201. *Hydrothermal Chemistry of the Silicates. Part IX.** *Nitrogenous Aluminosilicates.*

By R. M. Barrer and P. J. Denny.

By hydrothermal reaction, a number of crystalline ammonium and alkylammonium aluminosilicates have been synthesised. These are often of types analogous to alkali metal aluminosilicates and include ammonium analcites, harmotomes and micas. From methylammonium aluminosilicate gels, nitrogenous micas, montmorillonoid clays, harmotomes, sodalites, faujasites and Linde molecular sieve A were prepared. Under hydrothermal conditions methylammonium ions hydrolysed in part; but in appropriate methanol–water mixtures methylation of the ammonium base occurred. Hydrolysis and methylation of the organic base were found to play a part in determining the nitrogenous aluminosilicates produced. The ease of crystallisation tended, in the reaction mixtures used, to be correlated with the dissociation constants of the organic bases present. The crystals produced have been characterised in various ways.

Other phases identified included cristobalite, corundum, boehmite, and bayerite. Some mullite appeared when ammonium mica and certain of the methylammonium montmorillonites were sintered.

SEVERAL studies [1-4] from these laboratories have been particularly concerned with the crystallisation fields under hydrothermal conditions of lithium, sodium, potassium, rubidium, cæsium and thallium aluminosilicates, and with the properties and structures of the crystals produced. A limited study has also been made of the formation of germanium and gallium analogues of sodium aluminosilicates.[5] In the present paper we report conditions for synthesis of nitrogenous crystalline aluminosilicates in which there are no metal cations, but only ammonium or methylammonium ions. The literature contains little reference to such a possibility, although Merrill and Spencer [6] reported the formation of quaternary ammonium silicates such as $(NMe_4)HSiO_3,5H_2O$.

EXPERIMENTAL

Methylammonium hydroxides were employed as appropriately concentrated aqueous solutions. Mono-, di-, tri-, or tetra-methylammonium, or ammonium, hydroxide was stirred

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* Part VIII, *J.*, 1959, 195.

[1] Barrer, *Trans. Brit. Ceram. Soc.*, 1957, **56**, 155.

[2] *E.g.*, Barrer and Langley, *J.*, 1958, 3804, 3811, 3817.

[3] Barrer, Bultitude, and Kerr, *J.*, 1959, 1521.

[4] Barrer and Kerr, *Trans. Faraday Soc.*, 1959, **55**, 1915.

[5] Barrer, Baynham, Bultitude, and Meier, *J.*, 1959, 195.

[6] Merrill and Spencer, *J. Phys. Colloid Chem.*, 1951, **55**, 187.

in the correct proportions with freshly prepared amorphous alumina gel into " Syton " silica sols. In this way hydrous ammonium or alkylammonium aluminosilicate gels were produced of compositions $3(\mathrm{NMe}_x\mathrm{H}_{4-x}\mathrm{OH}),\mathrm{Al}_2\mathrm{O}_3,n\mathrm{SiO}_2 + \mathrm{aq.}$, where $1 < n < 9$ and $x = 0$—4. A number of these gels were relatively stiff, and often after hydrothermal treatment, especially at lower temperatures, the filtrates contained colloidal material amorphous to *X*-rays. The base was provided in excess of the 1 : 1 ratio between it and alumina to maintain the pH and so to promote dissolution and recrystallisation of solids.

The aqueous gels were heated in stainless steel autoclaves of about 16 c.c. capacity. After reaction the autoclaves were chilled rapidly, and the solids filtered off, washed, and dried. The solids were then examined optically, in the electron microscope, by electron diffraction, and by *X*-ray diffraction, as necessary. By these means they were normally identified according to the structures of the aluminosilicate frameworks. In some instances the crystals were further characterised by thermogravimetry and by differential thermal analysis. Some details of the equipment and procedures used in this examination have been briefly described in earlier papers.[2]

RESULTS

Crystallisation of Ammonium Aluminosilicates.—The species identified are given in Table 1. There were three nitrogenous aluminosilicates, based on the three-dimensional network zeolites analcite and harmotome, and on the layer-lattice of mica, severally. These minerals were formed in highly alkaline conditions, since the pH's of the cold mother-liquors after reaction were > 10·5 in all cases. The crystallisation of ammonium harmotome was poor, so that its *X*-ray pattern was not suitable for its full identification; however, the few lines obtained showed correspondence with this zeolite. Although the material termed NH_4-H (see Table 1) is similar to cristobalite, some weak *X*-ray diffractions were also present which indicated a further, unidentified species. *d*-Spacings of this species and of NH_4-H are given in Table 2. The crystallisation conditions are summarised in Table 3 and emphasise the dominance of the micaceous crystals throughout the crystallisation field.

TABLE 1. *Crystalline phases in the ammonium aluminosilicate field.*

Symbol	Identification	Yields	Symbol	Identification	Yields
NH_4-A	Boehmite	Fair	NH_4-H	Cristobalite	Fair
NH_4-B	Corundum	Poor	NH_4-K	Mica	V. good
NH_4-D	Cubic NH_4-analcite	Fair to poor	NH_4-L	Harmotome	V. poor

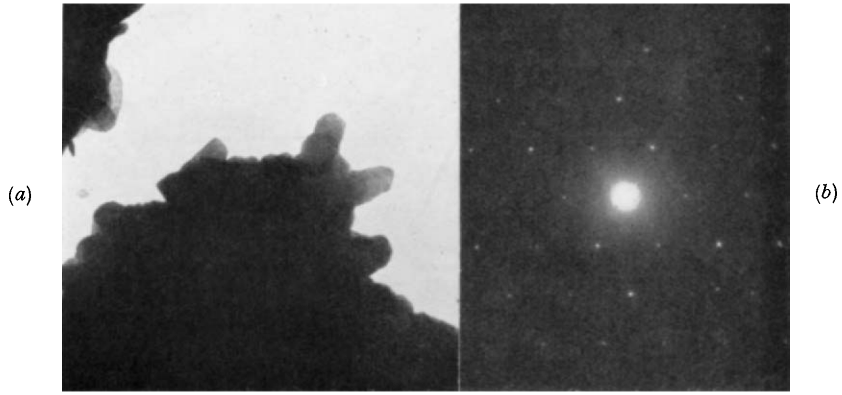
TABLE 2. d-*Spacings* (*in* Å) *of some ammonium aluminosilicates.*

NH_4-D (analcite)				NH_4-H (cristobalite)		Unidentified phase occurring with NH_4-H	
d	*I*	*d*	*I*	*d*	*I*	*d*	*I*
5·54	s	$2{\cdot}40_7$	vw	$4{\cdot}02_5$	vs	4·24	w
4·81	mw	$2{\cdot}20_1$	w	$3{\cdot}12_6$	m	$3{\cdot}73_8$	vw
3·63	vw	$1{\cdot}88_3$	w	$2{\cdot}83_7$	ms	$3{\cdot}51_8$	vw
$3{\cdot}39_3$	vs	$1{\cdot}72_3$	m	$2{\cdot}11_1$	mw	$3{\cdot}23_7$	vw
$3{\cdot}02_8$	vw	$1{\cdot}60_6$	m	$2{\cdot}01_3$	w	$3{\cdot}19_1$	vw
$2{\cdot}89_5$	ms	$1{\cdot}57_9$	w	$1{\cdot}92_7$	mw	$1{\cdot}34_4$	w
$2{\cdot}66_5$	vw	$1{\cdot}43_0$	w	$1{\cdot}86_6$	mw	$1{\cdot}33_1$	vw
$2{\cdot}49_6$	mw			$1{\cdot}53_1$	w		

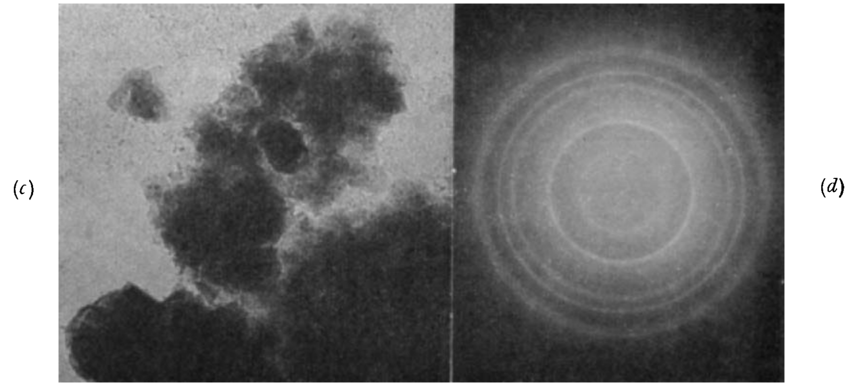
NH_4-D. This species was a cubic variety of analcite having a unit cell edge 13·57 Å. It appeared at 450° c at times between 7 and 11 days. The *d*-spacings are recorded in Table 2.

NH_4-K. The micaceous species, NH_4-K, resembles the illites about as closely as the muscovites. The *d*-spacings are compared with those of illite and of muscovite in Table 4. The monoclinic unit cell dimensions were: $a = 5{\cdot}22$; $b = 9{\cdot}02$; $c = 20{\cdot}02$ Å; $\beta = 95° \; 27'$. It was obtained in 100% yield, the best conditions being at 450° for $n = 2$. Differential thermal analysis curves are shown in Fig. 1*a* and *b*, and the corresponding thermogravimetric curve in Fig. 2*a*. Up to about 300° the weight loss is 1·3%, being endothermic. The material lost

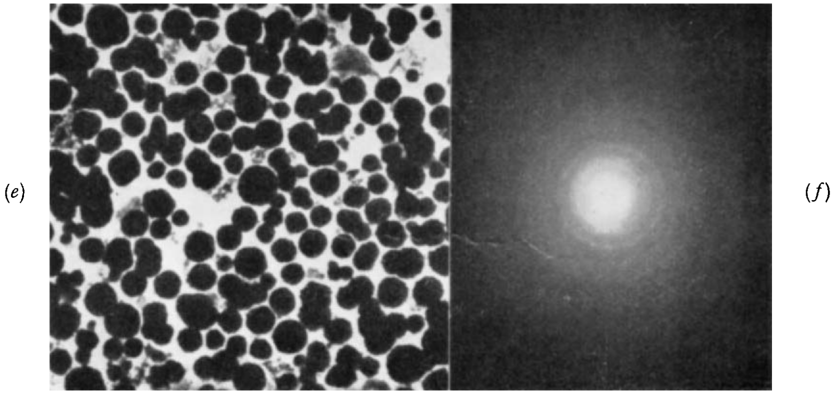
PLATE 1.



a and b, Photomicrograph and electron diffraction pattern of ammonium mica.

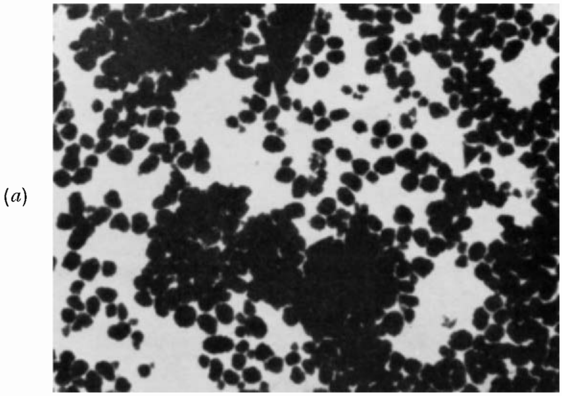


c and d, Photomicrograph and electron-diffraction pattern of nitrogenous montmorillonite.

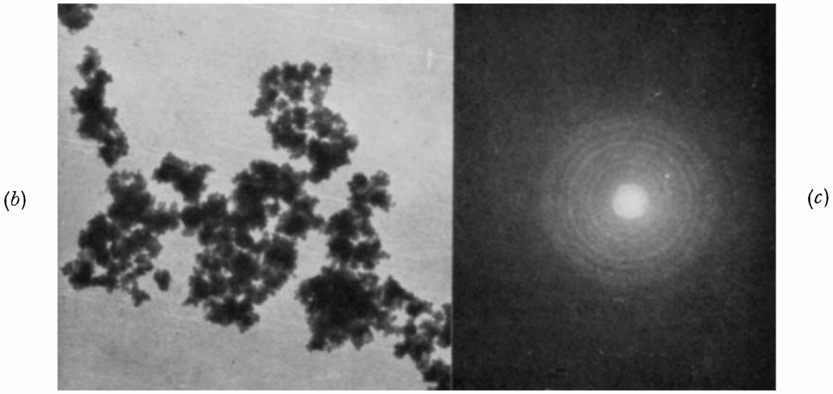


e and f, Photomicrograph and electron-diffraction pattern of nitrogenous hermotome.

PLATE 2.



a, Photomicrograph of nitrogenous Linde molecular sieve A.



b and c, Photomicrograph and electron-diffraction pattern of nitrogenous faujasite.

TABLE 3. *Crystallisation conditions for gels* $3NH_4OH,Al_2O_3,nSiO_2$ + aq., *and yields.*

n	200° 6 days	250° 4 days	271° 6 days	300° 3 days	350° 2 days	400° 2 days	450° 2 days	450° 7 days	450° 11 days
1	U *	Poor A Poor K	Fair A Fair K	Fair A Fair K	Fair A Fair K	Fair A Fair K	Good K Poor B	—	—
2	U	Poor K	Good K	Good K	V. good K	V. good K	V. good K	Good K	Good K
3	U	U	Fair K	Fair K	Good K	Good K	Good K	—	—
4	U	U	V. poor K	Fair K	Good K	Good K	Good K	Good K	Good K Fair H Poor D
5	U	U	V. poor L	V. poor K	Poor K	Fair K	Fair K	—	—
6	U	U	V. poor L	V. poor L	V. poor K	Poor K	Fair K	—	Fair K Fair H Fair D
7	U	U	U	U	U	V. poor K	Fair K	—	—
8	U	U	U	U	U	V. poor K	Poor K	—	—
9	U	U	U	U	U	U	V. poor K	—	—

* U denotes non-crystalline. The terms " poor," " fair," and " good " in this and similar Tables refer to the yields of the crystals. Yields were estimated visually, and from the intensities of the *X*-ray diffraction patterns. For A, B, D, H, K, L see Table 1.

below 300° is considered to be water. The main weight loss is associated with a strong endothermic peak, while at ~980° a sharp exothermal reaction occurs which yields mullite. The total weight loss at temperatures approaching 1000° corresponds with the formula

$$\tfrac{1}{3}(NH_4)_2O,Al_2O_3,2SiO_2,\tfrac{2}{3}H_2O(\text{structural}),0{\cdot}17H_2O(\text{surface})$$

A microanalysis showed that a specimen of NH_4-K, crystallised at 300°, contained 5·15% of nitrogen, compared with a theoretical value of 6·04% for the above formula.

TABLE 4. d-*Spacings of species* NH_4-K, *and of muscovite and illite.*

	d-Spacing (Å) and intensity					
hkl	Muscovite [7]		NH_4-K		Illite [7]	
002	9·99	s	10·37	s	9·98	s
004	4·98	m	5·17	m	4·97	w
110	4·47	vs	4·50	vs	4·47	s
111	4·29	w	4·36	m	—	—
022	4·11	w	—	—	4·11	vw
112	3·95	vw	—	—	—	—
$11\bar{3}$	3·87	m(B)	—	—	—	—
023	3·72	m	3·70	ms	3·7	vw
113	3·55	vw	—	—	—	—
$11\bar{4}$	3·48	m	3·45	m(B)	3·4	vw
006	3·32	vs	—	—	3·31	m
114	3·20	ms	—	—	3·2	vw
$11\bar{5}$	3·1	vw	3·12	m	—	—
025	2·98	s	—	—	2·98	w
115	2·86	m	—	—	2·84	vw
$11\bar{6}$	2·78	m	2·74	vw	—	—
200	$2{\cdot}58_5$	w	—	—	—	—
$20\bar{2}$	$2{\cdot}56_0$	vs	2·56	s(B)	2·56	s
008	2·49	w	$2{\cdot}49_5$	vw	—	—
133	2·46	w	$2{\cdot}45_6$	w	2·44	w
$20\bar{4}$	$2{\cdot}39_0$	m	$2{\cdot}41_2$	w	—	—
$13\bar{3}$	$2{\cdot}37_6$	m	—	—	2·38	m
221	$2{\cdot}24_5$	w	$2{\cdot}25_6$	vw	2·24	m
$22\bar{3}$	$2{\cdot}18_5$	w	$2{\cdot}18_0$	vw	2·18	w
$20\bar{6}$	2·14	m(D)	—	—	—	—
043	2·13	m(D)	—	—	2·11	w
223	2·05	vw	—	—	—	—
0010	$1{\cdot}99_1$	s	$1{\cdot}98_6$	vw	1·98	m
206	1·95	w	—	—	—	—
$04\bar{6}$	1·83	vw	$1{\cdot}85_5$	vw	—	—
138	1·76	w	—	—	—	—
$13\overline{10}$	$1{\cdot}65_4$	w	$1{\cdot}69_7$	w	1·65	w
312	1·64	m	—	—	1·64	m
313	1·60	w	—	—	—	—
314	1·55	w	—	—	—	—
1310	1·52	w	—	—	—	—
060	$1{\cdot}50_4$	s	$1{\cdot}50_2$	ms	1·50	s
335	$1{\cdot}34_4$	m	$1{\cdot}37_2$	vw	1·34	vw
—	$1{\cdot}33_5$	w	—	—	—	—
400	1·295	w(B)	$1{\cdot}29_8$	vw	1·29	m
0016	1·245	w(B)	$1{\cdot}24_9$	vw	1·24	w

When material NH_4-K was crystallised at 250° from a gel containing originally only NH_3Me^+ ions (Tables 5 and 6) the thermogram, shown in Fig. 1*b*, is very similar to that of NH_4-K in Fig. 1*a*. There is no exothermal peak such as characterises the pyrolysis of organic ions (Figs. 1*c* and *d*), so that at 250° hydrolysis of monomethylammonium ions must be extensive.

From crystallisations of NH_4-K at 300°, electron diffraction gave only ring patterns, but single-crystal patterns could be obtained from a product grown at 400°. Plates 1*a* and *b* show a typical electron-micrograph and electron-diffraction photograph of the micaceous

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[7] Cf. Grim, Bradley, and Brown, " X-ray Identification and Structure of Clay Minerals," Min. Soc., G.B., 1951, Chap. V.

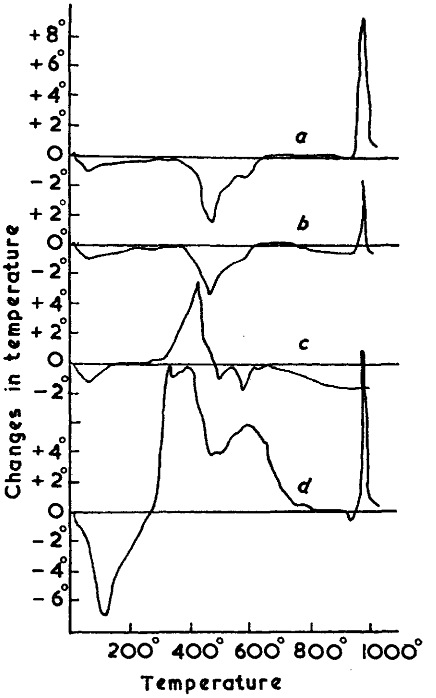
crystals. The *X*-ray powder diffraction photograph suggested that NH_4-K is dioctahedral. Thus the 060 line is close to 1·50 Å, and the 002 line is strong.

Crystallisations involving Methylammonium Bases.—The bases introduced into the gels were $NMeH_3{\cdot}OH$, $NMe_2H_2{\cdot}OH$, $NMe_3H{\cdot}OH$, and $NMe_4{\cdot}OH$. It became apparent that under hydrothermal conditions the substituted bases tend to be hydrolysed:

$$Me_xNH^+_{4-x} + H_2O \rightleftharpoons Me_{x-1}NH^+_{5-x} + MeOH \quad . \quad . \quad . \quad . \quad . \quad (1)$$

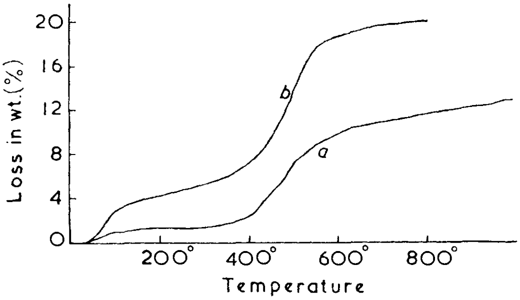
The higher the temperature the more rapidly such a hydrolysis can occur, and a series of alkylammonium ions and also NH_4^+ may result in solution. Accordingly the dominant cation in the crystalline products is in doubt and is represented by the symbol N in the following account. Nevertheless the products obtained depended upon the base used.

FIG. 1. *Thermograms of ammonium micas (curves a and b) and of methylammonium montmorillonites (curves c and d).*



a: $3NH_4{\cdot}OH,Al_2O_3,2SiO_2$ + aq. *at* 300° *for* 3 *days.*
b: $3NMeH_3{\cdot}OH,Al_2O_3,2SiO_2$ + aq. *at* 250° *for* 4 *days.*
c: $3NH_4{\cdot}OH,Al_2O_3,2SiO_2$ + aq. + 13% *of* MeOH *at* 300° *for* 4 *days.*
d: $3NMe_4{\cdot}OH,Al_2O_3,2SiO_2$ + aq. *at* 300° *for* 5 *days.*

FIG. 2. *Thermogravimetric curves of ammonium mica (curve a) and of dimethylammonium harmotome (curve b).*



The dominant species were montmorillonoid clays and mica-like crystals. A notable feature of this behaviour was the relatively low temperature of formation of these layer-lattice compounds. In addition to the layer-lattice crystals, however, it was possible to grow three-dimensional network zeolites and a felspathoid. The species obtained are summarised in Table 5. The pH's of the cold mother-liquors after reaction were all >10·5. Crystallisations proceeded fairly easily, excellent yields of some species being obtained. In all systems the ease of crystallisation decreased as the proportion of silica to base and alumina became large. The phase N-L is analogous to the Na-Pl of ref. 5, which was a cubic harmotome. This zeolite could be prepared by appropriate crystallisation of aluminosilicate gels containing initially all of the four methylammonium bases. Species N-Q and N-R are analogues of Na-Q and Na-R of ref. 5, and thus are nitrogenous varieties of Linde sieve A and Linde sieve X respectively.

The crystallisation fields of the various species in Table 5 are indicated in Figs. 3—6. The variety of the phases grown from gels containing tetramethylammonium hydroxide makes it expedient for reasons of clarity to give Fig. 6 in two parts. The conditions of growth and associated crystal yields are summarised in Tables 6 and 7. Of the layer lattice species it is seen that from ammonium, monomethylammonium, and dimethylammonium gels a mica-like phase is produced, whereas trimethyl- and tetramethyl-ammonium gels give montmorillonite-type clays.

TABLE 5. *Crystalline phases formed from alkylammonium aluminosilicate gels.*

Base in cold parent gel	Products		Maximum yield	Base in cold parent gel	Products		Maximum yield
	Symbol	Identity			Symbol	Identity	
$NMeH_3$·OH	N-C	Bayerite	Poor	NMe_4·OH	N-A	Boehmite	Poor
	N-K	Mica	Good (100%)		N-C	Bayerite	Fair
	N-L	Harmotome	Fair		N-T	Sodalite	Poor
NMe_2H_2·OH	N-A	Boehmite	Poor		N-V	Montmorillonite	Good (100%)
	N-C	Bayerite	Poor		N-L	Harmotome	Fair
	N-K	Mica	Good (100%)		N-Q	Zeolite, like Linde sieve A	Small yield, but obtained pure
	N-L	Harmotome	Good (100%)		N-R	Zeolite, analogue of faujasite	Small yield, but obtained pure
NMe_3H·OH	N-A	Boehmite	Poor				
	N-T	Sodalite	Fair				
	N-V	Montmorillonite	Fair to Good				
	N-L	Harmotome	Fair				

TABLE 6. *Crystallisation conditions of, and yields from, aqueous methylammonium aluminosilicate gels.*

(*a*) *Gels* $3NMeH_3$·OH,Al_2O_3,$n$$SiO_2$.

n	125°, 5 days 175°, 6 days 200°, 6 days	225°, 5 days	250°, 4 days	300°, 4 days
1	Poor C	Fair K Poor L	Fair K	Good K
2	U	Fair K Fair L	Good K V. poor L	Good K
3	U	U	Poor K	Poor K Good L
4	U	U	Poor K	Poor K Good L
5	U	U	V. poor K	V. poor K Poor L
6 to 9	U	U	U	U

(*b*) *Gels* $3NMe_2H_2$·OH,Al_2O_3,$n$$SiO_2$.

n	150°, 9 days	175°, 8 days	200°, 6 days	250°, 4 days	300°, 3 days
1	U	Fair L Poor C	Good L Poor A	Good K	Good K Poor A
2	U	Fair L V. poor C	Good L	Good K V. poor L	Good K Poor L
3	U	Poor L	Good L	Poor K Fair L	Fair K Fair L
4	U	Fair L	Good L	Poor K Fair L	Good L Poor K
5	U	Fair L	Good L	—	Good L Poor K
6	U	Poor L	Good L	U	Good L Poor K
7	U	V. poor L	Fair L	U	Good L V. poor K
8	U	V. poor L	V. poor L	U	Good L V. poor K

The Tetramethylammonium Aluminosilicate System.—The gels in this system were particularly prone to thixotropy. On hydrothermal treatment up to 150° the gels tended to remain stable and translucent as at room temperature. However, these gels became milky after several days (the time increasing with the silica content), owing to the formation of fine, white crystals. These could be centrifuged off and although obtained only in low yield could be obtained pure. These products were the zeolites N-R and N-Q of Table 7. Gels of different concentrations were tried from about 0·75 g. dry weight to 2·0 g. dry weight per 10 ml. of water. The more concentrated gels gave larger amounts of crystals, but they also tended to solidify to stiffer gels and since no crystal separation was possible after such solidification the yield of crystalline material was limited. The gels of higher silica content (n = 6—9) first formed stiff gels, after about 6 days, and the other gels after progressively increasing times as n decreased.

FIG. 3. *Crystallisation fields of nitrogenous aluminosilicate gels derived from monomethylammonium aluminosilicate gels. Boundaries in this and subsequent figures are approximate only; the abscissae, n, equal the molar ratios* SiO_2 *to* Al_2O_3 *in the crystallising gels (also in* Figs. 4—6).

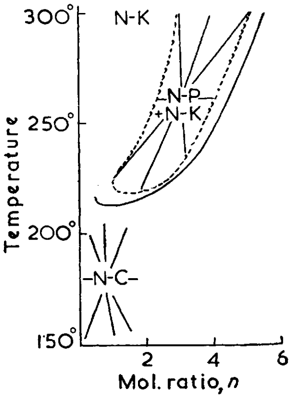


FIG. 4. *Crystallisation fields of nitrogenous aluminosilicates derived from dimethylammonium aluminosilicate gels.*

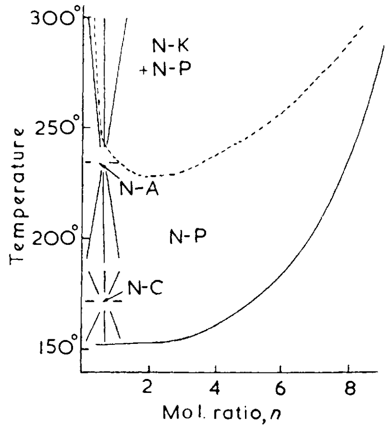


FIG. 5. *Crystallisation fields of nitrogenous aluminosilicates derived from trimethylammonium aluminosilicate gels.*

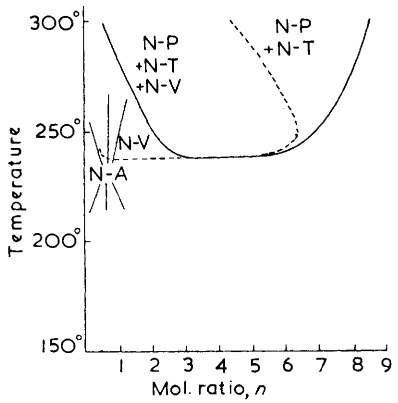


FIG. 6. *Crystallisation fields of nitrogenous aluminosilicates derived from tetramethylammonium aluminosilicate gels.*

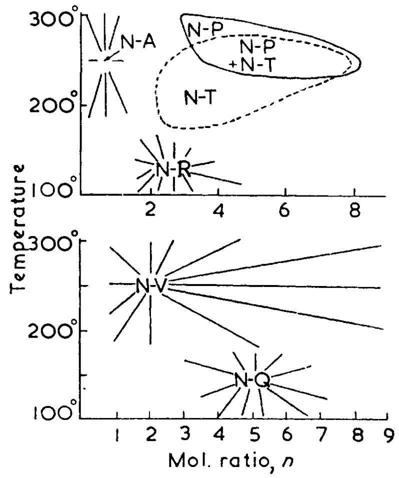


TABLE 7. *Crystallisation conditions of, and yields from, aqueous methylammonium aluminosilicate gels.*

(*a*) *Gels* $3NHMe_3{\cdot}OH,Al_2O_3,nSiO_2$.

n	175°, 6 days	220°, 5 days	225°, 4 days	250°, 4 days	300°, 3 days
1	U	U	Poor A	Poor A Fair V	Fair L Poor T Poor V
2	U	U	U	Fair V Fair T Poor L	Fair V Poor T Poor L
3	U	U	U	Fair V Fair T Poor L	Fair T Poor L Poor V
4	U	U	U	Fair V Poor T Poor L	Fair L Fair T V. poor V
5	U	U	U	Fair V Poor T Poor L	Good L
6	U	U	U	Fair V Poor T Poor L	Good L Poor T
7	U	U	U	Poor V	Good L. V. poor T
8	U	U	U	U	Poor L V. poor T
9	U	U	U	U	U

(*b*) *Gels* $3NMe_4{\cdot}OH,Al_2O_3,nSiO_2$.

n	100° 9 days	125° 10 days	150° 8 days	200° 5 days	225° 4 days	250° 7 days	300° 3 days
1	U	U	U	Fair A Fair V V. poor T?	Fair A Fair V	Fair A Fair V	Fair A Fair V
2	Poor R	Poor R	Poor R	Good V	Good V	Good V	Good V
3	Poor R	Poor R	Poor Q	Good V V. poor T?	Good V Poor T	Fair V Fair T Poor L	Good V Poor L
4	Poor R Poor Q	Poor R Poor Q	Poor Q	Good V V. poor T?	Good V Poor T	Fair V Poor T Poor L	Good V
5	Poor Q	Poor Q	Poor Q	Good V V. poor T?	Good V Poor T	Fair V Poor T Poor L	Good V
6	Poor Q	Poor Q	Poor Q	Good V V. good T	Good V V. poor T	Fair V Poor T Poor L	Good V
7	U	U	Poor Q	Good V V. poor T	Good V	Fair V Poor T Poor L	Good V
8	U	U	U	Good V V. poor T	Good V	Fair V Poor T Poor L	Good V
9	U	U	U	Good V	Good V	Good V	Good V

TABLE 8. *Crystallisation of* $3NH_4{\cdot}OH,Al_2O_3,2SiO_2$ *at* 300° *in aqueous methanol.*

Methanol (vol. %)	Product	Methanol (vol. %)	Product
0	N-K (mica)	33	N-V + poor N-M
6·6	N-K	60	N-V + poor N-M
13	N-V (montmorillonite type)		

Even at temperatures above 150° the gels tended to remain stable, or else the products were in fine colloidal suspension. This was particularly true when the product was, or contained, montmorillonite. The montmorillonite tended to persist as a sol which could not all be centrifuged off even after 3 or 4 hr. Thus, in a crystallisation from a gel of composition $3NMe_4{\cdot}OH,Al_2O_3,2SiO_2$ + aq. at 200° the product, montmorillonite, although obtained pure, was only isolated in about a 25% yield, the rest remaining in colloidal suspension. If non-thixothropic gels were used as the starting material, then bayerite was usually one of the products.

The nature of the crystalline products tended to vary with the method of mixing of the gels. Normally the organic base and alumina were first mixed and then were stirred into the silica sol. In another procedure, used in a few experiments only, water was added to the alumina gel, followed by silica sol and then by tetramethylammonium hydroxide, always while stirring. After crystallisations at 200° N-T (sodalite-type crystals) and N-V (montmorillonite) were obtained from compositions $3NMe_4{\cdot}OH,Al_2O_3,nSiO_2$ + aq. in which $n = 1$—3, while for $n = 5$—7 fair N-Q (Linde sieve A analogue) and a trace of montmorillonite were obtained. When $n = 4$, N-Q, N-T, and N-V were all formed. After crystallisation at 150° bayerite was found mixed with other crystalline species which were N-T for $n = 2$ and N-Q for $n = 3$ or 4. This sequence shows considerable variations on the results summarised in Table 7 for the normal method of mixing.

Hydrothermal Crystallisation of Gels in Presence of H_2O–MeOH *Mixtures.*—The hydrolysis of alkylammonium ions as indicated in eqn. 1 should be arrested or reversed in presence of methanol. Accordingly crystallisation was studied at 300° for 4 days with gels $3NH_4{\cdot}OH,Al_2O_3,2SiO_2$ and the various water–methanol mixtures of Table 8. Since montmorillonite did not crystallise from systems in which the only base present was $NH_4{\cdot}OH$, but was formed when the bases were $NMe_3H{\cdot}OH$ and $NMe_4{\cdot}OH$, the results in Table 8, lines 3—5, indicate methylation of the ammonium ion under hydrothermal conditions.

Microanalysis of the layer-lattice compound N-V crystallised from the 13% methanol–water gave a nitrogen : carbon ratio by weight of 1 : 0·56, to be compared with 1 : 0·86 for $NMeH_3^+$ ions. Thus the cations present are probably mainly ammonium and monomethylammonium. However, the total nitrogen content was 6·78%, quite near that expected for a mica, whereas the X-ray pattern is nearest to montmorillonite. Therefore in this one specimen there is much absorbed base or, more probably, the aluminosilicate sheets carry the charge density of mica sheets but have the turbostratic arrangement and interlayer distance of montmorillonite sheets.

The species N-M of Table 8 was not identified. The main *d*-spacings in Å, and their intensities, were: 4·13w; 3·94w; 2·57w; 2·52vw; and 2·46vw. A small amount of species N-K was also detected by electron microscopy amongst the products containing N-V.

TABLE 9. *Some* d-*spacings in* Å *of* N-T *and* N-V *and comparison with natural counterparts.*

Natural sodalite (A.S.T.M. index)			N-T		Natural montmorillonite[10]			N-V (X-ray)		N-V (electron diffraction)		Natural[10] beidellite	
d	*I*	*hkl*	*d*	*I*	*d*	*I*	*hkl*	*d*	*I*	*d*	*I*	*d*	*I*
6·3	17	110	6·33	s	4·5	s	11,02	4·45	vs(B)	—	—	4·45	vs
4·42	3	200	—	—	4·3			—	—	—	—	—	—
3·63	100	211	$3{\cdot}64_4$	vs	—	—	—	—	—	2·83	m	—	—
2·81	5	301	$2{\cdot}82_6$	mw	2·56	s	13,20	2·55	s(B)	2·55	s	2·60	vs
2·56	13	222	$2{\cdot}58_0$	ms	2·50			2·46	w(B)	—	—	2·49	
2·37	17	312	—	—	—	—	—	—	—	—	—	2·38	—
2·08	33	303	$2{\cdot}10_4$	w	2·20	vw	22,04	—	—	$2{\cdot}21_7$	w	$2{\cdot}24_0$	vw
1·98	2	402	—	—	—	—	—	—	—	—	—	$2{\cdot}16_4$	
1·88	2	332	$1{\cdot}90_5$	vw	—	—	—	—	—	—	—	$2{\cdot}09_0$	
1·80	2	224	—	—	—	—	—	—	—	—	—	$1{\cdot}89_0$	—
1·73	2	314	$1{\cdot}75_0$	mw	1·69	m	31,15,24	$1{\cdot}68_5$	w(B)	$1{\cdot}68_9$	s(B)	$1{\cdot}69_4$	m
1·61	1	215	$1{\cdot}62_8$	vw	1·67			—	—	—	—	$1{\cdot}65_4$	
1·56	10	404	$1{\cdot}57_6$	vw	1·49	s	33,06	$1{\cdot}47_5$	m(B)	$1{\cdot}48_9$	m	$1{\cdot}48_8$	vs
1·52	5	334	—	—	1·48			—	—	—	—	—	—
1·48	7	600	—	—	$1{\cdot}28_5$	m	26,40	$1{\cdot}27_5$	m(B)	$1{\cdot}28_6$	m	$1{\cdot}28_4$	m
1·43	8	611	—	—	$1{\cdot}27_5$			—	—	—	—	—	—
1·40	1	620	—	—	$1{\cdot}23_5$	w	35,17,42	$1{\cdot}23_5$	m(B)	$1{\cdot}24_1$	s	$1{\cdot}24_1$	m
1·37	2	541	—	—									
1·33	2	622	$1{\cdot}34_7$	vw									
1·31	2	631	—	—									
1·28	1	444	$1{\cdot}28_6$	vw									
1·20	7	—	$1{\cdot}21_4$	vw									
$a = 8{\cdot}88$ Å			$a = 8{\cdot}93$ Å					$a_0 = 5{\cdot}10$ $b_0 = 8{\cdot}90$				$a_0 = 5{\cdot}14$ $b_0 = 8{\cdot}93$	

Some Individual N-Aluminosilicates.—Species N-A (boehmite, Al_2O_3,H_2O) and N-C (bayerite, $Al_2O_3,3H_2O$) will not be described; they are common products from gels in which freshly prepared aluminium hydroxide is one of the constituents.[8]

Species N-T. This was a somewhat expanded form of sodalite. The cubic unit cell had $a = 8{\cdot}93$ Å (compared with 8·77—8·90 Å for natural sodalites and 8·94 Å for a basic sodalite [9]). *d*-Spacings and intensities are given in Table 9, and are compared with those of a natural sodalite. The crystals could be grown only from the gels originally containing tri- and tetramethylammonium hydroxide, and could not be obtained as sole product.

TABLE 10. d-*Spacings* (Å) *of species* N-P *and comparison with natural counterparts.*

Na-Pl [3, 5]			N-L		Na-Q [5]			N-Q		Na-R [5]			N-R	
d	*I*	*hkl*	*d*	*I*	*d*	*I*	*hkl*	*d*	*I*	*d*	*I*	*hkl*	*d*	*I*
7·1	s	110	$7{\cdot}0_9$	vs	12·36	vs	100	12·1	s	14·52	vs	111	—	—
—	—	—	[$6{\cdot}6_9$	w]	8·77	s	110	8·60	s	8·84	ms	220	8·80	vs
5·0	m	200	$5{\cdot}0_0$	ms	7·15	s	111	7·02	s	7·56	ms	311	7·51	s
4·10	s	112	$4{\cdot}0_9$	vs	6·35	w	200	6·08	vw	5·74	s	331	5·72	ms
3·45	vw	220	3·54	w	5·52	s	210	5·44	w	4·81	m	511	4·80	m
—	—	221	3·34	vw	5·02	w	211	4·97	w	4·42	ms	440	4·41	ms
3·18	vvs	310	3·17	vs	4·36	m	220	4·30	mw	4·20	vvw	531	4·27	mw
2·90	vw	222	—	—	$4{\cdot}10_2$	s	300	4·05	vs	$3{\cdot}95_4$	w	620	3·93	m
2·68	s	321	$2{\cdot}67_7$	s	$3{\cdot}89_9$	w	310	$3{\cdot}83_3$	mw	$3{\cdot}81_3$	ms	533	—	—
2·52	vw	400	$2{\cdot}51_1$	w	$3{\cdot}71_2$	s	311	$3{\cdot}65_9$	vs	$3{\cdot}76_9$	mw	622	3·79	vs
2·41	vw	410,322	—	—	$3{\cdot}41_3$	m	320	$3{\cdot}36_5$	ms	$3{\cdot}62_1$	vvw	444	—	—
2·36	w	411,330	—	—	$3{\cdot}28_7$	ms	321	$3{\cdot}24_3$	s	$3{\cdot}51_5$	vvw	551	$3{\cdot}48_4$	vw
2·23	vw	204	$2{\cdot}23_8$	vw	$3{\cdot}07_2$	vw	400	—	—	—	—	642	$3{\cdot}32_2$	vs
			$2{\cdot}13_6$	w	$2{\cdot}98_2$	vs	410	$2{\cdot}94_1$	s	—	—	731	$3{\cdot}24_0$	vw
			$2{\cdot}04_7$	vw	$2{\cdot}90_0$	m	411	$2{\cdot}85_6$	m	$3{\cdot}08_4$	m	733	$3{\cdot}03_8$	m
			$1{\cdot}96_2$	m	$2{\cdot}75_1$	m	420	$2{\cdot}71_2$	mw	$2{\cdot}94_1$	m	660	$2{\cdot}93_1$	mw
			$1{\cdot}82_9$	vw	$2{\cdot}68_1$	mw	421	$2{\cdot}64_6$	mw	$2{\cdot}88_1$	s	555	$2{\cdot}86_7$	s
			$1{\cdot}77_2$	mw	$2{\cdot}62_3$	s	332	$2{\cdot}58_5$	ms	$2{\cdot}79_0$	m	480	$2{\cdot}77_9$	m
			$1{\cdot}71_7$	m	$2{\cdot}51_2$	mw	422	$2{\cdot}47_9$	w	$2{\cdot}74_5$	w	753	$2{\cdot}73_0$	vw
			$1{\cdot}66_9$	mw	—	—	500	$2{\cdot}42_9$	w	$2{\cdot}72_5$	vw	842	—	—
			$1{\cdot}62_4$	w	$2{\cdot}36_9$	mw	511	—	—	$2{\cdot}66_2$	m	664	$2{\cdot}64_8$	m
			$1{\cdot}47_9$	mw	$2{\cdot}24_7$	w	521	$2{\cdot}21_5$	mw	$2{\cdot}61_7$	mw	931	$2{\cdot}60_7$	vw
			$1{\cdot}39_0$	w	$2{\cdot}17_4$	m	440	$2{\cdot}14_4$	m	$2{\cdot}54_5$	mw	844	$2{\cdot}53_8$	w
			$1{\cdot}36_3$	mw	$2{\cdot}14_5$	mw	441	—	—	$2{\cdot}40_3$	m	1022	$2{\cdot}39_2$	m
			$1{\cdot}31_3$	vw	$2{\cdot}10_9$	mw	433	—	—	—	—	1040	$2{\cdot}30_8$	vw
			$1{\cdot}27_1$	mw	$2{\cdot}07_8$	mw	531	—	—	$2{\cdot}20_6$	m	880	$2{\cdot}19_6$	w
					$2{\cdot}05_0$	m	600	$2{\cdot}02_4$	m	$2{\cdot}18_1$	m	955	$2{\cdot}17_0$	w
$a = 10{\cdot}0_1$ Å			$a = 10{\cdot}02$ Å		$a = 12{\cdot}30$ Å			$a = 12{\cdot}13$ Å		$a = 24{\cdot}96$ Å			$a = 24{\cdot}85$ Å	

Species N-V (*alkylammonium montmorillonites*). The unit cell dimensions of a specimen of tetramethylammonium montmorillonite were $a = 5{\cdot}10$, $b = 8{\cdot}90$, and $c = 11{\cdot}6$ Å. The *d*-spacings are given in Table 9, where they are compared with those of natural montmorillonite and beidellite. The *c*-spacing of N-V varies, in the same way as that of natural montmorillonites, according to the inter-layer cation. The *c*-spacings for samples of N-V crystallised at different temperatures are shown in Fig. 7 as a function of these temperatures. At 200° the *c*-spacing corresponded to that of tetramethylammonium montmorillonite prepared from the natural clay, while at 300° it corresponded to that of the monomethylammonium form,[11] in both cases for products crystallised from gels originally containing only tetramethylammonium cations. This variation in cations present, when one original base was used, can be ascribed to hydrolysis of the organic bases. Microanalysis of the crystals confirmed that the cation mainly present was that indicated by the measurement of the *c*-spacing. Thus the product crystallised at 200° from the gel $3NMe_4{\cdot}OH,Al_2O_3,SiO_2$ gave C 6·55, H 3·20, and N 1·96%, the C : N ratio being 3·29 compared with 3·43 for the NMe_4^+ ion.

Crystals of species N-V were obtained free from other species, but were prepared only from gels containing originally NMe_3H^+ and NMe_4^+ ions. The thermograms and the thermogravimetric curves of tetramethylammonium-V are shown in Figs. 1*d* and 8*a*. There are

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[8] Barrer and White, *J.*, 1951, 1167.

[9] Barrer and White, *J.*, 1952, 1561.

[10] Cf. McEwan, "X-ray Identification and Structure of Clay Minerals," Min. Soc., G.B., 1951, Chap. IV.

[11] Reay, Ph.D. Thesis, London, 1956.

exothermal peaks at 333°, 396°, and 590° on the thermogram which are characteristic of the pyrolysis of the organic ions.[12] The endothermic peak at 120° is associated with the loss of interlayer water. The thermogram and thermogravimetric curves of monomethylammonium-V (prepared from $3NH_4{\cdot}OH,4Al_2O_3,2SiO_2$ + aq. + 13% of methanol) are also shown in Figs. 1*c* and 8*b*. On the thermogram one exothermal peak with a maximum at 427° was observed. Endotherms with peaks at 500° and 580° are characteristic of the loss of structural water from montmorillonites. In NMe_4-V these peaks are smothered by the exothermal pyrolysis peaks. The essential lattice structure of N-V was stable to ~900°. After being heated to this temperature the material had unit cell dimensions $a = 5{\cdot}14$, $b = 9{\cdot}00$, and $c \approx 9{\cdot}6$ Å. In the thermogram of NMe_3-V, a sharp exothermic peak at 980°, preceded by a small endothermic peak, marks the partial recrystallisation to mullite. The NH_3Me-V also recrystallises to mullite below 1050° although without an exothermal peak.

An electron micrograph and diffraction pattern of N-V are shown in Plates 1*c* and *d*. The heat of interlayer water loss from NH_3Me-V (peak temperature 70°) was estimated from the thermogram and thermogravimetric curve, after calibration of the differential thermal analyser,[2] 24·8 kcal. per mole of water lost.

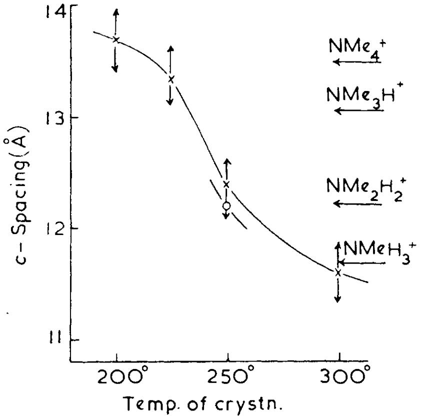

FIG. 7. *c-Spacings of nitrogenous montmorillonites crystallised at various temperatures from tetramethylammonium* (×) *and trimethylammonium aluminosilicate gels* (○). *On the right of the diagram the arrows are drawn at c-spacings observed for the indicated methylammonium ion-exchanged montmorillonites, prepared from natural montmorillonites.*[11]

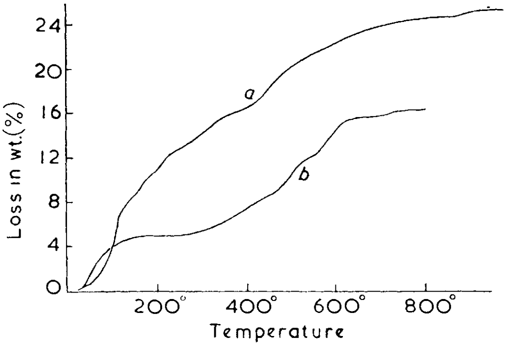

FIG. 8. *Thermogravimetric curves of synthetic tetramethylammonium montmorillonites* (*curve a*) *and monomethylammonium montmorillonite* (*curve b*).

Species N-L. This is the cubic variety of harmotome which was obtained from certain alkylmmonium aluminosilicate gels in almost 100% yield (Tables 5 and 6). It is analogous to the zeolite Na-Pl which served to determine the essential structure of the aluminosilicate framework of the harmotome-phillipsite zeolites.[3] The best yields were obtained from aqueous gels $3NH_2Me_2{\cdot}OH,Al_2O_3,nSiO_2$ ($2 \leqslant n \leqslant 6$) at 200°. The unit cell edge was 10·02 Å and did not vary in products grown from gels of different compositions and at different temperatures. The *d*-spacings are compared with those of Na-Pl in Table 10.

Microanalysis of a specimen crystallised at 200° from the above gel with $n = 3$ gave N 3·97, C 5·32, and H 2·84%. The C : N ratio is 1·34, compared with C : N = 1·71 for $NH_2Me_2^+$ and 0·86 for NH_3Me^+, so that dimethylammonium ions predominate slightly in this structure. The thermogram of a sample of N-L is shown in Fig. 9 and the thermogravimetric curve in Fig. 2 (*b*). The large exotherm with its peak at 475° is associated with pyrolysis of the organic ions. The endotherm with its peak at 88° is associated with loss of zeolitic water. At 850° an amorphous phase appears (admixed with carbon) which persists at least to 1050°. The

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[12] Allaway, *Proc. Soil Sci. Soc. Amer.*, 1948, **13**, 183.

photomicrograph of N-L, and the electron diffraction pattern, are shown in Plates 1*e* and *f*. The *d*-spacings derived from this pattern agreed with the *X*-ray *d*-spacings of Table 10.

Species N-Q. This was the nitrogenous analogue of Na-Q,[5] and therefore of Linde molecular sieve A. It was obtained pure but in low yield, and by microanalysis it was established that the cation mainly present in the sample analysed was $NH_2Me_2^+$. Thus, the C : N ratio was 1·89, to be compared with 1·71 for $NH_2Me_2^+$ and 2·57 for $NHMe_3^+$. Species N-Q crystallised only from tetramethylammonium aluminosilicate gels and the low yield may be governed by the rate of hydrolysis of NMe_4^+ which must be very slow at the low temperatures (~100—150°) at which it was obtained. The *d*-spacings are compared with those of Na-Q in Table 10, and a photomicrograph is shown in Plate 2*a*.

Species N-R. This was identified as an alkylammonium analogue of faujasite, and hence of Na-R [5] and Linde sieve X. As with N-Q it was obtained pure but in low yield. Microanalysis of a particular sample gave a C : N ratio of 1 : 3·44, to be compared with 3·43 for NMe_4^+. This ion should therefore be the only organic cation present. The cavities and channels in faujasite are filled by about 33 CMe_4 molecules per unit cell; [13] a comparable number of NMe_4^+ ions might therefore also fill this structure. This corresponds to a silica-rich aluminosilicate framework, which would therefore be the only possible form of faujasite structure containing only tetramethylammonium ions.

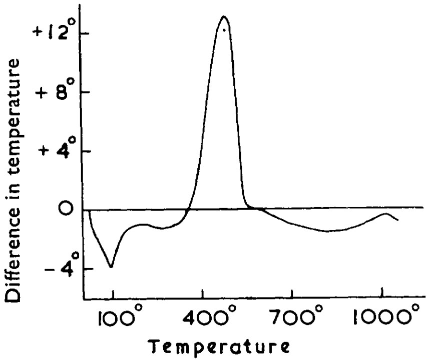

FIG. 9. *Thermogram of nitrogenous harmotome from* $3NMe_2H_2{\cdot}OH,Al_2O_3,3SiO_2$ + *aq. at* 200°.

The *d*-spacings of species N-R are given in Table 10, in which they are compared with those of Na-R.[5] The cubic unit cell edge is 24·85 Å. Plates 2*b* and *c* show a photomicrograph and the electron diffraction pattern of N-R. The *d*-spacings so determined agreed well with those obtained by *X*-ray diffraction. The material is excellently crystalline.

DISCUSSION

Ease of Crystallisation.—The ease of crystallisation varied greatly from one base to another. Crystallisation was, for instance, observed down to 150° in the dimethylammonium aluminosilicate system, but only down to 250° in the ammonium aluminosilicate system. If the basic dissociation constants are estimated at the minimum crystallisation temperatures by means of Pitzer's equation [14] there is a correlation between them, as shown in Table 11.

Appearance of Layer Lattices.—In hydrothermal systems the crystallisation of layer-lattice species related to montmorillonite, beidellite, and other clay minerals, occurs from alkali-metal aluminosilicates only when the amount of alkali-metal base is limited or, for kaolinites, virtually absent.[15] The framework minerals (*e.g.*, zeolites, felspars, felspathoids) replace layer-lattice minerals when the amount of alkali is increased and particularly when it is in excess. However, among the ammonium and methylammonium

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[13] Barrer and Sutherland, *Proc. Roy. Soc.*, 1956, **237***A*, 439.

[14] Pitzer, *J. Amer. Chem. Soc.*, 1937, **59**, 2365.

[15] Norton, *Amer. Mineral.*, 1939, **24**, 1; Ewell and Insley, *J. Res. Nat. Bur. Stand.*, 1935, **15**, 173; Roy and Sand, *Amer. Mineral.*, 1956, **41**, 505.

aluminosilicates we have shown not only that diverse framework structures can be formed, but that, even in presence of excess of base, layer-lattice species are formed very readily and can become the dominant crystalline phases. With smaller ions, notably in the case of NH_4^+, the important layer structure is a mica; as the ions increase in size, micas are replaced by montmorillonite-type clays. The tendency to form layer lattices is thus very differently manifested by the organic bases and by alkali-metal hydroxides.

TABLE 11. *Basic dissociation constants and minimum crystallisation temperatures,* T_m.

Base	T_m	Basic dissocn. const. at T_m	Base	T_m	Basic dissocn. const. at T_m
NH_4OH	~250	$1\cdot9_5 \times 10^{-6}$	$NH_2Me_2{\cdot}OH$	~150	$8\cdot5 \times 10^{-5}$
$NHMe_3{\cdot}OH$	~230	$4\cdot9 \times 10^{-6}$	$NMe_4{\cdot}OH$	~100	Strong base
$NH_3Me{\cdot}OH$	~210	$2\cdot0 \times 10^{-5}$			

The number of cations between the lamellæ in a montmorillonite having the ion-exchange capacity of Ross and Hendricks's ideal formula[16] is sufficiently low to be able to accommodate any methylammonium ion.[17] On the other hand, the cation density for micas of normal composition allows an area of only 23·4 Å^2 per ion. The areas of several alkylammonium ions have been estimated[11] as follows: NMe_4^+ 26 Å^2; NMe_3H^+ 26 Å^2; $NMe_2H_2^+$ 24 Å^2; $NMeH_3^+$ 17 Å^2. Therefore, of these ions, only ammonium, methylammonium (and possibly $NMe_2H_2^+$) could form micas having normal cationic compositions. Also, in mica the sheets do not expand readily and so the height of the ions may be important. The spherical ammonium ion, of similar diameter (2·86 Å) to K^+ (2·66 Å), should and evidently does form a stable mica structure. There is, however, difficulty when $NMeH_3^+$ is to be incorporated. The full cation density in mica has been realised in one preparation (p. 978) in which, however, the crystals were more like montmorillonite in the diffuseness of the *X*-ray pattern. This species represents an interesting intermediate phase. Finally, in accordance with the areas of the alkylammonium ions, layer-lattices rich in di-, tri-, and tetra-methylammonium ions were montmorillonoids in *c*-spacings (Fig. 7) and, from microanalysis for nitrogen, in cation density.

The Zeolites.—Among the various zeolitic phases the same problem arises of finding adequate intracrystalline space for packing in the number of alkylammonium ions needed to neutralise the framework charges. This difficulty has been commented upon in relation to N-R (faujasite). It arises equally in the cases of N-Q, N-T, and N-L. The possibility of incorporation only of small hydrolysis products (*e.g.*, NH_4^+ or $NMeH_3^+$ from NMe_4^+) is not fully supported by the microanalyses. It may be surmised that these zeolites tend to be silica-rich relative to their analogues containing only simple inorganic cations, although no proof of this can be offered. Alternatively, hydrogen ions may be incorporated along with larger alkylammonium ions. Species N-L (harmotome), for example, crystallised very readily from gels with $NMe_2H_2{\cdot}OH$ as base, and analysis showed much dimethylammonium ion to be present. However, the nitrogen content (3·97%) corresponds with a highly siliceous phase unless H_3O^+ is also present. The same is true of N-Q (4·2% N) and N-R (2·0% N).

The electron-microscopy and electron-diffraction studies reported in this and the following paper were carried out by Dr. I. S. Kerr of this Department, whom the authors thank.

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[16] Ross and Hendricks, U.S. Geol. Survey, Prof. Paper 205B, 1945.

[17] Barrer and Reay, *Trans. Faraday Soc.*, 1955, **51**, 1290.