of the MFI/calc sample into HF containing traces of either TEAF or TPAF was used for the purposes of this comparison. Johnson et al.<sup>33</sup> documented the effect of the HF concentration on the enthalpy of dissolution of calcined MFI and found that a difference in HF concentrations of 4.4% produced a discrepancy in the heat of solution of 0.95 kJ/mol, i.e., 0.22 kJ/mol SiO<sub>2</sub>/(%HF conc change). For a 0.6% HF concentration change (between 24.4 and 25), this contribution would be -0.13 kJ/mol, or much smaller than the difference between the two reported values. The literature data<sup>11,12,33</sup> are therefore irreconcilable within experimental error. Since the experimental conditions used here (sample synthesized in fluoride media, calorimeter containing ~5.4 g HF solution) are more similar to those used by Patarin et al. than to those used by Johnson et al., it is unclear why our value is closer to that of Johnson et al.

Based upon additional data reported by Johnson and co-workers,<sup>33</sup> it can be shown that the 6.8 kJ/mol discrepancy between the  $\Delta H_{\text{soln}}^{323}$  (MFI/calc) value reported here and in refs 11 and 12 is also not attributable to differences in silica concentration. Unlike Patarin et al., Johnson and co-workers were able to continuously stir their reaction mixture. Since the

TABLE 5: Comparison of Solution Enthalpies to Literature Values

reference	$\Delta H_{\text{soln}}^T$ (kJ/mol SiO <sub>2</sub> )	$T^a$	HF% <sup>a</sup>	correction <sup>b</sup> (kJ/mol SiO <sub>2</sub> )	$\Delta H_{\text{soln}}^{323}$ (kJ/mol SiO <sub>2</sub> )
Quartz					
this work	$-140.2 \pm 1.1$	323.15	25		$-140.2 \pm 1.1$
Johnson <sup>33</sup>	$-138.2 \pm 1.4^c$	298.15	24.4	-2.4	$-140.7 \pm 1.4$
Patarin <sup>11</sup>	$-138.0 \pm 1.0$	298.15	25	-2.4	$-140.4 \pm 1.0$
Hemingway <sup>29</sup>	$-137.7 \pm 0.2$	333.15	20.1	0.6	$-137.1 \pm 0.2$
Kilday <sup>30</sup>	$-139.1 \pm 0.1$	323.15	24.4	0.1	$-139.1 \pm 0.1$
Liou <sup>31</sup>	$-142.3 \pm 0.1$	322.62	24.4	0.1	$-142.4 \pm 0.1$
MFI/Calc					
this work	$-147.2 \pm 0.6$	323.15	25		$-147.2 \pm 0.6$
Johnson <sup>33</sup>	$-145.1 \pm 0.1$	298.15	24.4	-2.5	$-147.6 \pm 0.1$
Patarin <sup>11</sup>	$-138.0 \pm 1.8$	298.15	25	-2.4	$-140.4 \pm 1.8$
MFI/TPA					
this work	$-143.3 \pm 1.2$	323.15	25		$-143.3 \pm 1.2$
Patarin <sup>11</sup>	$-131.8 \pm 1.9$	298.15	25	-2.4	$-134.2 \pm 1.9$

<sup>a</sup> Experimental conditions of the reported solution experiments closest to 25% HF and 323.15 K. <sup>b</sup> Correction to 25% HF and 323.15 K. Temperature corrections for the MFI enthalpies of solution used the same correlations as for quartz.<sup>30</sup> <sup>c</sup> Combination of HF solution and F<sub>2</sub> combustion measurements.

value reported here is in good agreement with that of Johnson et al., and more exothermic than that of Patarin et al., it is plausible that molecular sieve dissolution may have been incomplete in the latter work. The value reported here and in ref 33 is believed to be a more accurate measure of the true  $\Delta H_{\text{soln}}^{323}$ (MFI/calc). The  $\Delta H_{\text{soln}}^{323}$ (MFI/TPA) value reported by Patarin et al. is also less exothermic (by 11.5 kJ/mol) than the value reported here. As-made molecular sieves dissolve slower than their calcined counterparts since their pores are filled with organics at the beginning of the calorimetry experiment. The larger discrepancy for the MFI/TPA data than for the MFI/calc data are therefore consistent with the hypothesis of incomplete dissolution in the previous work.<sup>11,12</sup>

**Enthalpy of Solution of Calcined MFI and \*BEA.** The enthalpies of solution of MFI/calc and \*BEA/calc were each determined in HF containing small amounts of two different organic cations. As noted above, the organic species in these solutions are always present at molalities less than 0.003 m. The final hexafluorosilicate molality after dissolution of the molecular sieves is 0.033 m. At such low concentrations, the SDA<sup>z+</sup> and SiF<sub>6</sub><sup>2-</sup> species are unlikely to interact with each other (for comparison the solvent molality is approximately 54.2 mol/kg). The  $\Delta H_{\text{soln}}^{323}$ (MFI/calc) and  $\Delta H_{\text{soln}}^{323}$ (\*BEA/calc) values per mol SiO<sub>2</sub> are therefore expected to be independent of the presence and identity of the SDA species. Examination of the data in Table 4 shows the pairs of values for each structure to indeed be within experimental error of each other. The average  $\Delta H_{\text{soln}}^{323}$  values for MFI/calc and \*BEA/calc are  $-147.2 \pm 0.7$  and  $-148.4 \pm 0.6$  kJ/mol SiO<sub>2</sub>, respectively.

**Enthalpies of Transition (Quartz → Calcined Molecular Sieve),  $\Delta H_{\text{trans}}^{323}$ .** The enthalpy of transition from quartz to other silica polymorphs at 323.15 K,  $\Delta H_{\text{trans}}^{323}$ , can be determined by the subtraction of the enthalpy of solution of the calcined molecular sieve from that of quartz:

$$\Delta H_{\text{trans}}^{323}(\text{quartz} \rightarrow \text{MS}) = \Delta H_{\text{soln}}^{323}(\text{quartz}) - \Delta H_{\text{soln}}^{323}(\text{MS/calc}) \quad (5)$$

Here, the average  $\Delta H_{\text{soln}}^{323}$ (MFI/calc) and  $\Delta H_{\text{soln}}^{323}$ (\*BEA/calc) values calculated above ( $-147.2 \pm 0.7$  and  $-148.4 \pm 0.6$  kJ/mol SiO<sub>2</sub>, respectively) were used. Table 6 compares the  $\Delta H_{\text{soln}}^{323}$  values calculated from the aqueous HF calorimetry in this work to the  $\Delta H_{\text{trans}}^{298}$  values determined by Piccione et al.<sup>8</sup> and Petrovic et al.<sup>7</sup> using high-temperature, molten calorimetry in lead borate near 974 K. On the basis of the heat capacity

TABLE 6: Enthalpies of Transition from Quartz to Other SiO<sub>2</sub> Polymorphs

framework	$\Delta H_{\text{trans}}^{323}$ (this work) kJ/mol SiO <sub>2</sub>	$\Delta H_{\text{trans}}^{298}$ (high- <i>T</i> calorimetry) kJ/mol SiO <sub>2</sub>
*BEA	$8.2 \pm 1.2$	$9.3 \pm 0.8^a$
MFI	$7.0 \pm 1.3$	$6.8 \pm 0.8^b$
MTW	$5.2 \pm 1.6$	$8.7 \pm 1.3^b, 7.0 \pm 2.7^c$
STF	$7.5 \pm 1.4$	$9.1 \pm 2.8^c$

<sup>a</sup> From ref 8. <sup>b</sup> From ref 7. <sup>c</sup> Estimated from the correlation in ref 8.

data of Boerio-Goates et al.,<sup>9</sup> the enthalpies of transition at 323.15 K differ from those at 298.15 K by no more than 0.5 kJ/mol SiO<sub>2</sub>. Within experimental errors,<sup>7,8</sup>  $\Delta H_{\text{trans}}^{298}$  and  $\Delta H_{\text{trans}}^{323}$  should therefore be equal. Since  $\Delta H_{\text{trans}}^{298}$ (STF) has not been determined experimentally, the value in Table 6 was obtained by using the molar volume– $\Delta H_{\text{trans}}^{298}$  correlation given in ref 8 to the STF framework, which has a molar volume of 34.86 cm<sup>3</sup>/mol.<sup>34</sup> The enthalpies of transition from quartz determined by the two methods are within experimental error of each other for all frameworks except MTW. The high-temperature calorimetry datum reported by Petrovic et al. is based on a sample that was made in fluoride media, but at basic pH.<sup>7</sup> As discussed by Barrett et al., molecular sieve materials made using fluoride as the mineralizing agent are only truly defect-free if the pH is sufficiently low.<sup>17</sup> The MTW sample used by Petrovic et al. may therefore have contained some silanol defect groups. Therefore, the enthalpy of the defect-free MTW framework may have been overestimated in ref 7 by up to 2.4 kJ/mol.<sup>8</sup> Correcting for the energetic destabilization due to an unknown density of defect sites would lead to a smaller disparity between the MTW data determined by HF and lead borate calorimetry. The presence of destabilizing silanol groups in the previously studied MTW sample is also suggested by the relatively large discrepancy between the experimental  $\Delta H_{\text{trans}}^{298}$ (MTW) value and that predicted from the molar volume– $\Delta H_{\text{trans}}^{298}$  correlation of ref 8. This correlation predicts a  $\Delta H_{\text{trans}}^{298}$ (MTW) value of 7.0 kJ/mol, significantly closer to the value calculated from the HF solution enthalpy in this work. In conclusion, the sets of  $\Delta H_{\text{trans}}^T$  data calculated from the two methods are in good agreement.

**Enthalpies of Interaction,  $\Delta H_{\text{int}}^{323}$ .** The interaction enthalpy  $\Delta H_{\text{int}}^{323}$  between each molecular sieve and its associated SDA are shown per mol SiO<sub>2</sub> and per mol SDA in Table 7. The standard errors were calculated according to  $\sigma = \sqrt{\sigma_3^2 + \sigma_4^2}$ , where  $\sigma_3$  and  $\sigma_4$  are the standard deviations for  $\Delta H_{\text{soln}}^{323}$ (MS/calc) and  $\Delta H_{\text{soln}}^{323}$ (MS/SDA), respectively.

**TABLE 7: Enthalpies of Interaction**

framework	organic SDA	$\Delta H_{\text{int}}^{323}$ (kJ/mol SiO <sub>2</sub> )	uncertainty (kJ/mol SiO <sub>2</sub> )	$\Delta H_{\text{int}}^{323}$ (kJ/mol SDA)	uncertainty (kJ/mol SDA)	$\Delta H_{\text{diff,diln}}$ (kJ/mol SiO <sub>2</sub> )
MFI	TPA	-3.2	1.4	-81	34	0.03
MFI	TEA	-1.1	1.4	-27	33	0.02
*BEA	TEA	-3.1	1.4	-32	15	-0.01
*BEA	BISPIP	-5.9	0.7	-181	21	-0.01
MTW	BISPIP	-1.6	1.3	-124	97	0.02
STF	SPIRO	-4.9	0.9	-83	16	0.02

The contribution of the differential heat of dilution between the calcined and as-made molecular-sieve samples,  $\Delta H_{\text{diff,diln}}$ , shown in the last column of Table 7, is less than 2.5% of the uncertainty in  $\Delta H_{\text{int}}^{323}$ . The simplifying approximation that the relative apparent molal enthalpy of HF solutions is independent of temperature in the 298.15–323.15 K range, therefore, cannot have significantly altered the calculated  $\Delta H_{\text{int}}^{323}$  values. Although the errors in  $\Delta H_{\text{int}}^{323}$  may appear large in relative terms, ranging from 12% to 125%, the absolute uncertainties are quite narrow ( $\leq 1.4$  kJ/mol SiO<sub>2</sub>) and are significantly smaller than those of Patarin et al.<sup>11,12</sup>

The  $\Delta H_{\text{int}}^{323}$  values in Table 7 range from -1.1 kJ/mol SiO<sub>2</sub> for the MFI/TEA interaction to -5.9 kJ/mol SiO<sub>2</sub> for the \*BEA/BISPIP interaction. All  $\Delta H_{\text{int}}^{323}$  values are negative and thus favorable for all inorganic/organic pairs studied here. At a typical synthesis temperature of 423.15 K, the available thermal energy per total number of moles in the system is  $RT$  and is 3.5 kJ/mol. Since there are many Si atoms per SDA in the as-synthesized molecular sieves, an appropriate quantity to compare to  $RT$  is  $\Delta H_{\text{int}}^{323}$  per mol SiO<sub>2</sub>. On such a basis, the interaction between the varied range of pure-silica molecular sieve frameworks and their SDAs studied here is seen to be in no case more exothermic than twice the thermal energy at synthesis conditions. Such a narrow  $\Delta H_{\text{int}}^{323}$  range may explain why certain SDAs, e.g., TEA and BISPIP, can direct syntheses toward several frameworks depending on the reaction conditions. The relatively small magnitude of  $\Delta H_{\text{int}}^{323}$  is consistent with the interpretation that the MS/SDA interaction consists predominantly of weak, van der Waals forces between the hydrophobic silica species and the hydrocarbon moieties of the SDA.<sup>35,36</sup>

The stabilizing effect of TEA toward the MFI framework is 2.1 kJ/mol SiO<sub>2</sub> less exothermic than that of TPA. This result is consistent with the observation that MFI is the sole product from pure-silica, TPA-directed syntheses whereas TEA frequently yields other phases. On a per mole of silica basis,  $\Delta H_{\text{int}}^{323}$ (\*BEA/TEA) is comparable to  $\Delta H_{\text{int}}^{323}$ (MFI/TPA) and is roughly 2 kJ/mol SiO<sub>2</sub> more exothermic than  $\Delta H_{\text{int}}^{323}$ (MFI/TEA). The stronger overall interaction between the \*BEA framework and TEA, however, is not due to a stronger stabilization of TEA in the \*BEA void spaces:  $\Delta H_{\text{int}}^{323}$ (\*BEA/TEA) per mol SDA is nearly identical to  $\Delta H_{\text{int}}^{323}$ (MFI/TEA). The more exothermic interaction energy of TEA within \*BEA likely reflects the greater number of guest molecules per SiO<sub>2</sub> in the larger \*BEA cages. Note that the occlusion of fluoride ions within molecular sieves has been shown by <sup>19</sup>F–<sup>29</sup>Si CP MAS NMR to result in the formation of five-coordinate Si units, SiO<sub>4/2</sub>F<sup>-</sup>.<sup>37</sup> Since all the materials studied in this work were prepared in fluoride media, it is not possible to separate the energetic effects of the interaction of the silica frameworks with the SDA cations and the F<sup>-</sup> anions.

The much larger organic, BISPIP, gives the highest enthalpy of interaction measured here when occluded inside \*BEA. The large negative  $\Delta H_{\text{int}}^{323}$ (\*BEA/BISPIP) may be related to a greater number of interactions between the organic molecule

and the silica framework when compared to TEA. Based on the unit cell (uc) compositions, there are 50 C atoms/uc in \*BEA/TEA and 60 C atoms/uc in \*BEA/BISPIP. This difference is too small for it alone to account for the factor of 2 difference in  $\Delta H_{\text{int}}^{323}$ (\*BEA/SDA) per mol SiO<sub>2</sub>. Instead, it is likely the quality of the spatial fit of the organic guest inside the inorganic host is important. Since the \*BEA structure is three-dimensional, the large BISPIP molecule is expected to have significant freedom to orient itself into a minimum energy configuration. Once such a conformation is found, the BISPIP cations are not expected to reorient themselves significantly away from it since such motion would require the simultaneous motion of a large number of atoms. By contrast, the TEA molecules inside the \*BEA cages have been shown by <sup>13</sup>C solid-state NMR to behave similarly to TEA cations in the liquid state.<sup>6</sup> Such fast rotating species would, on average, sample a larger number of less energetically favorable conformations, thus being consistent with a less exothermic  $\Delta H_{\text{int}}^{323}$  value for \*BEA/TEA.

The BISPIP SDA was also occluded inside MTW, a one-dimensional structure with a distorted, large pore. Table 7 shows the interaction between BISPIP and MTW to be considerably less exothermic than the \*BEA/BISPIP interaction.  $\Delta H_{\text{int}}^{323}$ (\*BEA/BISPIP) and  $\Delta H_{\text{int}}^{323}$ (MTW/BISPIP) are significantly different on a per mol SDA basis, so the difference is not solely due to a greater packing of SDA molecules in the \*BEA framework. Linear hydrocarbon chains can easily expand into one-dimensional pore systems, but bulkier groups, e.g., the *N*-benzyl substituted piperidinium groups of BISPIP, are less easily accommodated; such groups are expected to be more stable when residing within the intersections of multidimensional pore systems, or inside cage frameworks. Although the BISPIP SDA can undergo conformational changes, e.g., the ring-flipping mechanism proposed by Tsuji and Davis for BISPIP inside MTW,<sup>38</sup> before incorporation into a one-dimensional framework that is more constrained, portions of the large, bulky SDA may not be able to reside at the optimal distance to interact most favorably with the inorganic framework. Note further that MTW differs from the other three molecular sieves in this study in that one-seventh of the silica atoms are not accessible for interactions with the SDA from the pore channels.<sup>13</sup>

The bicyclic derivative used to make STF is representative of a class of relatively small, globular, yet rather rigid, SDAs used by researchers at Chevron to make novel molecular sieve materials.<sup>20</sup> Such molecules do not lead to the crystallization of as varied a set of frameworks as more flexible molecules, and it has been suggested that the high specificity of the more rigid SDAs may be due to their role in preventing polymorphs of lower activation energy from crystallizing.<sup>39</sup> The comparatively strong exothermic  $\Delta H_{\text{int}}^{323}$ (STF/SPIRO) value (the second highest per mol SiO<sub>2</sub> in this work) is consistent with the view that highly rigid SDAs such as SPIRO are occluded inside molecular sieves when they have significant favorable interactions. Such organics are simply not flexible enough to be easily accommodated into other frameworks. For SPIRO, this lack of



flexibility translates into the formation of STF that is best described as stacked cages connected by 10-ring portals.<sup>34</sup> These cages presumably provide necessary space for the rigid spiro moiety.

Lewis et al. used energy minimization techniques to calculate nonbonded energies of interaction between the symmetric tetramethylammonium (TMA), TEA, TPA, and tetrabutylammonium (TBA) cations and the pure-silica MFI, \*BEA, and ZSM-11 (MEL) frameworks.<sup>40</sup> They reported interaction energies for MFI/TEA, MFI/TPA, and \*BEA/TEA of  $-92.1$ ,  $-133.9$ , and  $-104.7$  kJ/mol SDA, respectively. These values are several times more exothermic than the corresponding  $\Delta H_{\text{int}}^{323}$  values of  $-27$ ,  $-81$ , and  $-32$  kJ/mol SDA measured here. Nevertheless, the calculated values follow the correct energetic trends, suggesting that the stabilization of charged organic SDA cations within molecular sieves, at least in their pure-silica form, can be viewed as consisting primarily of nonbonded interactions as was assumed by Lewis et al.<sup>40</sup>

**Gibbs Free Energies of MS/SDA Interaction.** The Gibbs free energies of interaction between organic SDAs and calcined molecular sieve,  $\Delta G_{\text{int}}(\text{MS/SDA})$ , are related to the interaction enthalpies determined in this work by

$$\Delta G_{\text{int}}(\text{MS/SDA}) = \Delta H_{\text{int}}(\text{MS/SDA}) - T\Delta S_{\text{int}}(\text{MS/SDA})$$

where  $\Delta S_{\text{int}}(\text{MS/SDA})$  represents the entropy of interaction between framework MS and its SDA. Unfortunately, no entropy data are available at this time for any organic-containing molecular sieve at any temperature. To calculate Gibbs free energies of interaction,  $\Delta S_{\text{int}}(\text{MS/SDA})$  was approximated. Note that the entropies for most tetraalkylammonium salts are only available at 298.15 K, whereas the  $\Delta H_{\text{int}}^{323}$  values determined above refer to interactions at 323.15 K. In the interest of simplicity, we assumed that the interaction enthalpies at 298.15 K are not significantly different from those at 323.15 K, i.e.,  $\Delta H_{\text{int}}^{298} = \Delta H_{\text{int}}^{323}$ . Such an assumption is reasonable since the major contributor to the heat capacity on either side of reaction 1 is that of the solid molecular sieve, and is expected to be relatively unaffected by the presence or absence of organic guest molecules. Following the same procedure as Helmkamp and Davis,<sup>14</sup> the entropies of interaction between organic SDA fluoride in the solution state and empty molecular sieve were estimated by the negative of the entropy of hydration of the solid SDA fluoride, i.e., per mol SDA  $\Delta S_{\text{int}}^{298}(\text{MS/SDAF}_2) = -\Delta S_{\text{soln}}^{298}(\text{SDAF}_2)$ . Tetraalkylammonium ions in aqueous solutions are well-known to order water around their alkyl chains.<sup>14,41,42</sup> The above approximation takes into account the gain in entropy of the water liberated by desolvation of the SDA cations as well as the change in environment experienced by the SDA cations upon enclathration in the molecular sieve framework.<sup>14</sup> It explicitly assumes that the entropy of the SDA fluoride occluded inside the molecular-sieve framework is the same as that for the solid salt. Using these approximations with a generic fluoride SDAF<sub>z</sub>:

$$\Delta S_{\text{soln}}^{298}(\text{SDAF}_z) = \Delta S_{\text{soln}}^{298}(\text{SDAI}_z) + z\{S[\text{F}^-(\text{aq})] - S[\text{I}^-(\text{aq})]\} + S^{298}(\text{SDAF}_z) - S^{298}(\text{SDAI}_z)$$

where SDAI<sub>z</sub> is the corresponding iodide. Johnson and Martin measured  $S(\text{TEAI}) = 311.1 \pm 1$  J/(mol K) and  $S(\text{TPAI}) = 432.1 \pm 1$  J/(mol K) by low-temperature heat capacity calorimetry.<sup>43</sup> They also calculated the entropies of solution for the two salts:  $\Delta S_{\text{soln}}^{298}(\text{TEAI}) = 78.7 \pm 1.5$  J/(mol K) and  $\Delta S_{\text{soln}}^{298}(\text{TPAI}) = 11 \pm 3$  J/(mol K).  $\Delta S_{\text{int}}^{298}$  can thus be estimated for the MFI/TPA,

TABLE 8: Gibbs Free Energies of Interaction

framework	organic SDA	$\Delta S_{\text{int}}^{298}$ (J/(mol SDA K))	$T\Delta S_{\text{int}}^{298}$ at 298.15 K (kJ/mol SiO <sub>2</sub> )	$\Delta G_{\text{int}}^{298}$ (kJ/mol SiO <sub>2</sub> )	$\Delta G_{\text{int}}^{423}$ a (kJ/mol SiO <sub>2</sub> )
MFI	TPA	$144 \pm 11$	$1.7 \pm 0.1$	$-4.9 \pm 1.4$	$-5.6$
MFI	TEA	$77 \pm 11$	$0.9 \pm 0.1$	$-2.0 \pm 1.4$	$-2.4$
*BEA	TEA	$77 \pm 11$	$2.2 \pm 0.3$	$-5.4 \pm 1.5$	$-6.3$

<sup>a</sup> Extrapolated assuming no temperature dependence of  $\Delta S_{\text{int}}^T$  or  $\Delta H_{\text{int}}^T$ .

MFI/TEA and \*BEA/TEA molecular sieve/SDA pairs. The absolute entropies of aqueous F<sup>-</sup> and I<sup>-</sup> were taken from *The NBS Tables of Chemical Thermodynamic Properties*: their values are  $-13.8$  and  $111.3$  J/(mol K), respectively.<sup>44</sup> The entropies of the solid fluorides were unavailable, doubtlessly due to the difficulties in preparing these salts in the anhydrous state. Piccione used group additivity methods to calculate the enthalpies and entropies of a collection of symmetric tetraalkylammonium salts and estimated  $S(\text{TEAF}) = 280.9 \pm 10.5$  J/(mol K) and  $S(\text{TPAF}) = 401.9 \pm 10.5$  J/(mol K).<sup>26</sup>

Table 8 lists the Gibbs free energies for the MS/SDA interactions,  $\Delta G_{\text{int}}^{298}$ , as well as the entropy and  $T\Delta S$  (at 298.15 K) contributions to the MS/SDA interactions. The entropy of interaction for the MS/SDA interaction is positive in all cases; as noted by Helmkamp and Davis, this may reflect the release of ordered water upon SDA enclathration.<sup>14</sup> The MS/SDA interaction is thus simultaneously favored by both enthalpic (exothermic van der Waals contacts between hydrophobic silica species and hydrocarbon chains) and entropic (disordering of water around the SDA) energies.  $T\Delta S_{\text{int}}^{298}$  ranges from 0.9 to 2.2 kJ/mol SiO<sub>2</sub> (54–92% of  $\Delta H_{\text{int}}^{298}$ ) so the enthalpy and entropy of interaction are of the same order of magnitude. Therefore, the entropy contribution cannot be neglected when quantitatively describing the thermodynamics of formation of molecular sieves.

The entropy of interaction per mol SDA is greater for TPAF ( $144 \pm 11$  J/(mol K)) than that for TEAF ( $77 \pm 11$  J/(mol K)). The more positive  $\Delta S_{\text{int}}^{298}$  per mol TPA is consistent with the expectation that larger, more hydrophobic cations would release a greater number of water molecules upon enclathration.<sup>14</sup> The magnitude of the entropy contribution to molecular sieve stabilization, however, is higher for the \*BEA/TEA interaction (2.2 kJ/mol SiO<sub>2</sub> at 298.15 K) than that for MFI/TPA. The reason for this apparent discrepancy is the greater organic content of the \*BEA sample. Within the approximations of this work, the entropy of interaction per mol SDA depends neither on the framework into which that SDA is occluded or on the amount of SDA occluded.  $\Delta S_{\text{int}}^{298}$  therefore scales linearly with the SDA/Si ratio when expressed per mol SiO<sub>2</sub>. The entropy contribution thus preferentially stabilizes higher organic contents, i.e., more porous frameworks. For the case of TEA, the entropy of the very mobile cations inside \*BEA is expected to be higher than for the more rigid TEA ions inside MFI. In fact, TEA inside \*BEA represents an extreme case where a rather small SDA is occluded inside a large-pore molecular sieve.

For comparison purposes, the last column of Table 8 shows  $\Delta G_{\text{int}}^{423}$  extrapolated from the data at 298.15 K to the more typical synthesis temperature of 423.15 K assuming that both the enthalpy and entropy of interaction are independent of temperature. While this assumption is open to criticism, sufficient data are not available to adequately correct  $\Delta H_{\text{int}}^{323}$  and  $\Delta S_{\text{int}}^{298}$  to synthesis conditions. No uncertainty for  $\Delta G_{\text{int}}^{423}$  is given since the assumption above is likely to lead to errors comparable to the uncertainties in the original data. Qualitatively,  $\Delta G_{\text{int}}^{423}$  follows the same trend as  $\Delta G_{\text{int}}^{298}$  with MFI/TPA

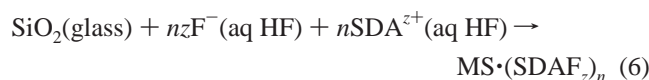
**TABLE 9: Gibbs Free Energies of Formation from Amorphous Precursors and SDAs**

framework		$\Delta H_{\text{trans}}^{298}$ (glass→MS) (kJ/mol SiO <sub>2</sub> )	$T\Delta S_{\text{trans}}^{298}$ (glass→MS) (kJ/mol SiO <sub>2</sub> )	$\Delta G_{\text{trans}}^{298}$ (glass→MS) (kJ/mol SiO <sub>2</sub> )
MFI		$-2.3 \pm 2.4$	$-1.0 \pm 0.3$	$-1.3 \pm 2.5$
*BEA		$0.2 \pm 2.4$	$-1.1 \pm 0.3$	$1.3 \pm 2.5$
framework		$\Delta H_{\text{rxn}}^{298}$ (glass→MS/SDA) (kJ/mol SiO <sub>2</sub> )	$T\Delta S_{\text{rxn}}^{298}$ (glass→MS/SDA) (kJ/mol SiO <sub>2</sub> )	$\Delta G_{\text{rxn}}^{298}$ (glass→MS/SDA) (kJ/mol SiO <sub>2</sub> )
MFI	TPA	$-5.5 \pm 2.8$	$0.7 \pm 0.1$	$-6.2 \pm 2.8$
MFI	TEA	$-3.4 \pm 2.8$	$-0.1 \pm 0.1$	$-3.3 \pm 2.8$
*BEA	TEA	$-2.9 \pm 2.8$	$1.2 \pm 0.2$	$-4.1 \pm 2.9$

<sup>a</sup> Extrapolated assuming no temperature dependence of  $\Delta S_{\text{rxn}}^T$  or  $\Delta H_{\text{rxn}}^T$ .

and \*BEA/TEA approximately more stable than MFI/TEA by  $RT$ . Within this approximation, higher temperatures only lead to slightly more favorable interactions ( $\leq 0.9$  kJ/mol SiO<sub>2</sub>). Unless the enthalpy and entropy of interaction themselves change significantly with temperature, the relative importance of these two terms is only slightly altered.

**Molecular Sieve Formation from Amorphous Precursors.** The Gibbs free energy of reaction between silica glass and an organic SDA leading to the formation of an as-made molecular sieve can be represented as



The Gibbs free energy for this reaction,  $\Delta G_6 = \Delta G_{\text{rxn}}^{298}(\text{glass} \rightarrow \text{MS/SDA})$ , is obtained by taking the sum of reaction 1 using the ions in aq HF as references and the following reaction:



The enthalpy and entropy of transition from quartz to silica glass are  $9.1 \pm 2.3$  kJ/mol SiO<sub>2</sub> and  $7.0 \pm 1.0$  J/(mol K), respectively,<sup>45</sup> and at 298.15 K the Gibbs free energy for reaction 7 is  $\Delta G_{\text{trans}}^{298}(\text{glass} \rightarrow \text{MS}) = \Delta G_{\text{trans}}^{298}(\text{quartz} \rightarrow \text{MS}) - \Delta G_{\text{trans}}^{298}(\text{quartz} \rightarrow \text{glass})$ . Therefore, the Gibbs free energy of formation of an organic-containing molecular sieve from amorphous precursors is

$$\Delta G_{\text{rxn}}^{298}(\text{glass} \rightarrow \text{MS/SDA}) = \Delta G_{\text{int}}^{298}(\text{MS/SDA}) + \Delta G_{\text{trans}}^{298}(\text{quartz} \rightarrow \text{MS}) - \Delta G_{\text{trans}}^{298}(\text{quartz} \rightarrow \text{glass})$$

Table 9 lists the various contributions to  $\Delta G_{\text{rxn}}^{298}(\text{glass} \rightarrow \text{MS/SDA})$  for MFI/TPA, MFI/TEA, and \*BEA/TEA. The large uncertainties in Table 9 are due to uncertainties in the literature values for the enthalpy and entropy of silica glass.<sup>45</sup> Since the energetic data for silica glass were obtained by high-temperature calorimetry, the  $\Delta H_{\text{trans}}^{298}(\text{quartz} \rightarrow \text{MS})$  values measured by high-temperature calorimetry<sup>7,8</sup> were used to calculate  $\Delta G_{\text{rxn}}^{298}(\text{glass} \rightarrow \text{MS/SDA})$ . Since the entropies of pure-silica molecular sieves are nearly identical,<sup>9</sup> the stabilities of calcined frameworks differ mostly because of enthalpy differences.

The Gibbs free energies of formation of MS/SDA from silica glass are not significantly more exothermic than the Gibbs free energies of interaction; they do not lead to stabilization energies greater in magnitude than  $2RT$ . The most favorable Gibbs free energy for assembly among the materials listed in Table 9 is that for MFI/TPA. Additionally, the interaction between \*BEA and TEA is sufficiently exergonic for the formation of \*BEA/

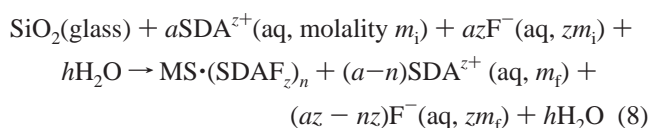
**TABLE 10: Synthesis Mixture Compositions**

framework	organic SDA	initial composition	final composition
MFI	TPA	1 SiO <sub>2</sub> /0.44 TPAF/ 8.44 H <sub>2</sub> O	1 MFI·(TPAF) <sub>0.039</sub> / 0.401 TPAF/8.44 H <sub>2</sub> O
MFI	TEA	1 SiO <sub>2</sub> /0.5 TEAF/ 15 H <sub>2</sub> O	1 MFI·(TEAF) <sub>0.041</sub> / 0.459 TEAF/15 H <sub>2</sub> O
*BEA	TEA	1 SiO <sub>2</sub> /0.5 TEAF/ 7.25 H <sub>2</sub> O	1 *BEA·(TEAF) <sub>0.098</sub> / 0.402 TEAF/7.25 H <sub>2</sub> O

TEA from amorphous precursors to occur spontaneously even though calcined \*BEA is less thermodynamically stable than glass.

#### Thermodynamic Analysis of the Full Synthesis Mixtures.

The  $\Delta G_{\text{rxn}}^{298}(\text{MS/SDA})$  values discussed above represent only part of the actual synthesis reaction. To perform a more complete analysis, the energetic effects of the changes in state of the other components (water and free SDA<sup>z+</sup> and F<sup>-</sup> ions in the mixture) must be considered. The crystallization of a pure-silica molecular sieve from a fluoride containing reaction mixture can be symbolized per mol silica as



where the hydration of the molecular sieve is again neglected. Here  $m_i$  and  $m_f$  denote the initial and final molalities of the SDA fluoride in the synthesis gel. The letters h and a are the initial amounts of SDAF<sub>z</sub> and water, respectively.  $m_{\text{cal}}$  (see below) is the molality of the SDA fluoride in the calorimeter at the end of the solution experiments. Table 10 lists the initial and final concentrations of the three synthesis mixtures considered. It is assumed that all the silica in each system is present as silica glass at the beginning and as MS/SDA at the end of the crystallization. This assumption is reasonable since the synthesis yield (on a silica basis) was greater than 85% for all three systems considered. Equation 8 is the sum of eq 6 and the following steps

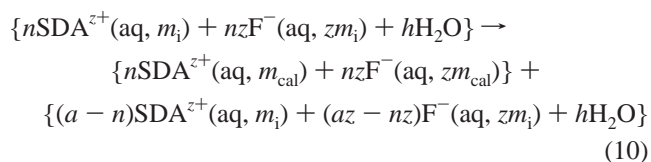
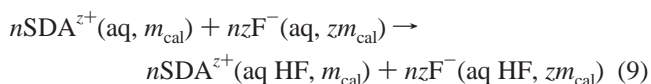




TABLE 11: Gibbs Free Energies of Formation and Effective Dilution for Complete Synthesis Mixtures

framework	organic SDA	$\Delta G_{\text{SYN}}^{298}$ (MS/SDA) (kJ/mol SiO <sub>2</sub> )	$\Delta G_{10}$ (effective dilution) (kJ/mol SiO <sub>2</sub> )	$\Delta G_{10}$ (kJ/mol SDA incorporated)	$\Delta G_{10}$ (kJ/mol SDA in synthesis mixture)
MFI	TPA	$-8.1 \pm 2.8^a$	-2.0	-50	-4.4
MFI	TEA	$-4.9 \pm 2.8$	-1.6	-39	-3.2
*BEA	TEA	$-8.5 \pm 2.9$	-4.4	-45	-8.9

<sup>a</sup> The largest error is contributed by  $\Delta G_{\text{rxn}}^{298}(\text{glass} \rightarrow \text{MS/SDA})$ .

Equation 6 is the idealized self-assembly of MS/SDA from silica glass and the SDAF<sub>z</sub> in its reference state (25% aqueous HF solution). Equation 9 represents the transfer of SDA and fluoride ions from 25% aqueous HF to water at the concentrations present in the solution calorimetry experiments. Equation 10 is the fictitious dilution of *n* moles SDA and fluoride ions (in *h* moles of water) from the initial concentration in the hydrothermal synthesis mixture to the concentration present in the solution experiments, and simultaneously of (*a*−*n*) moles of SDA and fluoride ions (in *h* moles of water) at the initial concentration of the hydrothermal synthesis mixture to (*a*−*n*) moles of SDA and fluoride ions (in *h* moles of water) at the final concentration of the hydrothermal synthesis mixture.

No data are available to estimate the energetics of SDAF transfer from water to 25% aqueous HF. The most similar compound to the SDA fluorides for which data are available is TEAI, and its Gibbs free energy of transfer from water to methanol is 7.5 kJ/mol SDA at 298.15 K.<sup>46</sup> For the MS/SDA pair with the highest organic content (\*BEA/TEA) such a value would lead to  $\Delta G_9 = 0.7$  kJ/mol SiO<sub>2</sub>. Since 25% aqueous HF is considerably more polar than methanol, the magnitude of  $\Delta G_9$  is expected to be significantly smaller than the value calculated from the transfer to methanol of TEAI.  $\Delta G_9$  was therefore neglected in the calculation of the energetic changes of the complete synthesis mixture due to the lack of data and to its small size. The Gibbs free energy of eq 10 is equal to

$$\Delta G_{10} = \Delta G_{\text{mix}}(m_f) + n\mu(m_{\text{cal}}) - \Delta G_{\text{mix}}(m_i) = \Delta G_{\text{mix}}^{\text{id}}(m_f) - \Delta G_{\text{mix}}^{\text{id}}(m_i) + \Delta G^{\text{EX}}(m_f) - \Delta G^{\text{EX}}(m_i) + 2RTn \ln(m_{\text{cal}}\gamma_{\text{cal}})$$

The Gibbs free energies of mixing are based on one mole of SiO<sub>2</sub>, and the standard state of the organic fluoride salts is the hypothetical ideal one molal solution. The excess Gibbs free energies of mixing were obtained from Pitzer's correlations for TEAF and TPAF,<sup>47</sup> as were the activity coefficients at the calorimetric concentration. The ideal Gibbs free energies of mixing for uni-univalent electrolytes at molality *m* are given by  $2RTn(\ln m - 1)$ .

Table 11 shows the Gibbs free energy of self-assembly for the synthesis mixture,  $\Delta G_8 = \Delta G_{\text{SYN}}^{298}(\text{MS/SDA})$ , as well as the contribution from the effective dilution of the SDA and fluoride ions,  $\Delta G_{10}$ . Dilution is exergonic for all cases, with  $\Delta G_{10}$  ranging from −1.6 to −4.4 kJ/mol SiO<sub>2</sub>, a range comparable to that of  $\Delta G_{\text{rxn}}^{298}(\text{glass} \rightarrow \text{MS/SDA})$ . Thus, each of the three energetic contributions considered in this work (silica→empty frameworks, MS/SDA interaction, and dilution of SDA fluorides in the synthesis mixture) contributes similarly in magnitude to the overall energetics. Note that at the high molalities present in these synthesis mixtures, the activity coefficients of the SDAF species in aqueous solution are among the highest reported for univalent electrolytes.<sup>48</sup> The magnitudes of  $\Delta G_{10}$  are therefore more negative than the corresponding dilutions for ideal solutions.

The Gibbs free energy changes during molecular-sieve synthesis range from −4.9 to −8.5 kJ/mol SiO<sub>2</sub>. While more exergonic than  $\Delta G_{\text{rxn}}^{298}(\text{glass} \rightarrow \text{MS/SDA})$ , these values still imply only slight thermodynamic differences between various phases. The  $\Delta G_{\text{SYN}}^{298}(\text{MS/SDA})$  values are comparable for MFI/TPA and \*BEA/TEA, the more readily synthesized materials. Although the interaction between TPA and glass to produce MFI/TPA is more favorable, the changes experienced by the water and SDAF not incorporated in the framework ( $\Delta G_{10}$ ) are more exergonic for the \*BEA/TEA pair.

**Implications for Molecular Sieve Synthesis.** Piccione et al. have shown that all crystalline silica polymorphs have Gibbs free energies within  $2RT$  of each other.<sup>9</sup> The Gibbs free energies of interaction between inorganic host and organic guest calculated here are of comparable magnitude. The MS/SDA interaction thus significantly alters the free energy landscape during molecular sieve self-assembly. In some cases, the relative stability of silicate frameworks is modified to such an extent that structures less stable than silica glass become energetically favorable when their self-assembly takes place with the proper SDA (\*BEA/TEA). While the interaction energies measured here are all favorable, they are not sufficiently exergonic to explain the strong selectivity that many organic cations have toward a relatively small subset of porous silica frameworks. The role of organic SDAs in zeolite synthesis cannot therefore be to provide preferential stabilization for one structure with respect to others: the  $\Delta H$  and  $\Delta G$  differences observed here are too small in magnitude to totally explain the frequent formation of pure molecular sieve phases. By contrast, the moderate magnitude of the Gibbs free energy changes during crystallization are consistent with the fact that most organocations are able to direct syntheses toward more than one molecular sieve framework.

The relative magnitudes of the enthalpy and entropy contributions to the Gibbs free energy of self-assembly are similar, so the crystallization thermodynamics depend on the delicate interplay between a large number of interactions. The energetics of the empty molecular sieves, those of the organic/inorganic interaction, and the additional stabilizing factor contributed by the effective dilution of high-activity SDAF species upon enclathration must all be considered to fully describe molecular sieve syntheses. No single factor dominates  $\Delta G_{\text{SYN}}^{298}(\text{glass} \rightarrow \text{MS/SDA})$ .

## Conclusions

The enthalpies of solution (25% HF at 323.15 K) for a series of pure-silica molecular sieves in their as-made and calcined forms have been determined by calorimetry. The relative enthalpies measured for the calcined frameworks confirm previous findings<sup>7,8</sup> that crystalline silica polymorphs are within twice the available thermal energy ( $RT$ ) of each other. Such a low barrier to transformation explains the large diversity (over 20 structures) of silica polymorphs.

Enthalpies of interaction between organic guests and inorganic hosts were obtained by measuring the difference between the enthalpies of solution of the as-made and calcined materials. The enthalpies of interaction span the narrow, exothermic range of  $-1.1$  to  $-5.9$  kJ/mol  $\text{SiO}_2$ . None of these values is more negative than  $-2RT$ , and such modest magnitudes explain why many SDAs can direct molecular sieve syntheses toward several frameworks.

Entropies of interaction were estimated and Gibbs free energies of interaction calculated for \*BEA/TEA, MFI/TEA, and MFI/TPA. The entropy of interaction is found to be positive in all cases. Within the approximations of this work, the entropy of interaction varies linearly with the organic content. The magnitudes of the enthalpy and entropy contributions to the Gibbs free energy of interaction are comparable, showing that both must be included in thermodynamic descriptions of MS/SDA interactions. The organic/inorganic interactions can thus provide a thermodynamic stability field for some  $\text{SiO}_2$  polymorphs that are less stable than glass, e.g., \*BEA, relative to amorphous precursors. When all the components present in the synthesis mixture are considered, additional stabilizing contributions ( $-1.6$  to  $-4.4$  kJ/mol  $\text{SiO}_2$ ) due to the effective dilution of the SDA and fluoride ions are recognized. Thus, the organic SDAs do not select one structure over others by strongly stabilizing a particular framework as the final product.

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