

**778.** *Reactions and Stability of Chabazite-type Phases.  
Part III.\* Intracrystalline Water.*

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The intracrystalline water in a series of non-stoichiometric hydrates based on the chabazite lattice has been studied by differential thermal analysis, thermogravimetry, and X-ray powder photography applied to a variety of ion-exchanged forms and, in some cases, for a variety of  $\text{Al}_2\text{O}_3 : \text{SiO}_2$  ratios, all equilibrated at a relative humidity of  $\sim 0.51$ .

In a natural chabazite the affinity for water decreased for a range of ion-exchanged forms in the sequence  $\text{Ca} > \text{Li} > \text{Na} > \text{K}, \text{Rb} > \text{Cs}$ . With increasing  $\text{Al}_2\text{O}_3 : \text{SiO}_2$  ratio the actual water content per structural cage increased for Ca and Li forms. For all forms there was a tendency, despite some irregularities, for the number of water molecules per cation to decrease with increasing number of cations per cage, with increasing cation radius, and with decreasing primary hydration number of the solvated cations.

Integral heats associated with water loss have been determined for various forms of a natural chabazite and of chabazite-type phases of varying  $\text{Al}_2\text{O}_3 : \text{SiO}_2$  ratios. These heats do not depend in a simple way on cation radius or on the number of cations per unit cell. It is suggested that cation positions may alter as cation radius changes and that some crystals undergo perturbations during water loss. Heats are influenced by ion-dipole interactions whose magnitude is however reduced in the intracrystalline environment.

CRYSTALLOHYDRATES may be stoichiometric or non-stoichiometric in water content. The zeolites comprise a diverse group of non-stoichiometric hydrates, and the behaviour of their intracrystalline water has been studied in relation to diffusion,<sup>1</sup> dielectric relaxation,<sup>2</sup> infrared absorption,<sup>3</sup> optics,<sup>4</sup> crystallography,<sup>5</sup> sorption equilibria,<sup>6,7</sup> sorption heats,<sup>7,8</sup> and exchange of light and heavy water.<sup>9</sup> Nevertheless, the detailed properties of crystal water remain obscure in many respects.

As a result of studies of hydrothermal crystallisation of aluminosilicates it has been possible<sup>10</sup> to prepare a series of chabazite-type phases in which (a) the alumina : silica ratio varies over a wide range, (b) the cation density varies to correspond with this ratio, (c) the cations present may be exchanged, to vary the ion radius and valency, and (d) the water content can be varied continuously in the crystals of all exchange forms.

We now report a comparative study of the intracrystalline water in these phases, having used differential thermal analysis, thermogravimetry, and X-ray powder photography, as in Parts I and II.<sup>11</sup> It has been our principal interest to obtain comparative values of integral heats for water loss in relation to alumina : silica ratios and cation

\* Parts I and II, preceding papers.

<sup>1</sup> Tiselius, *Z. physik. Chem.*, 1934, **A**, **169**, 425; 1935, **A**, **174**, 401; Barrer, "Diffusion in and through Solids," Cambridge Univ. Press, 1951, p. 97 *et seq.*

<sup>2</sup> Wetzlar, *Z. angew. Mineralog.*, 1938, **1**, 125; Cook and Meakins, *Trans. Faraday Soc.*, 1955, **51**, 1483.

<sup>3</sup> Pickett, *Amer. Mineralog.*, 1949, **34**, 861; Passerini, *Gazzetta*, 1935, **65**, 534.

<sup>4</sup> Rinne, *Neues Jahrbuch Mineralog.*, 1897, **I**, 41; **II**, 28; 1899, **I**, 1; Weigel, *Sitzungsber. Akad. Wiss. München, Math.-Phys. Klasse*, 5 Oct. 1919; Slawson, *Amer. Mineralog.*, 1925, **10**, 305.

<sup>5</sup> Taylor, *Proc. Roy. Soc.*, 1934, **A**, **145**, 80; Bragg, "Structure of Minerals," Cornell Univ. Press, New York, 1937, p. 262.

<sup>6</sup> Hey, *Mineralog. Mag.*, 1935, **24**, 99.

<sup>7</sup> Barrer, *Ann. Reports*, 1944, **41**, 31.

<sup>8</sup> Tiselius and Brohult, *Z. physik. Chem.*, 1934, **A**, **168**, 248.

<sup>9</sup> Kraft, *Z. Physik*, 1938, **110**, 303; Duhm, *Götting. Nach.*, 1936, **2**, 123; Faucher and Thomas, *J. Phys. Chem.*, 1955, **59**, 189.

<sup>10</sup> Barrer and Baynham, *J.*, 1956, (a) 2882, (b) 2892.

<sup>11</sup> Barrer and Langley, preceding papers.

type and radius. Various difficulties are associated with attempts to obtain quantitative heat data by differential thermal analysis, although suggestions have been made from various sources for improving the technique as a quantitative procedure.<sup>12</sup> It is however probable that useful comparative data will follow when a series of structurally very similar phases, all based on one aluminosilicate framework, is the subject of study, and if these phases remain structurally unaltered over the temperature interval required for water loss. These criteria are largely fulfilled by the crystals studied in this research.

## EXPERIMENTAL

*Materials.*—The crystalline zeolites examined were those already described in Parts I and II, *i.e.*, they were cation-exchanged forms of a natural chabazite with an alumina : silica ratio of 1 : 5.05, and of synthetic chabazite-type phases where this ratio is 1 : 4.15 (species G1), 1 : 2.72 (G2), 1 : 2.65 (G3), 1 : 2.56 (G4), and 1 : 2.30 (G5). In addition, Linde molecular sieve 4A kindly supplied by Linde Air Products Co. Ltd. was examined.<sup>13</sup> This sieve is a synthetic zeolite: the composition<sup>14</sup> of the specimen used in this work can be represented as  $\text{Na}_{12}[(\text{AlO}_2)_{12}(\text{SiO}_2)_{12}]\text{NaAlO}_2 \cdot 27\text{H}_2\text{O}$ , the water content being however rather variable.

*Determination of Water Content.*—The crystalline ion-exchanged forms of the chabazite-type phases were all brought into equilibrium with saturated calcium nitrate solution, by leaving

TABLE 1. Weight losses (%) by ignition and by thermogravimetry.

Sample	Ignition	Thermo- gravimetry	Sample	Ignition	Thermo- gravimetry
Li-chabazite .....	20.86	20.44	K-G4 .....	15.66	14.84
Na-chabazite .....	19.06	18.76	Ca-G1 .....	21.14	19.94
K-chabazite .....	15.66	15.16	Ca-G2 .....	23.74	23.15
K-G1 .....	15.91	15.35	Ca-G3 .....	23.16	22.56
K-G2 .....	19.59	19.10	Ca-G4 .....	22.05	21.86
K-G3 .....	16.76	16.01	Ca-chabazite .....	21.11	20.50

TABLE 2.

Sample	Total heat (cal.)	Area under curve (mm. <sup>2</sup> )	cal./10 <sup>3</sup> mm. <sup>2</sup>
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ .....	50.85	13,077	4.112 <sup>a</sup>
$\text{H}_2\text{O(I)}$ .....	32.25	7,732	4.172
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ .....	13.76	3,445	3.996
$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ .....	58.18	14,324	4.061 <sup>b</sup>
Mixture I .....	75.65	18,856	4.012
Mixture II .....	70.18	18,252	3.845

<sup>a</sup> Mean of three determinations. <sup>b</sup> Mean of two determinations.

them in desiccators containing the solution. Water contents were originally determined by ignition in platinum crucibles, over a Meker burner. However, weight losses by such ignition were all slightly, but significantly, greater than those obtained from thermogravimetric curves with temperatures rising to about 1100° (Table 1), probably owing to a small loss of alkali at 1250°; water contents were therefore determined from the thermogravimetric curves (Parts I and II).

*Standardisation of the Apparatus for Differential Thermal Analysis.*—The apparatus for differential thermal analysis was calibrated as follows. Its accuracy for our purpose was first assessed. Several reactions (*A—D*) having known heats were employed for this purpose, also mixed reactions (*A + C*) with known amounts of each reactive component. The water in reaction *D* was dispersed in ignited kaolin powder. The powdered reactants were prepared and packed as described in Part I. The curves for the reactions used in calibration are shown in Fig. 1. The double endothermic peaks indicate a water loss in steps. Areas under these

<sup>12</sup> Wittels, *Amer. Mineralog.*, 1951, **36**, 615, 760; Eyraud, *Technica*, 1954, **177**, 2; Lodding and Sturm, *Amer. Mineralog.*, 1957, **42**, 78; Boersma, *J. Amer. Ceram. Soc.*, 1955, **38**, 281.

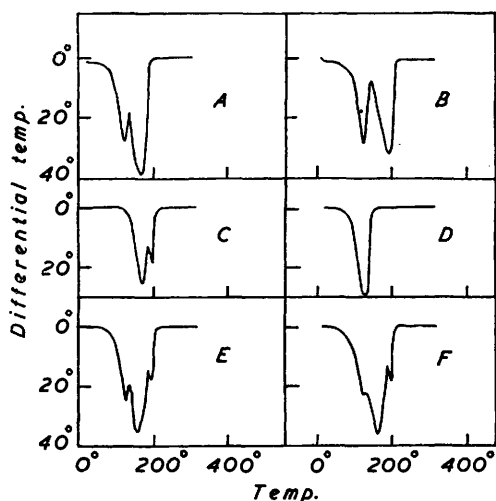
<sup>13</sup> Breck, Eversole, Milton, Reed, and Thomas, *J. Amer. Chem. Soc.*, 1956, **78**, 2338.

<sup>14</sup> Barrer and Meier, unpublished work.

(A) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} \longrightarrow \text{CuSO}_4 \cdot 3\text{H}_2\text{O} + 2\text{H}_2\text{O}(\text{g})$	$\Delta H_{373}$	26.4 <sub>9</sub>	kcal./mole	
$\longrightarrow \text{CuSO}_4 \cdot \text{H}_2\text{O} + 4\text{H}_2\text{O}(\text{g})$	$\Delta H_{388}$	27.3 <sub>4</sub>	"	
$\longrightarrow \text{CuSO}_4 + 5\text{H}_2\text{O}(\text{g})$	$\Delta H_{502}$	17.3 <sub>4</sub>	"	
	overall $\Delta H$	71.1 <sub>7</sub>	"	(ref. 15)
(B) $\text{BaCl}_2 \cdot 2\text{H}_2\text{O} \longrightarrow \text{BaCl}_2 \cdot \text{H}_2\text{O} + \text{H}_2\text{O}(\text{g})$	$\Delta H_{333}$	13.1 <sub>4</sub>	"	
$\longrightarrow \text{BaCl}_2 + 2\text{H}_2\text{O}(\text{g})$	$\Delta H_{425}$	14.8 <sub>9</sub>	"	
	overall $\Delta H$	28.0 <sub>3</sub>	"	(ref. 16)
(C) $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \longrightarrow \alpha\text{-CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O} + 1\frac{1}{2}\text{H}_2\text{O}(\text{g})$	$\Delta H_{401}$	19.52	"	
$\longrightarrow \alpha\text{-CaSO}_4 + 2\text{H}_2\text{O}(\text{g})$	$\Delta H_{436}$	7.31	"	
	overall $\Delta H$	26.8 <sub>3</sub>	"	(ref. 17)
(D) $\text{H}_2\text{O}(\text{l}) \longrightarrow \text{H}_2\text{O}(\text{g})$	$\Delta H_{373}$	9.72	"	(ref. 18)

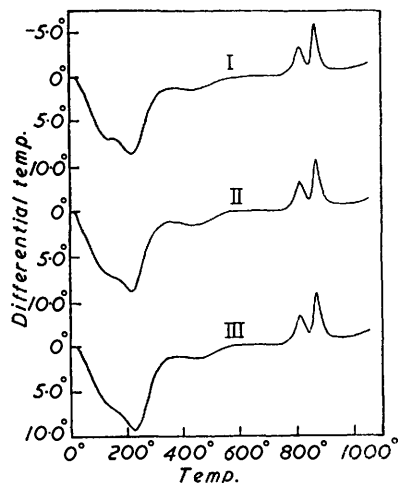
curves were evaluated graphically. If these areas are proportional to the heat of reaction we may hope to find the same constant of proportionality over the group of reactions, and can then extend the method to measure heats associated with water loss from the zeolites. The results, summarised in Table 2, show an average value of 4.06 cal. per  $10^3 \text{ mm.}^2$ , with maximum

FIG. 1. Thermograms for hydrates whose heats of hydration are known.



A,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . B,  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ . C,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ . D,  $\text{H}_2\text{O}$ . E, Mixture I (A + C). F, Mixture II (A + C).

FIG. 2. Thermograms for Linde molecular sieve 4A (Na form).



I, 0.2779 g. ( $\Delta H = 18.5_1$  kcal. per mole of  $\text{H}_2\text{O}$ ).  
 II, 0.2868 g. ( $\Delta H = 18.4_6$  kcal. per mole of  $\text{H}_2\text{O}$ ).  
 III, 0.2861 g. ( $\Delta H = 18.4_6$  kcal. per mole of  $\text{H}_2\text{O}$ ).

deviations of about  $-5.4$  and  $+3.8\%$ . Since the thermal conductivities of the several chemically distinct powders may differ appreciably this result is satisfactory. Probably most of the heat of reaction is removed *via* the gas and the vapour phase, rich in water vapour, and common to all reacting species.

*Reproducibility of Heat Determinations.*—The reproducibility of endotherms and integral heats associated with water loss was next investigated. The curves for differential thermal analysis of three samples of Linde molecular sieve 4A (Na form) are shown in Fig. 2. From the areas of the endotherms and the constant 4.06 cal. per  $10^3 \text{ mm.}^2$  integral heats of 18.5<sub>1</sub>, 18.4<sub>6</sub>, and 18.4<sub>6</sub> kcal./mole of water were obtained. The thermogram for the Ca form (sieve 5A) is shown in Fig. 3, and gives an integral heat of 17.0<sub>0</sub> kcal./mole of water removed. The

<sup>15</sup> International Critical Tables, 1926 Edn., Vol. VII, p. 263 (section on Free Energies).

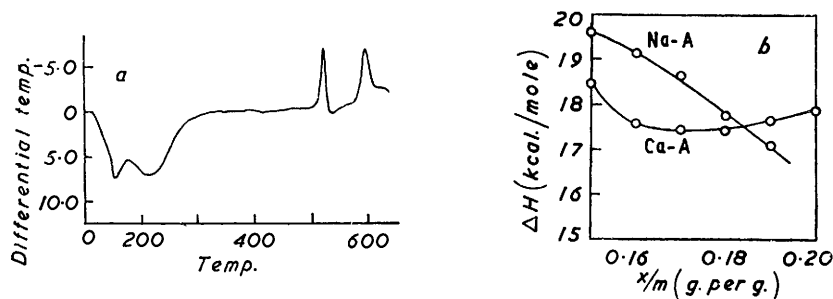
<sup>16</sup> "Selected Values of Chemical Thermodynamic Properties," Nat. Bur. Stand., Washington, 1949, Series I, Vol. I, Table 87—5.

<sup>17</sup> *Op. cit.*, Tables 89—2, 89—3, 89—4.

<sup>18</sup> Ref. 15, p. 232; also Richards and Matthews, *Proc. Amer. Acad. Arts Sci.*, 1911, **46**, 511; Smith, *Phys. Rev.*, 1911, **33**, 173.

figure also reproduces the *differential* heats obtained from sorption data, as a function of amounts sorbed ranging from 0.5 up to 0.62 and 0.67 of saturation, by Breck *et al.*<sup>13</sup> Integral heats between these limits can be found by graphical integrations from this value and are of the same order as our integral heats, although the different ranges in amounts sorbed preclude any close comparison. Still more satisfactory, however, is the agreement between the three integral heats determined from the endotherms of Fig. 2.

FIG. 3. (a) Thermogram for Linde molecular sieve 5A (Ca form) leading to integral heat. (b) Differential heat as a function of amount sorbed (ref. 13).



(a) refers to 0.2875 g.;  $\Delta H = 17.0_0$  kcal. per mole of  $H_2O$ .

*Stability of Phases to Heating and Cooling Cycles.*—Natural chabazite was heated in the cell of the differential thermal analysis apparatus to  $\sim 600^\circ$ , then cooled to room temperature, and equilibrated over saturated calcium nitrate solution. The heating and cooling cycles were repeated. Samples of the Na and the K form of the natural chabazite were taken through three such cycles. The curves were reproducible and X-ray examination showed that the materials remained unaltered, so that these natural chabazite phases show considerable stability

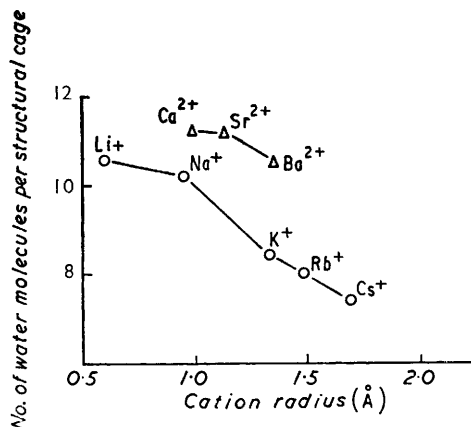


FIG. 4. Variation of water content of natural chabazite enriched in different cations, with cation radius.

under conditions obtaining during dehydration in the cell. X-Ray results reported in Part II show that the aluminous chabazite-type phases are sometimes less stable than the siliceous forms.

*Water Content and Cation Type and Density.*—Some equilibrium water contents at a relative humidity of  $\sim 0.51$  are given in Table 3. The chabazite structure contains large cavities, each able to hold a cluster of water molecules.<sup>19,20</sup> The Table shows the average number of water molecules per cage. The cluster size (in terms of number of molecules at  $p/p_0 \sim 0.51$ ) decreases as the cation size increases, although with several irregularities, and also as cation valency decreases. The effect of cation size could indicate that larger cations occupy a significant fraction of the volume of the cages. However, cation size is clearly not the only factor involved

<sup>19</sup> Wyart, *Bull. Soc. franç. Mineralog.*, 1933, **56**, 106.

<sup>20</sup> Dent and Smith, *Nature*, 1958, **181**, 1794.

because, as the number of Ca and Li cations per cage increases, so also does the number of water molecules per cage. These two cationic forms of the zeolite contain the ions most likely to bind water energetically, and evidently the more of these ions in the cages the greater the water retentivity at  $p/p_0 \sim 0.51$ .

TABLE 3. Water molecules per structural cage at  $p/p_0 \sim 0.51$ .

$\text{Al}_2\text{O}_3 : \text{SiO}_2$ ratio	Univalent cations per cage <sup>10</sup>	Ca form	Li form	Na form	K form
1 : 5.05	3.44	11.24	10.56	10.20	8.44
1 : 4.15	4.02	11.02	9.40	10.58	8.80
1 : 2.72	4.84	13.54	11.44	10.94	11.82
1 : 2.65	5.10	13.22	11.36	10.48	9.68
1 : 2.56	5.84	12.96	12.02	11.36	9.18
1 : 2.30	5.14	13.48	12.12	9.78	9.54

For the natural chabazite having an  $\text{Al}_2\text{O}_3 : \text{SiO}_2$  ratio of 1 : 5.05 a more extensive series of cation forms was investigated. A correlation then appeared between water retentivity at  $p/p_0 \sim 0.51$  and cation radius, as indicated in Fig. 4. In this Figure the results for Ca, Sr, and Ba forms fall on an upper curve and those for the univalent ions Li, Na, K, Rb, and Cs on another. Reference to Table 1, Part I, shows that in all cationic forms exchange was virtually complete save in the following instances: Sr (79% exchange); Ba (90%); Cs (89.7%). In the first two of the preceding three ion-exchanged chabazites the residual ion was  $\text{Na}^+$ ; in the third it was  $\text{Ca}^{2+}$ .

From Table 3 we may calculate, per Avogadro number of cubo-octahedral cages in chabazite, the total volume of cations plus water molecules contained in them at a relative pressure of  $\sim 0.51$ . To the nearest whole number we then have, assuming a molecular volume of 18  $\text{cm}^3$  for water: Ca form 208; Li form 194; Na form 192; K form 172; Rb form 172; Cs form 168  $\text{cm}^3$ . This volume varies with cation size more than could reasonably be attributed to deviations of the molecular volume of intracrystalline water from its normal value. Thus, the cages in the Ca form are probably nearly saturated, at  $p/p_0 \sim 0.51$ , but this is not true of the other forms. These results show the different intrinsic water retentivities of the various cation forms.

The intracrystalline environment of the cations necessarily restricts the extent of cation solvation. Nevertheless there is a general correlation between the numbers of water molecules per cation in natural chabazites and primary hydration numbers of the same cations in aqueous solution,<sup>21</sup> as shown in Table 4. Because of the restricted environment of the intracrystalline cations we should also expect to find fewer water molecules per cation as the number of cations increases, so that the aluminous chabazite-type crystals should contain less highly hydrated cations. Despite certain irregularities this is confirmed by the data in Table 5.

TABLE 4.

	$\text{Ca}^{2+}$	$\text{Li}^+$	$\text{Na}^+$	$\text{K}^+$	$\text{Rb}^+$	$\text{Cs}^+$
$\text{H}_2\text{O}$ mols. per cation in natural chabazite ...	6.5	3.1	3.0	2.5	2.3	2.0*
Primary hydration nos. of cations .....	6-8	6	5	3	2	—

\* Calc. for the homoionic Cs form.

TABLE 5.

$\text{Al}_2\text{O}_3 : \text{SiO}_2$ ratios in crystals	Water mols. per cation			
	Ca form	Li form	Na form	K form
1 : 5.05	6.5	3.1	3.0	2.5
1 : 4.15	5.5	2.3	2.6	2.2
1 : 2.72	5.6	2.4	2.3	2.4
1 : 2.65	5.2	2.2	2.1	1.9
1 : 2.56	4.4	2.1	1.9	1.6
1 : 2.30	5.2	2.4	1.9	1.9

*Heats Associated with Water Loss in Natural Chabazites.*—We may assume, from the results in Table 2 and from the reproducibility of the endotherms for Linde molecular sieve 4A, that the areas of the endotherms for the various chabazite-type phases are proportional to the resultant of the heat terms for all processes occurring during removal of water from the crystals.

<sup>21</sup> Bockris and Conway, "Modern Aspects of Electrochemistry," Butterworths, London, Chapter 2.

We may also assume that the constant of proportionality obtained from the reactions of Table 2 (4.06 cal. per  $10^3$  mm.<sup>2</sup>) is nearly the same for all the water desorption reactions, especially since the phases studied are based on the same structure. The resultant heats associated with water will be integral heats, and will be mean values over a considerable temperature interval, weighted towards the temperatures of maximum rate of water loss.

In Parts I and II the differential thermal analysis endotherms and corresponding thermogravimetric curves were presented for typical instances and discussed qualitatively. From the endotherms the areas enclosed with the base-line were evaluated and heats associated with water loss derived. These heats can be considered in different ways, of interest from different points of view. The results are given in Table 6. In the Cs-, Sr-, and Ba-rich form there were other cations present in smaller amount; and estimates, of which the following is typical, were made of heats for the homoionic forms.

The Sr-rich form is 79% exchanged and there is the equivalent of 3.44 univalent cations per cage, with 11.18 water molecules. The heat associated with water loss from a structural cavity was found from the endotherm of Part I to be 171.8 kcal./Avogadro no. of cavities. In the 79% Sr-form there are 1.36  $\text{Sr}^{2+}$  and 0.72  $\text{Na}^+$  ion per cavity. In a homoionic Na form there are 3.0 water molecules per ion. As an approximation therefore we assume that there are  $10.2 \times 0.72/3.44 = 2.14$  water molecules associated with  $\text{Na}^+$  in the heteroionic crystal. The removal of these 2.14 molecules requires 30.6 kcal., so that 141.2 kcal. were involved in the loss of the remaining 9.04 water molecules, associated with 1.36  $\text{Sr}^{2+}$  ions. This gives 15.6 kcal. per mole of water, a ratio of 6.6 molecules of water per  $\text{Sr}^{2+}$  ion, and the other heats of Table 6 for the homoionic Sr-form. Similar calculations gave for the homoionic Cs and Ba forms 2.0 and 6.1 water molecules per cation, and the heats of Table 6.

The thermogravimetric data (Part I) for Ca, Sr, and Ba forms of chabazite indicate that water losses are 99.1% and 99.6% complete respectively, at temperatures approaching 800°. The endotherms of the Li and the Ba form are complex and rather similar, and probably indicate that water loss is associated with other changes, such as re-arrangement of cations (Part I). Perturbations of the crystal of this type could modify heat changes associated with water loss, as may also minor alterations of the aluminosilicate framework. One therefore refers to heats associated with water loss rather than to heats of dehydration.

Despite possible thermal effects of crystal perturbations during water loss it is of interest to compare overall heats associated with water loss and heats of solvation of anhydrous ions by water in bulk (columns 3 and 5 of Table 6). The intracrystalline environment of the cations restricts their solvation (Table 4), but also they are probably partially shielded by the negative charge mosaic of the aluminosilicates. On both counts heats associated with water removal per g.-ion are reduced more than ion solvation in bulk water. Indeed, since a substantial part

TABLE 6.

Cationic form	Heat			Heat of solvation of cation <sup>22</sup> (kcal./g.-ion)
	kcal./mole of $\text{H}_2\text{O}$	kcal./g.-ion	kcal./A. no. of cavities	
Li .....	12.7	39.0	134	136
Na .....	14.3	42.4	146	114
K .....	14.9	36.6	126	94
Rb .....	13.3	30.8	106	87
Cs(0.897)Ca(0.103) .....	13.7 *	27.4 *	94.5 *	80
Ca .....	20.3	134.2	230	410
Sr(0.79)Na(0.21) .....	15.6 *	103.8 *	178 *	376
	16.0 *†	108.3 *†	186 *†	—
Ba(0.90)Na(0.10) .....	22.3 *	135.6 *	233 *	346
	20.9 *‡	129.3 *‡	222 *‡	—

\* Calc. for homoionic Cs, Sr, and Ba forms. † For first 98.19% of water loss, reached at 700°.

‡ For first 94.72% of water loss, reached at 550°.

of the heat associated with water loss may arise from interaction of water molecules with the anionic framework, cation-water dipole interactions within the crystal are probably small compared with ion-water molecule interactions in bulk water.

The heats associated with dehydration of a cavity (column 4, Table 6) are of particular interest because they approximate to heats required to vaporise the cluster of water molecules

<sup>22</sup> Bernal and Fowler, *J. Chem. Phys.*, 1933, **1**, 515.

in the cavity. These clusters (cf. Table 3) range in size from 13.54 molecules for one of the Ca forms to 6.8 molecules estimated for the homoionic Cs form. In column 2 of Table 6 are given heats associated with water loss per mole of water removed. Heats for the Na, K, Rb, and Ca forms are particularly interesting because for these phases there is no evidence of important lattice perturbation during water loss, and no assumption is involved in calculation, these forms being homoionic.

TABLE 7. Heats associated with water loss ( $\Delta H_1 = \text{kcal. per mole of H}_2\text{O}$ ;  
 $\Delta H_2 = \text{kcal./g.-ion}$ ).

Al <sub>2</sub> O <sub>3</sub> : SiO <sub>2</sub> ratio	$\Delta H_1$				$\Delta H_2$			
	Li form	Na form	K form	Ca form	Li form	Na form	K form	Ca form
1 : 5.05	12.7	14.3	14.9	20.3	39.0	42.4	36.6	134.2
1 : 4.15	21.7	21.5	17.9	18.0	52.6	56.7	39.1	98.5
1 : 2.72	23.3	24.3	17.6	22.1	55.0	54.8	43.0	123.4
1 : 2.65	19.0	16.6	16.0	22.0	42.3	35.0	30.4	114.2
1 : 2.56	24.2	21.6	14.7	23.9	49.7	42.0	23.1	106.1
1 : 2.30	25.9	21.2	—	21.7	61.0	40.3	—	114.0

*Heats Associated with Water Loss in Relation to Al<sub>2</sub>O<sub>3</sub> : SiO<sub>2</sub> Ratios.*—The more aluminous a chabazite-type phase the greater the density of negative charges on the aluminosilicate framework and of the cations needed for electrical neutrality. This could modify the binding energy of intracrystalline water. Heats for Li, Na, K, and Ca forms of a series of chabazite-type phases of varying Al<sub>2</sub>O<sub>3</sub> : SiO<sub>2</sub> ratios are shown in Table 7. For the synthetic phases rich in Li, Na, and Ca nearly all the heats  $\Delta H_1$  have higher values than for the corresponding forms in the natural chabazite having Al<sub>2</sub>O<sub>3</sub> : SiO<sub>2</sub> = 1 : 5.05. The heats for the K forms show some increases, but with a different trend. Higher heats may be due to the greater charge density in the more aluminous phases, but there are modifying factors, which may be related to lattice perturbations in some of the phases during water loss.

The heats  $\Delta H_2$  show other trends.  $\Delta H_1$  depends mainly upon the energy of bonding of water in the structure, but  $\Delta H_2$  depends on this energy and on the number of water molecules per cation. As the cation density increases the amount of water per cation, despite some irregularities, shows a tendency to decrease (Table 5).  $\Delta H_2$  is largest for the Ca-rich phases, and least for the K forms, as would be expected from considerations of ion valency and size, if electrostatic forces were important in binding the water. However, evidence has been presented above that ion-dipole energies are much reduced within the crystal, and indeed values of  $\Delta H_1$  for Ca are often not very different from those for other cationic forms (Table 7).

#### DISCUSSION

It is of particular interest to compare the binding energy of water molecules in liquid water with that of water molecules in clusters within the chabazite. To do this we must estimate the energy required to remove a group of water molecules from the liquid equal to the group of water molecules per cavity in the zeolite, without the collapse of the cavity in liquid water. We may estimate this energy as follows. The latent heat of vaporisation of water at 100° is 9.7<sub>2</sub> kcal./mole.<sup>18</sup> At this temperature the co-ordination number will be assumed to be either 6 or 8. The removal of the first water molecule (leaving a cavity equal in volume to the molecule) requires an energy of 19.44 kcal., and breaks either 6 or 8 bonds according to the co-ordination number. If the co-ordination number is 6, the next six water molecules removed each break 5 bonds and so may be considered to require 16.2 kcal./mole while the next 12 molecules removed each break 4 bonds and require 13 kcal./mole. If the co-ordination number is 8, the next eight molecules removed each break 7 bonds, requiring 17.0 kcal./mole, and the following 8 break 4 bonds each, for an energy of 9.7<sub>2</sub> kcal./mole. Thus, as the cluster removed increases in size the heat per mole of water falls from 19.44 towards lower values, eventually for large enough clusters approaching 9.72 kcal./mole.

For the actual cluster sizes found in the cages of the Ca, Li, Na, and K forms of the natural chabazites and in the synthetic more aluminous phases, the energies per mole of water needed to remove clusters of equal size from liquid water range from 16 to 15 kcal. (co-ordination number 6) or 17.3 to 15.5 kcal. (co-ordination number 8). While this

estimate and comparison are not rigorous, it is seen that the binding energy of water in the cages in chabazite for the K forms (Table 7) is not very different from that in liquid water. That in the Ca, Li, and Na forms is usually greater, by differing amounts—up to ~50% in the extreme instance (Li-G5). Ion-dipole interaction terms may contribute significantly here, although this interaction is evidently not the major part of the total energy of interaction, which must include dispersion, dipole-dipole, and dipole-induced dipole contributions. The oxygen framework of the zeolite may well simulate the oxygen structure of the liquid water, so that the method of comparison developed above may be reasonably adequate.

Factors associated with apparatus and technique which operate to reduce the accuracy of differential thermal analysis as a quantitative method are, on the evidence of Table 2 and Fig. 2, not dominant in the conditions existing in this work. Other physicochemical factors associated with the experimental materials are likely to contribute to some irregularities in sequences of heat values and of hydration: (1) Complete chemical analyses of the Li, Na, and Ca forms of the synthetic phases were not available; although the conditions of exchange were those known to effect very extensive exchange,<sup>10</sup> there could be a little potassium in some of these forms. (2) The phases are not all equally stable under the conditions of differential thermal analysis, and there is evidence from the thermograms of lattice perturbation in the range associated with water loss for some but not all the phases (Parts I and II). (3) The synthetic phases, although produced in good yield,<sup>10</sup> are not necessarily 100% pure.

The results in Table 7 in particular must be considered in the light of the above factors. Nevertheless it is thought that this paper gives a perspective of the influence of cation type and of varying number of cations per unit cell on water retentively and energy of bonding in chabazite-type phases. There are small differences in the water contents of the crystals as given in Table 3 and those in Table 3 of ref. 10*b*. This arises because the phases in the earlier work were not in contact with a solution of fixed relative pressure before water determination, but were equilibrated with the atmosphere under necessarily more variable conditions.

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