

*Studies on the zeolites. Part III. Natrolite  
and metanatlolite.*<sup>1</sup>

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*Introductory.*

ONE of the most typical occurrences of natrolite, in the Puy-de-Dôme amygdaloids, formed the main type occurrence of R. J. Haüy's species Mesotype (1801); but when A. F. Gehlen and J. N. Fuchs (1813) and J. N. Fuchs (1816) recognized the individuality of soda-, lime-, and lime-soda-mesotypes, and divided Haüy's species into three, they discarded Haüy's name altogether, using for the three new species the names natrolite, scolecite, and mesolite. Natrolite was not a new name, having been given in 1803 by M. H. Klaproth to the well-known yellow-banded fibrous-radiating zeolite from Württemberg. The name mesotype has persisted for the whole group (in which sense it will be used here); and for long the names soda-, lime-, and lime-soda-mesotype were used as well as Gehlen and Fuchs's names. In France, however, the name mesotype is used in a more restricted sense for natrolite only.

The individuality of natrolite, mesolite, and scolecite, and especially of mesolite, has been repeatedly doubted, but the accumulated observations of Sir David Brewster,<sup>2</sup> P. Reiss and G. Rose (1843), A. Des Cloizeaux (1857), R. Görgey,<sup>3</sup> H. L. Bowman,<sup>4</sup> A. Cavinato (1927), and others leave no doubt that the mesotype group is not a single isomorphous series, but three distinct and separate species, with a limited degree of isomorphous replacement. This conclusion is fully supported by the present work.

<sup>1</sup> Part II, *Min. Mag.*, 1932, vol. 23, p. 51.

<sup>2</sup> Sir D. Brewster, quoted in F. Mohs, *Min.*, 1825, vol. 2, p. 237.

<sup>3</sup> R. Görgey, *Tschermaks Min. Petr. Mitt.*, 1908, vol. 27, p. 255; 1909, vol. 28, p. 79.

<sup>4</sup> H. L. Bowman, *Min. Mag.*, 1908, vol. 15, p. 216.

Several varieties of natrolite have been distinguished, and a number of supposed species have proved on further study to be merely natrolite. Thus *Högauite* (C. J. Selb, 1803) is a synonym for natrolite from Högau, the original Württemberg locality described by Klaproth.

The name *Bergmannite* (C. F. Schumacher, 1801) was applied to the pseudomorphs of natrolite, or natrolite and diaspore, after nepheline (and possibly other minerals), common in the Langesundfjord district of Norway. *Spreustein* (A. G. Werner, 1811) and *Radiolite* (H. M. T. Esmark, 1828) are similar impure occurrences,<sup>1</sup> in part at least pseudomorphous, while *Brevicite* (J. Berzelius, 1834) is a much purer, but still impure material; all these are from the same district. From this region also comes *Eisen-Natrolith* (C. Bergemann, 1851), which W. C. Brøgger (1889) showed to be ordinary natrolite coloured green by inclusions. These inclusions Brøgger believed to be chloritic, possibly allied to stilpnomelane, but if all the aluminium of Bergemann's analysis is set down as natrolite, the residue after deduction of the natrolite approaches an aegirine-augite in composition.

*Lehunte* of T. Thomson (1836) is shown by an analysis by J. Apjohn (1845) to be merely a compact natrolite. Many specimens carry a good deal of extra, occluded water. *Savite* of G. Meneghini and E. Bechi (1852) was shown by Q. Sella (1858) and by A. Des Cloizeaux (1867) to be natrolite; the impurity in Bechi's material has generally been supposed to be serpentine, but his analysis rather suggests enstatite.

*Galactite* (W. Haidinger, 1855)<sup>2</sup> is a milky-white variety of natrolite. The cause of its opacity is not known; some authors have supposed it to be due to a replacement of soda by lime, but several of M. F. Heddle's analyses (1856) of galactites show only small amounts of lime, less than have been found by the author and others in glassy natrolites unquestionably free from mesolite or other impurity. *Fargite* (M. F. Heddle, 1856) is a red variety of natrolite (coloured by iron) from Glen Farg, Perthshire. If Heddle's material was quite free from mesolite (which also occurs in Glen Farg), this must

<sup>1</sup> Some spreusteins, however, consist mainly of the doubtful zeolite hydronephele, which many authors hold to be a mixture of natrolite and diaspore; the author hopes to start a re-investigation of hydronephele shortly.

<sup>2</sup> The name was certainly given by Haidinger before 1847, as it is mentioned by E. F. Glocker, *Synopsis Min.* (Halle), 1847, p. 176. This appears to be the first publication of the name.

be one of the most lime-rich natrolites ever analysed, 30 % of the soda being replaced by lime.

*Mooraboolite* of G. B. Pritchard (1901), from Maude, Moorabool valley, Victoria, was shown by L. J. Spencer (1903) to be merely impure natrolite.

*Epinatrolite* of S. J. Thugutt (1911) was distinguished from natrolite solely by differences in the intensity of the stain it takes on application of methylene blue or of silver nitrate followed by potassium chromate, after it has been ignited for short periods.<sup>1</sup> This does not seem to the author sufficient ground for the establishment of a new species, and a re-investigation of the substance is called for, especially by X-ray and vapour-pressure methods. Unfortunately the author had no material available to carry this out.

#### *Composition.*

All the available analytical data, including nine new analyses by the author (table I), indicate that, unlike thomsonite, natrolite is a zeolite of fixed Si/Al-ratio, namely 1.5. In common with the other true zeolites, the ratio O/(Si + Al) is 2, indicating an indefinitely extended, non-polar bonded anionic framework. The X-ray data indicate a unit cell containing 80 oxygen atoms, 16 aluminium, and 24 silicon atoms, and the water content is also appreciably constant at 16 molecules per unit cell. The normal characteristic number of kations is 16, and occurrences in which 16 sodium atoms per unit cell form the only kationic content are not uncommon. But frequently a part of the sodium (up to 1.0 atom per unit cell<sup>2</sup>) is replaced by potassium, and the author's analyses tend to suggest that an appreciable replacement of this kind is more common than has been generally realized, many analysts not having troubled to separate the alkalis. A limited degree of replacement of two sodium atoms by one calcium atom may also occur, up to perhaps two atoms Ca per unit cell (replacing four atoms Na), but the precise limit to this replacement cannot be fixed, since so few analyses have been made on material of optically controlled purity. In two of the author's analyses, the natrolite was intimately associated with mesolite in the

<sup>1</sup> Thugutt has recently (1932) stated that there is a difference in the birefringence. It is, however, too small to be reliably measurable.

<sup>2</sup> The analysis by S. von Waltershausen (1853) showing 2.40 atoms K per unit cell is probably in error. The 20.35 % potash in C. G. Gmelin's analysis (1850) is clearly a misprint for 0.35 %.

one case, and calcite in the other (nos. 9 and 3 of table I respectively); these might be hoped to give some indication of the limit of replacement, but the analyses are not as satisfactory as could be wished. In the first, the amount of material available was very small, while in the second, the natrolite and calcite were so intimately intergrown that a complete separation was impossible, and the composition of the natrolite had to be arrived at by deduction of the calcite found. Even allowing for these sources of error, however, the difference between the two calcium contents is remarkably great. Probably the limit of replacement varies with temperature and other conditions.

TABLE I. New chemical data for natrolite.

	1.	2.	3.	4.	5.	6.	7.	8.	9.	
Percentage composition.	SiO <sub>2</sub> ...	47.60	47.38	46.52	47.33	47.15	47.29	46.96	47.22	47.1
	Al <sub>2</sub> O <sub>3</sub>	27.40	27.63	26.29	27.67	27.39	27.56	27.12	26.94	27.8
	Na <sub>2</sub> O	15.36	14.96	10.56	14.74	15.27	14.63	12.48	14.45	15.9
	K <sub>2</sub> O ...	0.23	0.41	0.46	0.50	0.50	0.59	1.25	1.27	—
	CaO ...	0.13	0.54	3.14	0.22	0.30	0.80	1.89	1.05	1.3
	H <sub>2</sub> O ...	9.47	9.58	9.63	9.64	9.53	9.40	10.80	9.28	9.35
Total	100.19	100.50	100.51*	100.10	100.14	100.27	100.50	100.21	101.4	
Oxygen % ...	42.21	42.31	42.32	42.14	42.06	42.17	41.54	41.99	42.09	
Oxygen, atoms per unit cell	80.94	80.94	80.90	80.91	80.83	81.01	79.41	80.52	—	
Atoms per unit cell, assuming oxygen 80.	Si ...	23.97	23.84	24.26	23.90	23.84	23.84	23.95	23.92	23.5
	Al ...	16.24	16.38	16.16	16.36	16.32	16.51	16.28	16.10	16.4
	Na ...	14.99	14.59	10.67	14.43	14.96	14.29	12.34	14.29	15.4
	K ...	0.15	0.26	0.29	0.33	0.33	0.37	0.82	0.82	—
	Ca ...	0.08	0.29	1.76	0.11	0.18	0.43	1.04	0.53	0.7
	H <sub>2</sub> O ...	15.91	16.08	16.74	16.23	16.07	15.80	18.38	15.68	15.6
Specific gravity	2.245	2.245	2.238	2.248	2.250	2.249	2.238	2.245	—	

1. B.M.39877. Puy de Marmant, Puy-de-Dôme, France. Clear stout prisms.
2. B.M.49545. Salesl, Leitmeritz, Bohemia. Crust of small clear prisms.
3. B.M.1925,489. Moore, Trenton, New Jersey. Glassy needles with calcite.
4. Benallt manganese mine, Rhiw, Carnarvonshire. Large translucent crystals.
5. B.M.52571. Cape Blomidon, King's Co., Nova Scotia. Clear crystals.
6. B.M.62763. De Beers diamond mine, Kimberley, S. Africa. Clear crystals.
7. B.M.1914,944. Seiser Alpe, Bozen, Tyrol. Radiating massive.
8. B.M.1914,769. Snake Hill, North Bergen, New Jersey. Clear crystals.
9. B.M.62354. Neubauerberg, Mickenhan, Böhmisch-Leipa. Long, hair-fine needles, each with a very thin cap of mesolite.

\* Including 3.91% CaCO<sub>3</sub>.

A collection was made of all the available analyses of natrolite, and the results, recalculated in atoms per unit cell of 80 oxygen

atoms, classified as was done for thomsonite. A survey of the whole of these data leads to the conclusions above set out; there is no evidence that the calcium content is due, or even partially due, to a substitution of the type  $\text{NaSi} \rightleftharpoons \text{CaAl}$ , nor is there any evidence that the water content increases with increase of lime content, as has

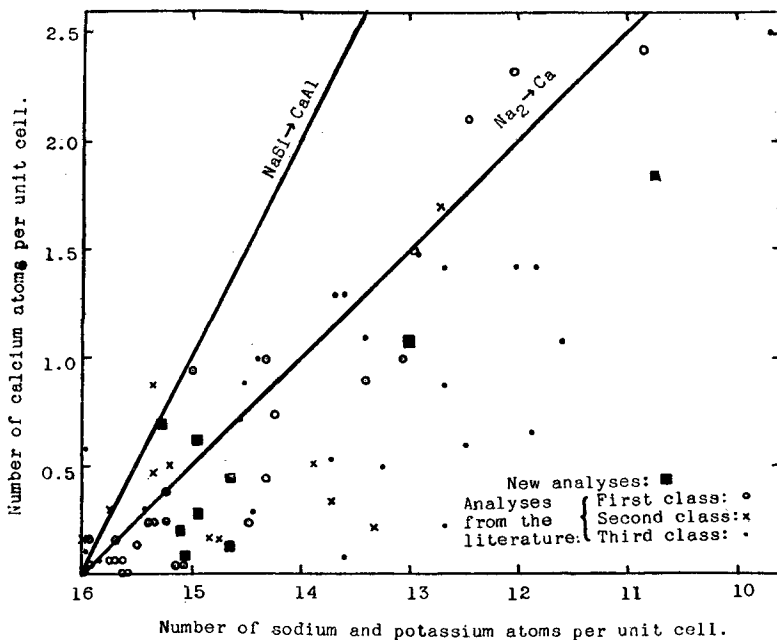


FIG. 1. A graphical representation of such analytical data for natrolite as take account of the lime content, to show that calcium replaces sodium in the proportion  $\text{Na}_2 \rightarrow \text{Ca}$ , and cannot be accounted for by a replacement of type  $\text{NaSi} \rightarrow \text{CaAl}$ .

been occasionally supposed. It seems unnecessary to give the actual recalculated figures here,<sup>1</sup> but fig. 1, in which the calcium content (for those analyses which take account of a possible calcium content) is plotted against the sum of the alkalis, presents the evidence for a  $\text{Na}_2 \rightarrow \text{Ca}$  rather than a  $\text{NaSi} \rightarrow \text{CaAl}$  substitution.

<sup>1</sup> 119 analyses were collected from the literature (see bibliography, p. 284), of which 45 were accounted as first-class, 23 second-class, 34 third-class, and 14 rejected as worthless. Of the first-class analyses, lime was estimated or shown to be absent in 30, potash in 15, and both in 11. The corresponding figures for the second-class analyses are 14, 10, and 8, and for the third-class, 24, 6, and 5.

*Crystallography, density, pyroelectricity, and X-ray work.*

Natrolite was originally believed by R. J. Haüy (1801) to be tetragonal, but was soon found to be really orthorhombic. O. Luedecke (1881), W. C. Brøgger (1889), and others brought forward evidence for the existence of monoclinic natrolites, but other workers, including the author, can find no confirmation of these results (cf. below, under optics).

A considerable number of goniometric measurements have been made on natrolite, the fullest being those of W. C. Brøgger (1879, 1889), who found an axial ratio of  $0.9785 : 1 : 0.3536$ ; but as G. Kalb (1930) points out, natrolite is very prone to the development of vicinal faces, and since the symmetry is fairly low, special precaution is necessary to obtain a reliable axial ratio. The cleavage angle, which will not be affected by vicinal development, has been measured by Dr. L. J. Spencer on the crystals from Benallt described below, and by W. C. Brøgger (1879) on crystals from Stokö, Langesundfjord, the angles found being  $88^{\circ} 55\frac{1}{2}'$  and  $88^{\circ} 51'$  respectively. Taking the mean,  $88^{\circ} 53'$ , the axial ratio  $a : b$  becomes 0.9807. From this and the values  $36^{\circ} 44'$ ,  $37^{\circ} 35'$ , and  $53^{\circ} 35'$  deduced by Kalb as the most probable values for the true angles  $(111) : (\bar{1}\bar{1}1)$ ,  $(111) : (\bar{1}\bar{1}1)$ , and  $(111) : (\bar{1}\bar{1}1)$ , three values for the axial ratio  $c : b$  may be calculated; the three agree closely, and the axial ratio may be safely taken as very nearly  $a : b : c = 0.9807 : 1 : 0.3537$ . This is in good agreement with the value obtained from Mr. F. A. Bannister's X-ray measurements of the cell-sides, which give  $a : b : c = 0.981 : 1 : 0.354$ , and will be adopted throughout the present work. The X-ray measurements of A. L. Parsons (1930), L. Pauling (1930), F. Halla and E. Mehl (1930), and J. Wyart (1931) differ considerably among themselves, and agree none too well with the above ratio, leading to axial ratios of  $0.9785 : 1 : 0.3572$ ,  $0.9769 : 1 : 0.3534$ ,  $0.9823 : 1 : 0.3544$ , and  $0.9865 : 1 : 0.3551$  respectively.

The normal habit of natrolite is the simple combination  $m(110)$ ,  $o(111)$ , as long needles parallel to the  $c$ -axis. Sometimes  $a(100)$  and  $b(010)$  are developed, and less often pyramids  $z(331)$  and  $\pi(551)$  and domes  $D(101)$  and  $e(011)$ ; other forms are decidedly rare. The natrolite of abnormal habit, elongated parallel to the  $b$ -axis, described by V. von Lang (1863) from the Langesundfjord district, Norway, and figured in most text-books (e.g. Dana, Syst. Min., 6th edn., 1892, p. 600, fig. 3), has been shown by the

author<sup>1</sup> to have been thomsonite. Twins of natrolite have been described with twin-planes: (110), by C. Stadtländer (1885), from Stempelberg, Marburg, and by A. Lacroix (1896) from several localities; (011), by G. Cesàro (1909), from Hohentwiel; and (031), by V. von Lang (1863), from the Langesundfjord region.

Of ten natrolite specimens measured by the author, on the three-circle goniometer, seven show the simple combination  $m$  (110),  $o$  (111) (or rather, one vicinal form near  $m$  and three near  $o$ ); two, from Jakuben, Bohemia, and De Beers diamond mine, Kimberley, show also the forms  $a$  (100) and  $b$  (010); and the tenth, from the Benallt manganese mine, Carnarvonshire, has a more complex habit. The measurements on the first nine are given in table II.

TABLE II. Goniometric measurements on natrolite.

	1.	2.	5.	6.	8.	10.	11.	12.	13.
$am$ ...	—	43 39	44 36	44 35	42 38	44 27	44 39	44 29	44 29
$cv_1$ ...	26 50	25 38*	26 42	26 43	26 46	26 46	26 47	26 42	26 32
$cv_2$ ...	28 36	—	27 25	27 39	27 6	27 55	27 16	27 39	26 45
$cv_3$ ...	25 47	—	25 35	26 13	25 57	26 5	25 52	26 19	—
$[ca]:[cv_1]$ ...	44 29	44 22*	44 0	44 38	43 50	44 50	45 2	45 27	43 25
$[ca]:[cv_2]$ ...	41 47	—	44 12	44 40	41 20	44 34	45 39	43 13	44 20
$[ca]:[cv_3]$ ...	41 34	—	36 11	42 39	40 54	42 51	43 19	40 58	—

\* Only approximate.

Specimens 1, 2, 5, 6, and 8, see table I; 10, B.M.1911,145, Jakuben, Tetschen, Bohemia; 11, B.M.1929,339, Zirkowitz, Bohemia; 12, B.M.1918,133, Salesl; 13, B.M.48663, Salesl.

The measurements were carried out as follows: the goniometer was adjusted with the axes of the first and third circles coincident and the axis of the second circle coincident with the reference line; the crystal was then mounted and the zone  $mm'$  brought into adjustment; this zone was measured with the third circle, and the bisector of the angle (110):(1 $\bar{1}$ 0) (the normal to the face  $a$ , which is not developed except on the South African and Jakuben crystals, for which it was accordingly adjusted direct) brought into coincidence with the reference line; then by rotating the first and second circles through 90°, the absent face  $c$  (001) is brought into face adjustment, and readings on the first circle give values of  $cp$  ( $p$  being any face), while the third circle gives the interzonal angles  $[ca]:[cp]$ .

Following G. Kalb (1930),  $v_1$ ,  $v_2$ , and  $v_3$  are used for the three vicinal planes replacing  $o$  (111); the largest and nearest to the true  $o$  (111) is  $v_1$ .

The calculated value of  $am$  and  $[ca]:[co]$  is 44° 26½', and of  $co$  26° 47½', from the adopted axial ratio.

Both the new measurements and the data from the literature show that the face  $m$  (110) is fairly often present in its true position, and

<sup>1</sup> Min. Mag., 1932, vol. 23, p. 66.

that when replaced by a vicinal face, the replacing face is on the  $a$  (100) side of the true position of  $m$  (110). The presence of the true  $m$ -face and a vicinal face together has not been observed. As Kalb observed,  $o$  (111) is commonly replaced by a three-faced vicinal pyramid, the faces of which are often approximately in the zones  $[10\bar{1}]$ ,  $[0\bar{1}1]$ , and  $[110]$ , and one face of which (that nearest the true

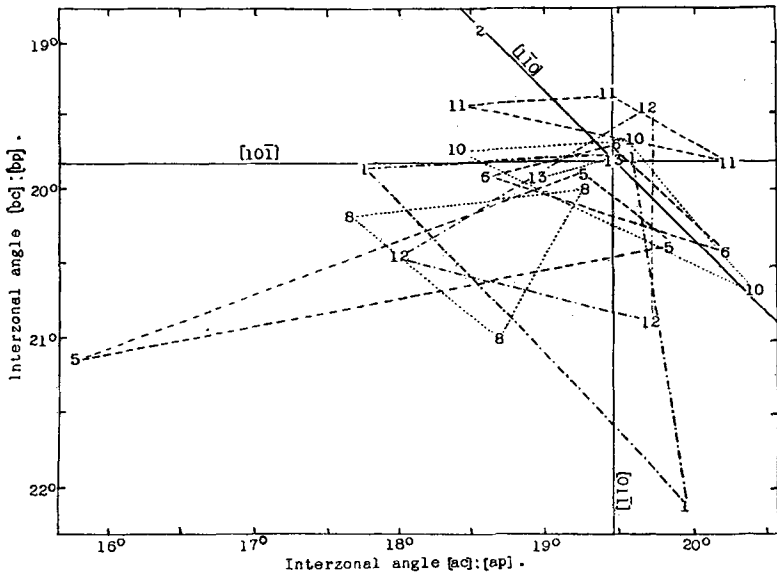


FIG. 2. A portion of a gnomonic projection (projection radius 100 cm.), showing the distribution of the faces vicinal to (111) on a number of natrolite crystals from different localities.

position of  $o$  (111), which is commonly approximately in the zone  $[0\bar{1}1]$  is always much larger than the other two. Sometimes one, and very occasionally both, of the smaller vicinal faces may be suppressed. The large face has commonly been assumed to be the true  $o$  (111), and the smaller faces have often been assigned indices such as (10.11.11), (40.40.39), &c.

The new measurements indicate that the two smaller vicinal faces are often decidedly out of the zones  $[10\bar{1}]$  and  $[1\bar{1}0]$ , especially the latter, which in several specimens has been observed to lie nearer zone  $[0\bar{1}1]$ . Fig. 2, in which the new data on the vicinal faces replacing  $o$  (111) are shown graphically in the form of a small section of a gnomonic projection on  $c$  (001) (with a radius of projection of



100 cm.), shows how the largest face of the three lies fairly near the true position of  $o$  (111), while the other two lie, one between  $o$  and  $m$ , but generally nearer  $a$  than the zone  $[1\bar{1}0]$ , and the other between  $o$  (111) and  $o'$  ( $1\bar{1}1$ ), often fairly closely in the zone  $[10\bar{1}]$ , but sometimes decidedly out in the direction of  $a$ .

Much more interesting results were obtained with the crystals from the Benallt manganese mine near Rhiw, Carnarvonshire. These magnificent crystals, up to 3.5 cm. in length and 0.4 cm. square, were discovered in 1911 by Mr. Arthur Russell, and have not hitherto been described. There are also unterminated crystal fragments up to 5 cm. in length and 1 cm. square. When first found, the crystals were water-clear, but they tend to become white and almost opaque unless kept in a closed tube. The cause of this change has not been elucidated; the opaque crystals do not appear to have lost any considerable amount of water, nor do they recover their transparency when kept over water for six months.

The measurements made on these crystals are summarized in table III, together with some observations made by Dr. L. J. Spencer in May 1911 and not hitherto published, and a typical crystal is shown in fig. 3. The forms developed are:  $m$  (110), reflects well, but is plentifully sprinkled with natural etch-figures;  $o$  (111), reflects fairly well, also carries numerous etch-figures;  $a$  (100) and  $b$  (010), narrow and rather dull;  $z$  (331) and  $\pi$  (551), matt, reflect poorly, and tend to alternate, occurring as plane patches in the curved tracts between  $o$  and  $m$  shown in the figure;  $D$  (101) and  $e$  (011), very narrow but fairly bright. From the curved tract between  $m$  and  $o$ , diffuse reflections are also obtained in the positions corresponding to  $\omega_1$  (332),  $\omega_2$  (441), and  $\omega_3$  (991) or (10.10.1).

The natural etch-figures on  $o$  (111) (fig. 4) are small triangular pits, bounded by faces of  $z$  (331),  $D$  (101), and  $e$  (011). Those on  $m$  (110) are quadrilaterals, and are of particular interest, as their shape and relative orientation on adjacent  $m$ -faces indicate the symmetry-class of natrolite to be didigonal polar,  $C_{2v}$ , with the  $c$ -axis as polar axis;<sup>1</sup> they are pits, generally bounded by four faces, and wedge-shaped, but the larger ones may have a plane bottom parallel to the  $m$ -face they are on. The other bounding planes are: at the side of the pits nearest  $a$  (100), usually  $\gamma_1$  (230), but a few pits show  $\gamma_2$  (340),  $\gamma_3$  (350),  $n$  (120), or  $\gamma_4$  (250); at the side of the pits nearest  $b$  (010), usually  $a$  (100),  $\delta_2$  (11.2.0), or  $\delta$  (310), but a few pits showed  $\delta_3$  (520),  $\delta_4$  (210),

<sup>1</sup> Cf., however, below, under pyroelectricity and X-ray work.

or  $\delta_5$  (10.7.0) ; at the lower end of the pits, nearest the attached end of the crystals, a face  $\alpha$  truly in the zone  $mo$   $[1\bar{1}0]$ , and inclined at

TABLE III. Goniometric measurements on Benallt natrolite, by the author and Dr. L. J. Spencer.

Angle.	Meas. (M. H. H.).	Meas. (L. J. S.).	Calc.
$ma$ (110)(100)	$44^\circ 45', 44^\circ 10'$	$44^\circ, 44\frac{1}{2}^\circ$	$44^\circ 26\frac{1}{2}'$
$mm'$ (110)( $1\bar{1}0$ )	$87^\circ 56'$ to $89^\circ 50'$	$\{88^\circ 28'$ to $89^\circ 4'$ (Cleavage, $88^\circ 55\frac{1}{2}'$	88 53
$mb$ (110)(010)	$45^\circ 3', 45^\circ 24'$	$45^\circ 20', 45^\circ 35', 45^\circ 46'$	45 33 $\frac{1}{2}$
$mo$ (110)(111)	$62\frac{1}{2}^\circ$ to $64^\circ$	$63^\circ 6', 63^\circ 7', 63\frac{1}{2}^\circ$	63 12 $\frac{1}{2}$
$m\omega_1$ (110)(332)	$52^\circ, 52\frac{1}{2}^\circ$	—	52 51
$mz$ (110)(331)	$33^\circ 20', 33\frac{1}{2}^\circ, 37^\circ$	$33\frac{1}{2}^\circ, 34^\circ, 36\frac{1}{2}^\circ$	33 25
$m\omega_2$ (110)(441)	$26^\circ, 24\frac{1}{2}^\circ, 27^\circ$	$27\frac{1}{2}^\circ$	26 20
$m\pi$ (110)(551)	$18^\circ$ to $21^\circ 20'$	$21\frac{1}{2}^\circ, 21^\circ 34'$	21 36
$m\omega_3$ (110)( $h\bar{h}1$ )	$12^\circ$	—	$\{12 24^*$ $\{11 12^\dagger$
$be$ (010)(011)	$72^\circ$	$70^\circ, 71^\circ$	70 31
$aD$ (100)(101)	$70^\circ, 72^\circ$	—	70 10
$[ma][mo]$	$90^\circ, 89\frac{1}{2}^\circ, 90^\circ, 89^\circ$	—	90 0
Angles of etch-figures on $m$ (110):—			
$ma$	$\{9^\circ, 10^\circ, 6\frac{1}{2}^\circ, 7\frac{1}{2}^\circ, 6^\circ,$ $\{8-13\frac{1}{2}^\circ$	$11^\circ 21', 11^\circ 5', 14^\circ$	—
$[mo][ma]$	$0^\circ, 0^\circ 10', 0^\circ 20', 0^\circ, 0^\circ$ $3^\circ 10', 2^\circ 30', 3^\circ 20',$	—	—
$m\beta$	$\{2^\circ 50', 4^\circ 30', 3^\circ 20',$ $\{3^\circ 20', 2^\circ, 3^\circ, 3^\circ$	$4^\circ 19'$	—
$[mo][m\beta]$	$\{3^\circ 50', 4^\circ 30', 4^\circ 10',$ $\{4^\circ 10', 2^\circ 40', 2^\circ 50',$ $\{2^\circ 20', 2^\circ 20', 2^\circ 40',$ $\{3^\circ, 2\frac{1}{2}^\circ$	$\neq 0^\circ$	—
$m\gamma_1$ (110)(230)	$\{10^\circ 50', 10^\circ 34', 10\frac{1}{2}^\circ-$ $\{11\frac{1}{2}^\circ, 10^\circ 40', 10^\circ 45',$ $\{10^\circ 15', 11^\circ$	—	11 21
$m\gamma_2$ (110)(340)	$8\frac{1}{2}^\circ, 7^\circ 30', 7^\circ$	—	8 9 $\frac{1}{2}$
$m\gamma_3$ (110)(350)	$14^\circ 12'$	$14^\circ$	14 6
$mn$ (110)(120)	$\{17^\circ 30', 17^\circ 15', 18^\circ,$ $\{19^\circ, 18^\circ$	—	18 32 $\frac{1}{2}$
$m\gamma_4$ (110)(250)	$21-22^\circ, 23-25^\circ$	—	23 22
$m\delta$ (110)(310)	$27\frac{1}{2}^\circ, 26^\circ, 26^\circ$	—	26 20
$ma$ (110)(100)	$\{43^\circ 42', 43^\circ 56',$ $\{43^\circ 42', 45^\circ$	—	44 26 $\frac{1}{2}$
$m\delta_2$ (110)(11.2.0)	$34^\circ 3', 34^\circ 20', 34^\circ$	$32\frac{1}{2}^\circ$	34 20
$m\delta_3$ (110)(520)	$22\frac{1}{2}^\circ$	—	23 2
$m\delta_4$ (110)(210)	$17^\circ 37'$	—	18 19
$m\delta_5$ (110)(10.7.0)	$9^\circ 34', 9^\circ 33'$	—	9 54 $\frac{1}{2}$

\* (110)(991).

† (110)(10.10.1).

various angles to  $m$  in different pits— $6^\circ$ ,  $10^\circ$ ,  $11\frac{1}{2}^\circ$ , and  $14^\circ$  inclinations were noted, while some pits appear to have this face curved, with a slope ranging from  $8^\circ$  to  $14^\circ$ , i.e. from (881) to (14.14.1); at the upper end of the pits, nearest the terminated end of the crystals, a curved vicinal tract  $\beta$ , the inclination of which to  $m$  (110) generally ranges from  $2^\circ 0'$  to  $4^\circ 30'$ , and which is decidedly out of the zone  $mo$  [ $1\bar{1}0$ ], the interzonal angle  $[mo]:[m\beta]$  being about  $2\frac{1}{2}$ – $4\frac{1}{2}^\circ$ . In fig. 4 are shown drawings of some of these etch-figures made with a camera lucida; their actual size is 1– $1\frac{1}{2}$  mm. in length.

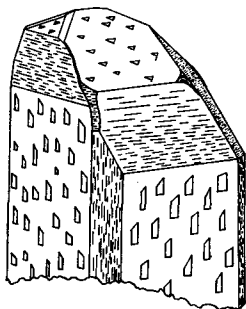


FIG. 3.

FIG. 3. Measured crystal of natrolite from Benallt, Carnarvonshire. Set up with  $a$  (100) in front.

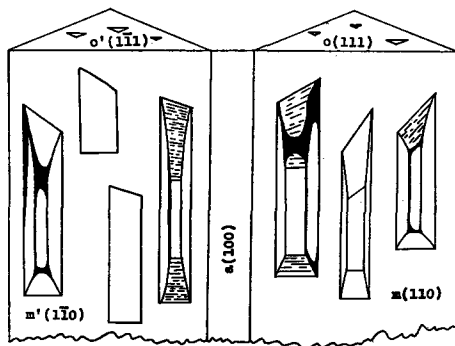


FIG. 4.

FIG. 4. Natural etch-figures on one of the measured crystals of natrolite from Benallt, Carnarvonshire.

R. J. Haiiy (1801) and J. D. Forbes (1834) found mesotype to be pyroelectric, but since mesotype included scolecite and mesolite as well as natrolite, this result is indefinite. P. Reiss and G. Rose (1843) studied crystals of natrolite from the Faeroe Isles, Fassa-thal, Langesundfjord, Puy-de-Dôme, and Jakuben, none of which they found to be pyroelectric. W. G. Hankel (1879), working with material from the Langesundfjord region, found certain pyroelectric effects, but they were not such as to enable any conclusions as to the symmetry-class to be made, and were probably false pyroelectricity, due to distortion of the crystal by uneven heating.

The available data being so unsatisfactory, it was evidently desirable to obtain new evidence of the pyroelectric behaviour of natrolite. Dr. W. H. Taylor kindly undertook to examine three plates of the Benallt material, cut perpendicular to the three

principal axes. The experiments, made by Mr. C. A. Meek in the Department of Physics of the University of Manchester, using the liquid air method,<sup>1</sup> showed conclusively that natrolite is weakly pyroelectric, with a single polar axis, the *c*-axis. This is in agreement with the results of the study of the natural etch-figures, showing that the *c*-axis is polar, and the symmetry class didigonal polar (orthorhombic hemimorphic),  $C_{2v}$ . Other work, however, suggests that natrolite is probably really monoclinic, though very closely pseudo-orthorhombic (see p. 283 below). The etch-figures and pyroelectric data would then fix the symmetry-class as digonal polar (monoclinic hemimorphic or sphenoidal),  $C_2$ .

Since this work was completed, F. Halla and E. Mehl (1932) have found that natrolite is piezoelectric; they do not, however, state which is the piezoelectric axis.

Parallel growths of natrolite with thomsonite have been observed by J. E. Hibsich (1917) on specimens from Jakuben, and from the Morwaner Bach, Salesl (both in Bohemia). Parallel growths with scolecite, from Bishopton, Renfrewshire, are described by G. Cesàro (1909). Needles of mesolite tipped with natrolite, from Kara-dagh, Crimea, are described by Miss O. A. Brinken (1914), while natrolite needles tipped with mesolite, from Fuchsberg, Salesl, are described by J. E. Hibsich (1917). The last type of association has been observed by the author on several specimens from the Neubauerberg, Mickenhan, Böhmisches-Leipa; the long (up to 2 cm.), hair-fine needles of natrolite are terminated by the pyramid  $o(111)$ , as usual, and an extension of mesolite in parallel position continues the needles, sometimes as much as 1 cm. farther in length; on other specimens, the mesolite forms a very thin coating over the whole of the natrolite needle (prism faces as well as pyramid). These parallel growths present a striking appearance under the polarizing microscope, the natrolite polarizing in brilliant colours, while the mesolite is apparently isotropic. I have since found that A. Scheit (1911) has also described this occurrence.

It may perhaps be noted here that whereas F. Zambonini (1908) doubts the occurrence of natrolite on Monte Somma, Vesuvius, there is a specimen in the British Museum (B.M. 95048), from the Vesuvian collection of T. Monticelli, which optical and chemical tests show to be definitely natrolite.

There are a fair number of determinations of the specific gravity

<sup>1</sup> A. J. P. Martin, *Min. Mag.*, 1931, vol. 22, p. 519.

of natrolite in the literature. The most reliable, twelve in number, range from 2.234 to 2.257, with a mean of 2.249. Less accurate determinations, and determinations made on impure or unsuitable material, 24 in number, range from 1.953 for a fine-grained lehuntite to 2.39 for an impure spreustein. The specific gravity of each of the analysed specimens (table I) has been determined, the results ranging from 2.238 to 2.250. The specific gravity must, however, be affected by the potassium content (the calcium content will have little effect, since two sodium atoms have nearly the same weight as one calcium atom); after allowing for the change of cell-size due to the replacement of sodium by potassium (see p. 278), there must be an increase in the specific gravity amounting to 0.0088 per potassium atom per unit cell replacing sodium; artificial base exchange produces just such an increase (see table VIII). After making this correction for all the specific gravity determinations for which the necessary chemical data are available (the eight of table I, and five from the literature<sup>1</sup>) we arrive at a mean figure of 2.242 for the probable specific gravity of fully hydrated potash-free natrolite.

Since the space-group determinations by A. L. Parsons (1930), L. Pauling (1930), F. Halla and E. Mehl (1930 and 1932), and J. Wyart (1931) do not agree, Mr. F. A. Bannister has undertaken a re-examination of the matter. Parsons's space-group results are definitely incorrect. Pauling and Wyart both assign the space-group  $C_{2v}^{19}$ , while Halla and Mehl concluded at first (1930) that it is  $C_{2v}^{18}$ ,  $D_{2d}^7$ , or  $D_{2d}^{23}$ , since they observed the diffractions (024), (028), (402), (802), and (204), which should be absent for  $C_{2v}^{19}$ ; but in their second paper (1932) they suggest that these observed diffractions are due to local lattice distortion ('Gitterstörungen'), or perhaps to small crystals attached to the principal one. Mr. Bannister has carefully examined several crystals, from Salesl and Kimberley; the diffractions (402), (042), (802), and (082) were observed repeatedly on rotation and oscillation photographs, but were always extremely weak. The first pair are stronger than the second, but their intensity is no more than perhaps 1/100 of that of an ordinary 'very weak' line. Diffractions (20.0.2), (10.0.4), and (14.0.4) could not be detected (Halla and Mehl found (802) stronger than (402)). Since the 'anomalous' diffractions appear with the same intensity on photographs of several crystals from two different localities, Halla and Mehl's explanations

<sup>1</sup> See G. J. Brush, 1861; A. Pelikan, 1902; B. J. Harrington, 1906; G. Tschermak, 1917; and T. L. Walker and A. L. Parsons, 1922.

(1932) seem untenable; the diffractions must be 'real', and the space-group cannot be strictly  $C_{2v}^{19}$ , though it approximates very closely to it.

The diffractions are all to be expected if the space-group is  $C_{2v}^{18}$ ; but W. H. Taylor<sup>1</sup> has found it impossible to build up a satisfactory structure for natrolite in this space-group, whereas in  $C_{2v}^{19}$  a good structure could be found. The most reasonable explanation seems to be that natrolite is not truly orthorhombic. It is monoclinic, elongated along the symmetry-axis, with  $\beta 90^\circ 0'$  and space-group  $C_2^8$ , but with an extremely close approximation to the orthorhombic symmetry  $C_{2v}^{19}$  of which  $C_2^8$  is a sub-group. This conclusion agrees with the X-ray data, but no optical evidence could be found to support it. On the other hand, it explains the continuity which vapour-pressure and X-ray work seem to indicate between natrolite and anhydrous metanatrolite, which is definitely monoclinic (see further under metanatrolite, below).

While this seems the most probable explanation of the anomalous diffractions, further work on the subject is desirable. It would be of particular interest to investigate whether they persist at liquid-air temperatures, and whether they are shown by the base-exchange products derived from natrolite, and by the most lime-free natrolites.

The unit-cell dimensions of natrolite are  $a 18.31 \pm 0.04$ ,  $b 18.66 \pm 0.04$ , and  $c 6.60 \pm 0.02$  Å., according to Mr. Bannister's measurements on crystals from Salesl (no. 2, table I) and Kimberley (no. 6, table I). From these values, together with the analytical figures and specific gravities, the number of oxygen atoms per unit cell was calculated for each specimen analysed, the results being included in table I. It will be observed that they all tend to be rather higher than 80, but the source of error could not be traced. The cell dimensions found by Parsons, Pauling, Halla and Mehl, and Wyart are all in fairly good agreement with the present figures.<sup>2</sup>

### Optics.

The first investigation of the optical properties of natrolite appears to have been by Sir David Brewster (1821, 1822), who examined material from Puy-de-Dôme and from Hohentwiel. He distinguished

<sup>1</sup> Private communication.

<sup>2</sup> Halla and Mehl's value for the unit cell content, 7.8 molecules of  $\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$ , is inaccurate owing to their use of an incorrect molecular weight; the true figure, from their cell-dimensions and specific gravity, is 8.17 molecules.

between natrolite and the other mesotypes and thomsonite, and also, for some reason, between natrolite from the two occurrences mentioned, but unfortunately never seems to have published the promised account of his results. The earliest available data are therefore those of A. Des Cloizeaux (1857, 1858, 1862), who showed that the optic axial plane is parallel to  $b$  (010) and the positive acute bisectrix perpendicular to  $c$  (001), the optic axial angle,  $2E$ , being  $90-100^\circ$ , with  $\rho < v$ .

Des Cloizeaux found straight extinction, and optics in all ways consistent with orthorhombic symmetry, but O. Luedecke (1881) found extinction-angles of  $5-6^\circ$  on  $m$  (110) on crystals from Aussig and Salesl; oblique extinction has also been observed by A. von Lasaulx (1881) on crystals from Trezza, Aci Castello, Sicily,  $3\frac{1}{2}-4\frac{1}{2}^\circ$ ; by W. C. Brøgger (1889) on Norwegian crystals,  $1\frac{1}{2}-3^\circ$ ; and by S. J. Thugutt (1911) on 'epinatrolite' from Sauerbrunnenstrasse, Karlsbad,  $5-6^\circ$ . On the other hand, O. Schmidt (1886) could find no evidence of monoclinic symmetry on crystals from Brevig, Aussig, or Salesl, nor could E. Artini (1887) on crystals from several localities, nor J. E. Hibsich (1917) on a large number of crystals from Salesl. The author has examined hundreds of crystals, from most of the localities represented in the British Museum collection, and has never met with any which failed to give perfectly straight extinction on  $m$ ; one or two sub-parallel groups gave anomalous effects, but on crushing these, the cleavage fragments all extinguished straight. Many of these crystals were potassiferous (Brøgger suggested that monoclinic natrolites were essentially potassiferous, the extinction-angle increasing with the potassium content). It cannot therefore be said that there is at present any satisfactory evidence for the existence of monoclinic natrolites with the symmetry-axis perpendicular to the elongation. But the causes of the observed extinction-angles are not yet clear; imperfect adjustment of apparatus, vicinal faces, and sub-parallel growths have all been suggested.

After the X-ray work had shown that the space-group of natrolite cannot be truly  $C_{2v}^{19}$ , and is probably  $C_2^8$ , the symmetry-axis being parallel to the elongation, several cut plates of the Benallt material were re-examined. No trace of monoclinic dispersion of the bisectrices could be found, nor any departure of the extinction on  $c$  from diagonal. The departure of the symmetry from orthorhombic must therefore be extremely small.

Several sets of measurements of the refractive indices of natrolite

have been published,<sup>1</sup> but with the exception of one by S. Di Franco (1929), all have been made on unanalysed material; it is not clear from Di Franco's analysis whether lime and potash were really absent, or merely left undetermined. There are several sets of optic axial angle determinations in the literature,<sup>2</sup> but only those by W. C. Brögger (1889) and E. Artini (1887) were made on analysed material (Artini's material was analysed by G. B. Negri (1890)).

The author has made refractive index determinations by the prism method on four, and optic axial angle determinations on six analysed specimens. The optic axial angle determinations were made with crystal fragments immersed in a liquid of refractive index equal to the refractive index  $\beta$  of the crystal, giving 2V direct, except for the Benallt material; a large plate of the latter, cut perpendicular to the *c*-axis, gave 2E. The figures for the Benallt material are decidedly the most accurate, since the prisms cut from these large crystals have polished refracting surfaces about 3 mm. square.

The large plate of the Benallt natrolite cut perpendicular to the *c*-axis also served for direct measurements of  $\beta - \alpha$ . These were made at the same time as the optic axial angle measurements, the wave-length of the light being adjusted by the monochromator so that the centre of the interference-figure (i.e. the Bx) was dark, and the order of the interference involved found by counting the rings between the bisectrix and an optic axis. Between  $\lambda$  4480 and 7320 Å., interferences in the 20th to the 35th order were obtained. The thickness of the plate (measured with a micrometer screw-gauge) is the chief source of error in these determinations, so that the relative values of  $\beta - \alpha$  found for various wave-lengths are considerably more accurate than the absolute values.

Unfortunately, those specimens richest in lime and in potash were not suitable for refractive index determinations by the prism method; determinations by the immersion method showed no differences outside the limits of error ( $\pm 0.003$ ) from the indices found for the Benallt material. The differences between the refractive indices of the Benallt natrolite and of the other specimens measured by the prism method are barely outside the limits of experimental error, and could not be accurately correlated with the small variations in

<sup>1</sup> A. Des Cloizeaux, 1862; W. C. Brögger, 1879; J. Lorenzen, 1889; K. Zimányi, 1894; S. Di Franco, 1929.

<sup>2</sup> A. Des Cloizeaux, 1862; W. C. Brögger, 1879, 1889; E. Palla, 1884; E. Artini, 1887, 1888; J. Lorenzen, 1889; S. Di Franco, 1929.



TABLE IV a. Optical measurements on Benallt and Puy de Marmant natrolites (refractive indices and optic axial angles).

λ.	Benallt, no. 4.					Puy de Marmant, no. 1.		
	α.	β.	γ.	2E.	2V.	α.	γ.	2V.
7682	1.4737	1.4772	1.4856	100° 40'	62° 49'	—	—	—
7200	1.4747	1.4781	1.4866	100 20	62 36	1.4769	1.4890	—
7000	1.4756	1.4786	1.4876	100 38	62 44	1.4773	1.4894	—
6708	1.4764	1.4795	1.4887	100 51	62 48	1.4777	1.4898	59° 14'
6563	1.4768	1.4798	1.4892	100 56	62 50	1.4779	1.4900	—
6250	1.4777	1.4809	1.4899	101 2	62 50	1.4783	1.4901	59 34
6000	1.4787	1.4819	1.4909	101 24	62 58	1.4789	1.4912	—
5893	1.4789	1.4822	1.4911	101 36	63 3	1.4799	1.4918	59 37
5780	1.4796	1.4830	1.4918	101 43	63 4	1.4804	1.4925	59 40
5461	1.4805	1.4838	1.4923	101 53	63 7	1.4813	1.4938	59 44
5350	1.4811	1.4846	1.4931	102 6	63 11	1.4821	1.4946	59 41
5000	1.4829	1.4864	1.4957	102 8	63 11½	1.4842	1.4973	59 30
4916	1.4835	1.4868	—	—	—	—	—	—
4861	1.4837	1.4871	1.4965	101 56	63 4	1.4856	1.4988	59 14
4550	1.4860	1.4896	1.4993	101 42	62 45	1.4878	1.5017	59 8
4358	1.4878	1.4912	1.5011	101 26	62 32	1.4894	1.5035	—
4200	1.4897	1.4933	1.5027	101 18	62 22	—	—	—
4047	1.4924	1.4946	1.5048	—	—	—	—	—

Probable errors (excluding wave-lengths λ7682, 7200, 4200, and 4047): in the refractive indices, Benallt material, maximum ± 0.0003, mean ± 0.0001; Puy de Marmant material, ± 0.0010; in the optic axial angles, Benallt material, maximum ± 4', mean ± 1½'; Puy de Marmant material, ± 10'.

TABLE IV b. Optical measurements on Cape Blomidon, Salesl, Kimberley, and Snake Hill natrolites (refractive indices and optic axial angles).

λ.	Cape Blomidon, no. 5.			Salesl, no. 2.		Kimberley, no. 6.	Snake Hill, no. 8.
	α.	γ.	2V.	α.	γ.	2V.	2V.
7000	—	1.4853	—	—	—	—	—
6708	1.4750	1.4865	61° 31'	1.4780	1.4891	63° 20'	—
6563	1.4764	1.4881	—	—	1.4898	—	—
6250	1.4780	1.4887	61 40	—	1.4905	63 51	—
6000	1.4792	1.4895	—	—	1.4912	—	—
5893	1.4800	1.4901	61 44	1.4806	1.4919	64 0	60° ± 1°
5780	1.4806	1.4907	61 45	—	1.4921	64 10	—
5461	1.4812	1.4916	61 45	—	1.4926	64 20	—
5350	1.4818	1.4922	61 48	1.4825	1.4935	64 25	—
5000	1.4836	1.4937	61 40	—	1.4948	64 23	—
4861	1.4842	1.4943	61 25	—	1.4957	64 7	—
4550	—	1.4960	—	—	—	—	—

Maximum probable error in the refractive indices, ± 0.0010.

TABLE IV c. Optical measurements on Benallt natrolite, no. 4 (birefringence).  
Interferences with a plate 4.55 mm. thick  $\perp c(001)$ , in several orders.

$\lambda$ .	$\beta - \alpha$ .	Order.	$\lambda$ .	$\beta - \alpha$ .	Order.
7320	0.003210	20th	5420	0.003328	28th
6960	3225	21	5250	3337	29
6708	3236	22	5110	3362	30
6470	3265	23	4970	3379	31
6220	3274	24	4830	3390	32
5990	3284	25	4700	3402	33
5780	3296	26	4590	3423	34
5610	0.003322	27th	4480	0.003439	35th

chemical composition; there is some evidence that increase in lime lowers the refractive index slightly, while potash has little effect (see further under base-exchange, below). No variations in the birefringence,  $\gamma - \alpha$ , or dispersion with the small amounts of lime and potash were detected. The optic axial angle shows fairly considerable variations, which appear to arise from variations in  $\beta - \alpha$ , but these again could not be correlated with the changes in chemical composition.

All these optical data are collected in tables IV *a*, *b*, and *c*. The refractive index and birefringence curves (fig. 5 shows those of the Benallt material only, the others falling too close to be distinguished) present nothing of particular note, but the measurements of 2E and 2V (fig. 6) for a large number of wave-lengths disclosed one point of some interest. The dispersion of the optic axial angle is usually given as  $\rho < \nu$ , and the angle does indeed increase steadily from the red to the blue-green, but on taking the measurements farther, it was found that 2E shows a maximum at  $\lambda$  5150 Å., decreasing again for blue and violet light. No measurements had previously been made in this portion of the spectrum. The internal angle, 2V, shows a similar behaviour (both in the Benallt material and in the other measured specimens); from the red to  $\lambda$  5150 in the blue-green it increases steadily, then falls sharply, and for the violet is less than for the red.

The exact orientation of the prisms used for refractive index measurements was in every case measured on the goniometer, and a correction for imperfect orientation applied to the refractive indices found by the usual formulae. The accuracy of the work on the Benallt material was checked by comparing the two values of  $\alpha$  found with the two prisms; a further check was obtained by comparing the

values of  $\beta - a$  and  $\gamma - a$  obtained as differences in the refractive index measurements with the directly determined values of  $\beta - a$  and the values of  $\gamma - a$  computed from  $\beta - a$ ,  $2E$ , and  $\beta$ . Except for the

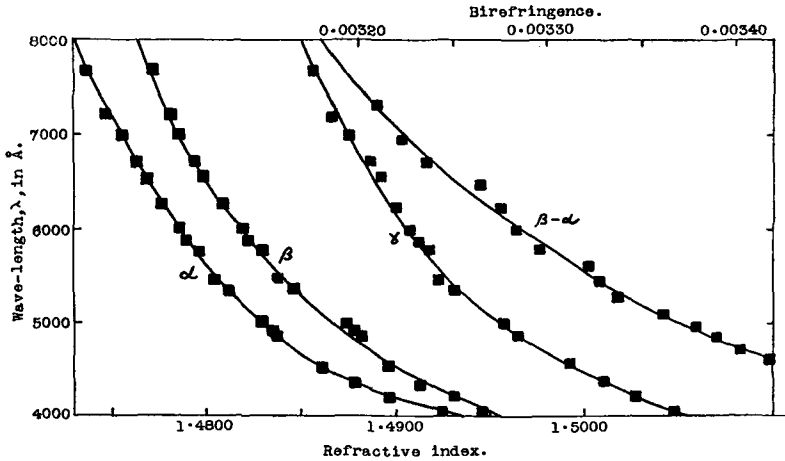


FIG. 5. The variation of the refractive indices and birefringence ( $\beta - a$ ) of natrolite from Benallt, Carnarvonshire, with the wave-length of the light.

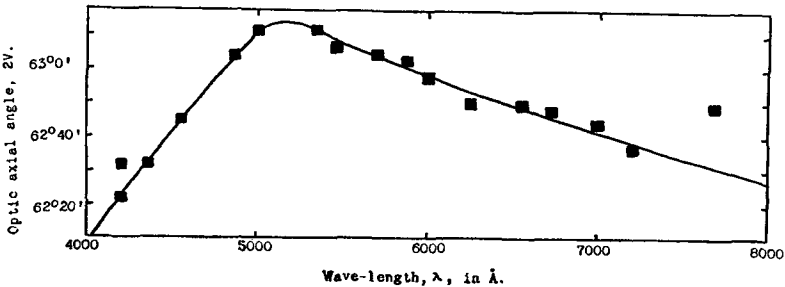


FIG. 6. The variation of the optic axial angle,  $2V$ , of natrolite from Benallt, Carnarvonshire, with the wave-length of the light.

far red and far violet, the agreement was very good. The maximum and average probable errors so found are noted in table IVa. The probable errors for the other specimens are estimated.

The mean dielectric constant of natrolite (a quantity closely related to the refractive index) has been measured by E. E. Fairbanks (1926), who found  $\epsilon = 11 \pm 1$  at  $31^{\circ} \text{C}$ .; measurements of the dielectric constant along the three crystallographic axes would be of considerable interest, but have never been attempted.

*Dehydration and vapour-pressure.*

Several studies have been made of the dehydration of natrolite. F. Rinne (1890) was interested only in the complete dehydration, which leads to metanatrolite (see below). G. Tammann (1897) made a set of isothermal observations at the ordinary temperature; his curve runs parallel to the isothermal dehydration curve for 20° C. deduced from the author's vapour-pressure observations, but there are two discrepancies. In the first place, the losses of water when the saturated zeolite was exposed over sulphuric acid of various concentrations are throughout higher than would be expected from the author's results by about 0.25%; this is the amount Tammann found to be lost at a water vapour-pressure of 12.5 mm. Hg. The author's curves show that the vapour-pressure of fully hydrated natrolite is considerably less than that of water, being about 8 mm. at 20° C. (that of water is 17.4 mm. at 20° C.), and it appears probable that the excess 0.25% water absorbed when natrolite is exposed to saturated water-vapour is merely adsorbed, not included in the lattice; this would account for the steep fall of this first part of Tammann's curve, followed by a more gradual slope as the true crystal water is removed.

The second discrepancy is that if this first 0.25% water is accepted as merely adsorbed, Tammann's water determination shows the fully hydrated natrolite as still containing 10.15% water, considerably in excess of 16 mols. per unit cell. But Tammann determined the water as loss on ignition, and it is readily shown that, on ignition, natrolite loses a part of its soda as well as the water, thus explaining Tammann's high result.

The isobaric dehydration of natrolite has been studied by F. Zambonini (1906, 1908) and by A. Cavinato (1927), with very different results. Observations by the rough method of dehydration in an oven without any attempt at control of the water vapour-pressure have been made by several workers,<sup>1</sup> with very variable results. The author has carried out a few isobaric dehydrations of natrolite which have only served to convince him that the approach to equilibrium is extremely slow, and that even so long as 8 hours is often insufficient for its attainment. The various studies, however,

<sup>1</sup> A. Damour, 1858; C. Hersch, 1887; W. H. Melville, 1892; G. Friedel, 1899; F. W. Clarke and G. Steiger, 1900; G. Stoklossa, 1918; A. Beutell, 1921; T. L. Walker and A. L. Parsons, 1922; S. Di Franco, 1929.

serve to show the general character of the isobaric curve; dehydration is at first very slow and gradual, until a temperature variously given as from 240 to 300° C. (for a water vapour-pressure of 10 mm.) is reached, when a rapid loss of water takes place, and the crystals, previously clear, become opaque, fragile, and porcellaneous. At about 350° C. dehydration is complete.

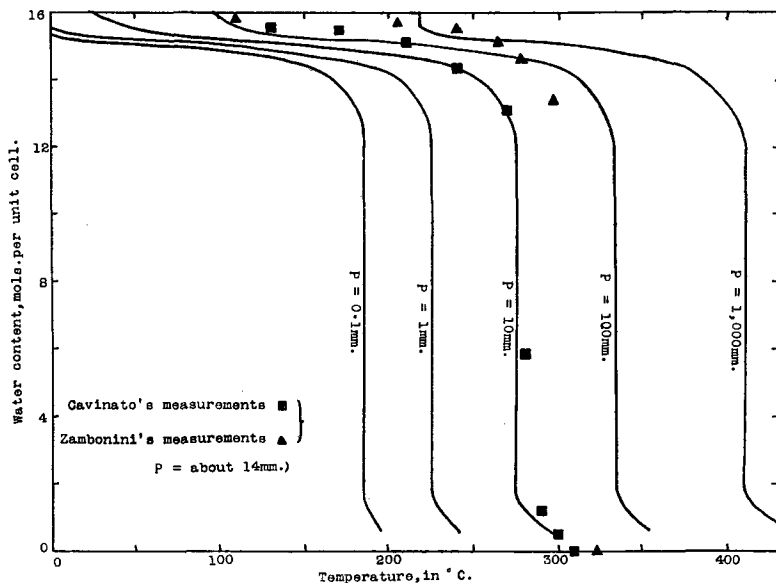


FIG. 7. Isobaric dehydration curves of natrolite (specimen no. 2, from Salesl, Bohemia), together with the isobaric dehydration results of Zambonini (1906, 1908) and Cavinato (1927).

The vapour-pressure experiments leave no doubt as to the true course of the isobaric curves, and the computed isobaric curve for a water vapour-pressure of 10 mm. Hg agrees quite well with Cavinato's results for temperatures above 240° C., but only badly below. The computed isobaric curves, from the vapour-pressure data, are shown in fig. 7, together with the experimental results of Zambonini and Cavinato for a vapour-pressure of about 14 mm.

The vapour-pressure measurements were made with the apparatus and in the manner previously described and figured,<sup>1</sup> and are tabulated and graphed in the same way. One or two slight modifications

<sup>1</sup> Part II of this series, loc. cit.

were, however, made in the apparatus, which experience had proved desirable. The narrow tube connecting the zeolite bulb, *Z*, with the null manometer was lengthened, to ensure avoidance of the trouble met with in the work on thomsonite, of uneven heating of the zeolite due to its shifting in the bulb and getting too near the outside of the oven.

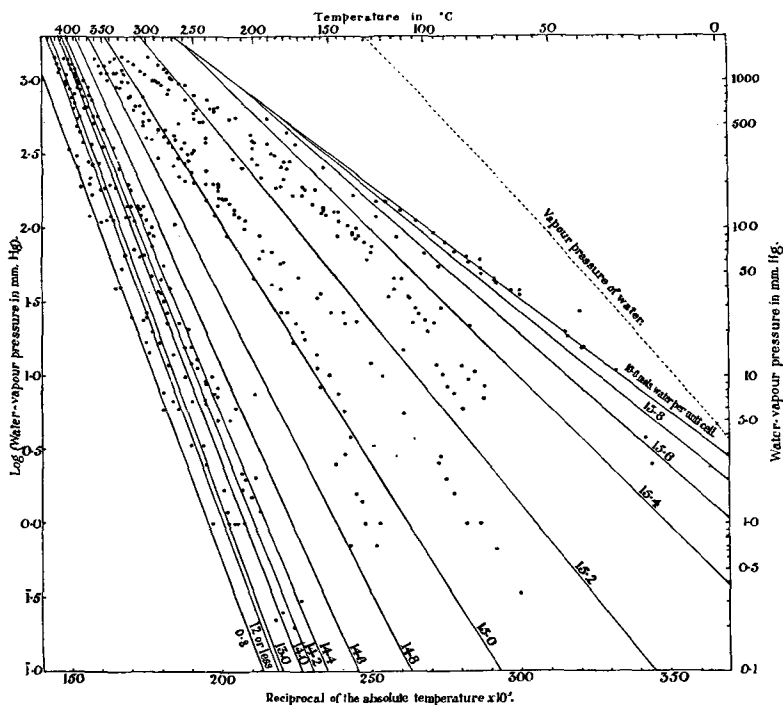


FIG. 8. Isohydric vapour-pressure curves of natrolite (specimen no. 2, from Salesl, Bohemia).

The tube between the bulb *B* and the tap *H* was lengthened and bent over at right angles, so as to avoid the heat rising from the auxiliary oven *O*, which tended to soften the tap-grease and make the tap leak in its former position. Lastly, a new main manometer was installed, with a range up to 1450 mm. Hg pressure, while a good high-temperature thermometer enabled the temperature range to be extended to about 420° C.

The results obtained (table V) were satisfactory, equilibrium being rapidly established with either rising or falling temperature, and

repeat observations were in good agreement. The greatest error is in measurement of the temperature, which may occasionally be out by as much as 5° C. A thermocouple would be more suitable for this measurement, but was not available.

Fig. 8 shows the isohydric curves plotted from the experimental data. The molecular heats of hydration,  $Q$ , for different degrees

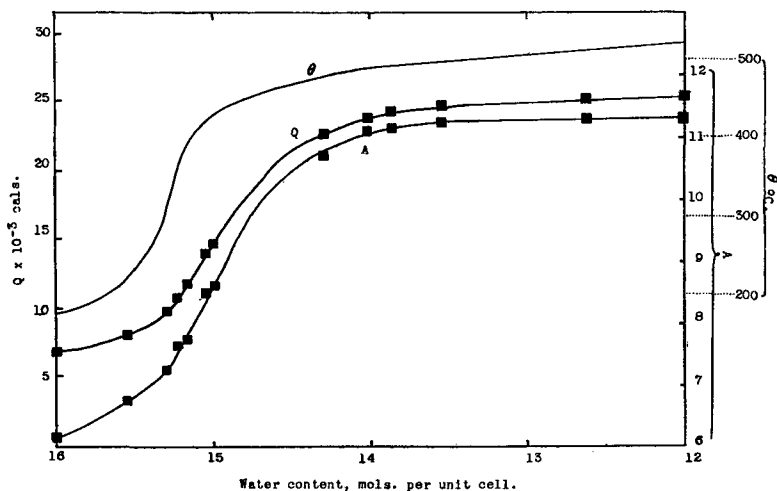


FIG. 9. The variation, with the water content, of the molecular heat of hydration ( $Q$ ) of natrolite, the integration constant ( $A$ ) of the equation

$$\log_{10} p = A - Q/RT(\log_e 10),$$

and the temperature ( $\theta$ ) at which the isohydric curve for fully hydrated natrolite cuts the isohydric curve for natrolite of a lower degree of hydration.

of hydration, and the integration constants,  $A$ , of the equation  $\log_{10} p = A - Q/RT(\log_e 10)$  (where  $T$  is the absolute temperature and  $p$  the water vapour-pressure in mm. Hg) are listed in table VI and plotted in fig. 9. As with thomsonite, the procedure adopted was to deduce  $Q$  and  $A$  from the low-pressure region of the experimental curves, then to plot  $Q$  and  $A$  against the degree of hydration, and to draw 'theoretical' isohydric lines, assumed straight, by means of  $Q$  and  $A$  values interpolated from this plot. Isothermal curves were also computed, but are not reproduced, as they give no additional information. Computed isobaric curves are shown in fig. 7. In the high-pressure region of the experimental data, where the dead-space loss of water causes an appreciable departure of the experimental

curves from the true isohydric lines,<sup>1</sup> the agreement between observed and calculated pressures is still quite good (see table V).

TABLE V. The vapour-pressure of natrolite (Salesl, B.M. 49545) at various degrees of hydration. (Results plotted in fig. 8.)

*c* = water content, mols. per unit cell; *t* = temperature, in °C.; *p* = water vapour-pressure in mm. Hg; *p*<sub>calc.</sub> = water vapour-pressure calculated from the isohydric curves of fig. 8; + temperature rising; - temperature falling; ? doubtful equilibrium.

Series 1.						Series 3.†					
<i>c.</i>	<i>p.</i>	<i>t.</i>	Log <i>p.</i>	Log <i>p</i> <sub>calc.</sub>	Notes.	<i>c.</i>	<i>p.</i>	<i>t.</i>	Log <i>p.</i>	Log <i>p</i> <sub>calc.</sub>	Notes.
16-00	3.8	19	0.58	0.87	? *	15-17	0.34	60	1.53	1.75	+
15-99	32	60	1.55	1.51	+	15-17	0.17	45	1.23	1.35	-
16-00	20	45	1.30	1.29	-	15-17	0.68	70	1.83	1.96	+
16-00	11	28	1.04	1.03	-	15-17	1.0	76	0.00	0.11	+
15-99	38	64	1.58	1.56	+	15-17	1.0	81	0.00	0.23	+
16-00	18.5	44	1.27	1.37	-	15-17	1.6	86	0.20	0.33	+
16-00	16	39	1.20	1.20	-	15-17	2.0	90	0.30	0.42	+
15-99	48.5	75	1.69	1.71	+	15-17	2.6	94	0.41	0.50	+
15-99	42	69	1.62	1.62	-	15-17	4.4	103	0.64	0.66	+
15-99	46	70	1.66	1.63	+	15-17	10.0	120	1.00	0.98	+
15-99	40	70	1.60	1.63	+	15-17	5.6	110	0.74	0.79	-
15-98	54	76	1.73	1.71	-	15-17	12.4	127	1.09	1.09	-
15-98	58.5	80	1.77	1.77	+	15-16	23	143	1.43	1.32	+
15-98	65	81	1.81	1.78	+	15-14	58	182	1.76	1.84	+
15-98	69	86	1.84	1.85	+	15-15	34	158	1.53	1.52	+
15-97	80	90	1.90	1.90	+	15-16	23	142	1.36	1.31	+
15-97	94	96	1.97	1.97	+	15-16	27	149	1.43	1.44	+
15-97	112	105	2.05	2.06	+	15-16	36	157	1.56	1.53	+
15-96	132	112	2.12	2.13	+	15-15	47	170	1.67	1.69	+
15-95	151	119	2.18	2.21	+	15-15	59	180	1.77	1.82	+
						15-14	69	188	1.84	1.92	+
						15-13	89	195	1.95	2.01	+
						15-12	161	229	2.21	2.37	+ ?
						15-13	148	220	2.17	2.31	-
						15-13	131	216	2.12	2.26	-
						15-13	111	208	2.05	2.17	-
						15-12	159	225	2.20	2.33	+
						15-13	135	216	2.13	2.26	-
						15-11	201	240	2.30	2.50	+
						15-09	277	258	2.44	2.69	+
						15-07	344	270	2.55	2.73	+

\* After standing 10 days at room-temperature.

† Owing to an accident to the apparatus, the water contents of these series are only approximate.

<sup>1</sup> With thomsonite, the maximal pressures measurable by the apparatus being so much lower, the dead-space loss was not noticeable.



TABLE V (continued).

Series 3 (continued).†						Series 4 (continued).					
c.	p.	t.	Log p.	Log p <sub>calc.</sub>	Notes.	c.	p.	t.	Log p.	Log p <sub>calc.</sub>	Notes.
15-07	380	275	2.58	2.76	+	15-22	530	242	2.72	2.85	+
15-06	415	280	2.62	2.78	+	15-21	555	246	2.74	2.86	+
15-05	470	286	2.67	2.84	+	15-20	610	250	2.78	2.87	+
15-03	540	295	2.73	2.91	+	15-20	743	268	2.87	2.91	+
15-02	600	300	2.78	2.93	+	15-20	823	276	2.91	3.04	+
15-00	680	310	2.83	2.99	+	15-19	927	285	2.97	3.07	+
15-00	680	305	2.83	2.96	-	15-19	1000	290	3.00	3.10	+
14-93	980	325	2.99	3.03	+	15-19	1000	294	3.00	3.12	+
14-91	1130	334	3.05	3.08	+	15-18	1100	300	3.04	3.14	+
14-86	1358	340	3.13	3.10	+	15-15	1281	311	3.11	3.18	+
						15-15	1350	318	3.13	3.22	+
Series 4.						15-14	1440	325	3.16	3.26	+
15-30	9.5	81	0.98	1.07	+	15-17	1180	306	3.07	3.15	-
15-30	30	100	1.48	1.38	+	15-19	989	287	2.99	3.09	-
15-29	41	114	1.69	1.58	+	15-19	873	275	2.94	3.03	-
15-29	79	126	1.88	1.74	+	15-20	630	249	2.80	2.86	-
15-28	99	135	2.00	1.84	+	15-25	350	202	2.54	2.58	+
15-28	128	146	2.11	1.98	+						
15-30	20	98	1.30	1.35	+	Series 5.†					
15-30	26	103	1.42	1.42	+	15-27	82	131	1.91	1.73	+
15-30	29	105	1.46	1.45	+	15-23	97	136	1.96	1.82	+
15-29	43	114	1.63	1.59	+	15-25	126	155	2.10	2.06	+
15-29	57	122	1.76	1.70	+	15-29	29	93	1.46	1.26	+
15-29	85	135	1.93	1.88	+	15-27	71	127	1.84	1.55	+
15-29	111	145	2.05	2.01	+	15-27	93	136	1.97	1.82	+
15-28	139	155	2.14	2.09	+	15-29	22	80	1.34	1.04	+
15-27	190	168	2.28	2.21	+	15-26	105	141	2.02	1.86	+
15-26	256	181	2.41	2.36	+	15-26	112	145	2.05	1.93	+
15-30	6.0	83	0.78	1.10	+?	15-26	133	154	2.12	2.04	+
15-29	35	108	1.54	1.49	+	15-25	145	161	2.16	2.12	+
15-30	5.4	74	0.73	0.94	+?	15-25	167	174	2.22	2.27	+
15-30	6.8	78	0.83	1.01	+	15-25	185	185	2.27	2.39	+
15-30	7.4	83	0.87	1.10	+	15-25	165	168	2.22	2.20	+
15-30	23	96	1.36	1.32	+	15-24	191	182	2.28	2.34	+
15-30	46	114	1.66	1.60	+	15-24	219	195	2.34	2.49	+
15-29	89	134	1.95	1.85	+	15-23	255	210	2.41	2.62	+
15-28	128	148	2.11	2.01	+	15-22	298	218	2.47	2.66	+
15-27	182	159	2.26	2.11	+	15-21	338	230	2.53	2.71	+
15-26	250	178	2.40	2.31	+	15-20	380	240	2.58	2.75	+
15-26	298	203	2.47	2.60	+	15-19	520	265	2.71	2.84	+
15-26	270	198	2.43	2.48	+						
15-25	406	220	2.61	2.54	+	Series 6.					
15-22	522	239	2.72	2.84	+	15-29	15.3	110	1.18	1.52	?
						15-29	12.0	95	1.08	1.28	?

† Owing to an accident to the apparatus, the water contents of these series are only approximate.

TABLE V (continued).

<i>Series 6 (continued).</i>						<i>Series 7 (continued).</i>					
<i>c.</i>	<i>p.</i>	<i>t.</i>	Log <i>p.</i>	Log <i>p</i> .calc.	Notes.	<i>c.</i>	<i>p.</i>	<i>t.</i>	Log <i>p.</i>	Log <i>p</i> .calc.	Notes.
15-29	10.4	92	1.01	1.23	+	15-08	39	182	1.59	1.72	+
15-29	8.5	90	0.93	1.20	-	15-07	63	196	1.80	1.90	+
15-29	7.5	87	0.88	1.15	+	15-07	100	207	2.00	2.05	+
15-29	23	106	1.36	1.46	+	15-06	126	216	2.10	2.12	+
15-29	35	117	1.54	1.63	+	15-06	157	223	2.20	2.18	+
15-28	62	129	1.79	1.75	+	15-05	190	230	2.28	2.24	+
15-28	88	145	1.95	1.98	+	15-08	18	166	1.25	1.48	+
15-27	123	152	2.09	2.03	+	<i>Series 8.</i>					
15-26	180	166	2.26	2.00	+	15-05	0.7	139	1.85	0.88	+ ?
15-26	190	167	2.28	2.20	+	15-05	2.5	147	0.40	1.04	?
15-25	282	179	2.45	2.34	+	15-05	8.5	156	0.93	1.19	+
15-24	320	189	2.51	2.41	+	15-05	11.5	158	1.06	1.22	+
15-24	280	175	2.45	2.27	+	15-05	23	172	1.36	1.44	+
15-24	310	186	2.49	2.39	+	15-05	27	178	1.43	1.53	+
15-23	375	191	2.57	2.42	+	15-04	46	188	1.62	1.64	+
15-22	430	203	2.63	2.51	+	15-04	70	195	1.85	1.73	+
15-21	566	215	2.75	2.57	+	15-03	122	213	2.08	1.95	+
15-20	650	231	2.81	2.65	+	15-02	200	229	2.30	2.15	+
15-19	743	237	2.87	2.66	+	15-01	246	239	2.39	2.24	+
15-20	667	230	2.82	2.64	-	15-00	336	250	2.53	2.35	+
15-21	550	220	2.74	2.62	-	15-00	382	258	2.58	2.44	+
15-23	384	200	2.58	2.54	-	15-00	326	252	2.51	2.36	+
15-20	640	236	2.81	2.66	+	15-03	140	230	2.15	2.16	+
15-23	380	202	2.59	2.55	-	15-02	206	250	2.31	2.39	+
15-21	610	233	2.79	2.64	+	15-01	236	254	2.38	2.41	+
15-29	7.0	74	0.84	0.92	+	15-01	314	262	2.50	2.44	+
15-18	793	250	2.90	2.71	+	14-99	426	269	2.63	2.54	+
15-16	989	265	2.99	2.80	+	15-00	400	268	2.60	2.54	-
15-16	1013	272	3.01	2.87	+	15-01	350	262	2.54	2.50	-
15-14	1143	277	3.06	2.89	+	15-01	286	251	2.46	2.44	-
15-13	1280	286	3.11	2.98	+	15-01	296	260	2.47	2.53	+
15-11	1430	296	3.16	3.05	+	14-99	470	278	2.67	2.64	+
15-14	1210	280	3.08	2.92	-	14-95	770	303	2.89	2.83	+
15-16	1060	273	3.02	2.88	-	14-94	980	318	2.99	2.97	+
15-17	930	260	2.97	2.74	-	14-92	1090	324	3.04	3.00	+
15-25	216	180	2.33	2.33	+	14-92	1181	325	3.07	3.02	+
<i>Series 7.</i>						14-89	1410	335	3.15	3.07	+
15-08	1.4	132	0.15	0.91	?	<i>Series 9.</i>					
15-08	3.8	138	0.58	1.03	?	15-02	0.7	124	1.85	0.44	?
15-08	5.8	142	0.76	1.09	+	15-02	1.0	122	0.00	0.41	?
15-08	7.5	146	0.88	1.15	+	15-02	3.4	126	0.53	0.47	+
15-08	10.2	151	1.01	1.24	+	15-02	1.0	130	0.00	0.57	?
15-08	14	158	1.15	1.36	+	15-02	1.6	136	0.20	0.68	+
15-08	20	168	1.30	1.48	+						

TABLE V (continued).

<i>Series 9 (continued).</i>						<i>Series 10 (continued).</i>					
c.	p.	t.	Log p.	Log p <sub>calc.</sub>	Notes.	c.	p.	t.	Log p.	Log p <sub>calc.</sub>	Notes.
15-02	2.9	142	0.47	0.79	+	14-28	182	316	2.26	2.16	+
15-02	17	173	1.23	1.34	+	14-28	142	308	2.15	2.06	-
15-02	27	182	1.43	1.47	+	14-29	116	300	2.06	1.92	-
15-02	46	200	1.66	1.76	+	14-29	90	291	1.95	1.82	-
15-01	90	221	1.95	2.01	+	14-30	1.7	210	0.23	0.41	+
15-00	120	232	2.08	2.11	+	14-30	5.0	220	0.70	0.50	+
15-00	154	240	2.19	2.21	+	14-30	7.5	232	0.88	0.76	+
14-99	210	258	2.32	2.42	+	14-30	5.9	215	0.78	0.40	-
14-99	258	270	2.42	2.55	+	14-30	10.0	234	1.00	0.81	+
14-99	226	264	2.35	2.49	-	14-30	6.8	252	0.83	1.14	+
14-98	300	286	2.48	2.71	+	14-30	27	277	1.43	1.13	+
14-97	406	300	2.61	2.84	+	14-30	46	282	1.66	1.67	+
14-96	522	303	2.72	2.88	+	14-30	104	291	2.01	1.82	+
14-95	624	312	2.80	2.91	+	14-28	142	303	2.15	1.95	+
14-94	765	320	2.88	2.96	+	14-28	200	320	2.30	2.21	+
14-92	880	329	2.94	3.03	+	14-27	250	330	2.40	2.35	+
14-91	1010	343	3.00	3.16	+	14-26	350	338	2.54	2.46	+
14-90	1140	353	3.05	3.21	+	14-25	470	349	2.67	2.62	+
14-89	1247	357	3.10	3.25	+	14-24	580	357	2.76	2.72	+
14-88	1380	362	3.14	3.29	+	14-22	750	365	2.87	2.80	+
14-89	1260	347	3.10	3.17	-	14-22	790	367	2.90	2.83	+
14-90	1110	338	3.05	3.15	-	14-20	920	370	2.96	2.87	+
14-92	900	331	2.95	3.05	-	14-20	1030	378	3.01	2.95	+
14-94	770	317	2.89	2.95	-	14-19	1120	381	3.05	3.01	+
14-96	486	301	2.69	2.90	-	14-18	1200	382	3.08	3.03	+
14-97	396	292	2.60	2.76	-	14-17	1300	386	3.11	3.06	+
						14-16	1420	395	3.15	3.16	+
<i>Series 10.</i>						<i>Series 11.</i>					
14-30	0.1	197	1.00	0.01	?	13-53	122	305	2.09	1.96	+
14-30	1.0	216	0.00	0.43	?	13-53	106	269	2.03	1.11	?
14-30	11.6	247	1.06	1.06	+	13-55	21	257	1.32	0.90	-
14-30	13.3	249	1.12	1.07	+	13-55	38	286	1.58	1.64	+
14-30	9.3	241	0.97	0.91	-	13-54	66	302	1.82	1.70	+
14-30	11.4	247	1.06	1.06	+	13-55	40	273	1.60	1.21	-
14-30	7.3	229	0.86	0.71	-	13-55	48	291	1.68	1.53	+
14-30	5.0	228	0.70	0.70	-	13-53	120	325	2.08	2.06	+
14-30	1.0	215	0.00	0.40	-	13-53	142	325	2.15	2.06	+
14-30	6.5	240	0.81	0.90	+	13-53	194	342	2.29	2.32	+
14-30	6.8	240	0.83	0.90	+	13-52	278	356	2.44	2.52	+
14-30	12.2	255	1.09	1.16	+	13-51	370	365	2.57	2.63	+
14-30	23	266	1.36	1.39	+	13-50	580	380	2.76	2.82	+
14-30	32	274	1.50	1.53	+	13-45	930	403	2.97	3.12	+
14-29	56	281	1.75	1.61	+	13-43	1240	412	3.09	3.22	+
14-29	94	294	1.97	1.87	+	13-44	1110	405	3.04	3.13	-
14-28	136	305	2.13	2.01	+						



TABLE V (continued).

Series 16 (continued).						Series 17.					
c.	p.	t.	Log		Notes.	c.	p.	t.	Log		Notes
			Log p.	p <sub>calc.</sub>					Log p.	p <sub>calc.</sub>	
1.86	32	280	1.51	1.09	+	0.82	39	332	1.59	1.67	+
1.86	37	284	1.57	1.17	+	0.82	14	269	1.15	0.59	-
1.85	72	312	1.86	1.66	+	0.82	25	315	1.40	1.40	+
1.85	120	338	2.08	2.06	+	0.82	40	326	1.60	1.58	+
1.84	180	352	2.26	2.27	+	0.81	120	370	2.08	2.22	+
1.83	280	368	2.45	2.50	-	0.80	190	380	2.28	2.36	+
1.82	380	375	2.58	2.59	+	0.79	260	388	2.42	2.46	+
1.81	490	385	2.69	2.72	+	0.78	340	400	2.53	2.62	+

The interpretation of the vapour-pressure (*pct*-) surface found offers some difficulties. At any given temperature (below a certain critical temperature  $\theta$ , discussed below) the vapour-pressure falls continuously with loss of water until only about 12 mols. per unit cell are left. As this water content is approached, the isohydric curves get closer and closer together, while the isothermals gradually become parallel to the pressure axis. From about 12 to somewhere between 1.8 and 0.9 mols. water per unit cell, the vapour-pressure remains constant within the accuracy of measurement, then falls off with further dehydration.

TABLE VI. The constants of the vapour-pressure surface of natrolite.

(The molecular heats of hydration\* ( $Q$ ), the integration constants,  $A$ , of the equation  $\log_{10} p = A - Q/RT(\log_{10})$ , and the temperatures ( $\theta$ ) at which the isohydric curve for fully hydrated natrolite cuts the isohydric curves for natrolites of lower degrees of hydration.)

Mols. water per unit cell.	$Q$ , cal.	$A$ .	$\theta$ .
16.00	$7.05 \times 10^3$	6.14	174°C.
15.55	8.47	6.75	220
15.30	10.05	7.25	310
15.17	12.22	7.76	390
15.05	14.42	8.50	420
15.00	15.07	8.63	430
14.30	23.16	10.92	480
14.02	24.34	11.10	490
13.87	24.67	11.21	492
13.55	25.08	11.24	497
12.63	25.90	11.31	511
8.04	25.86	11.31	520
1.86	25.85	11.30	520
0.82	$25.85 \times 10^3$	11.00	ca. 800

\* Heats of hydration per gram-molecule of water, for the combination of natrolite with water-vapour (*not* liquid water), and excluding the external work involved.

Now if there were a sharp break in the gradient of the isothermals at 12 mols. water, the vapour-pressure then remaining constant till all the water were removed, the interpretation would offer no difficulties; it would be evident that at 12 mols. water a discontinuity entered, a second, anhydrous solid phase appearing. Natrolite with less than 12 mols. water per unit cell would in that case be

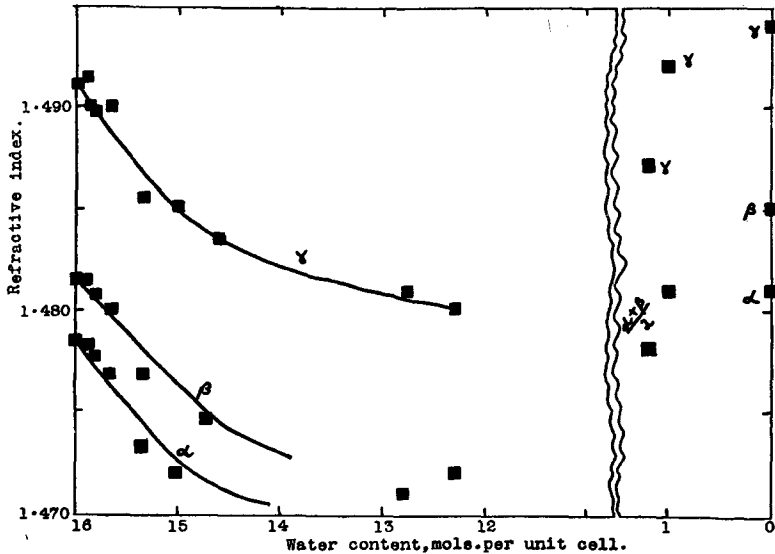


FIG. 10. The variation of the refractive indices of natrolite (for Na-light) with the degree of hydration.

heterogeneous, a mixture of an anhydrous phase and a phase with 12 mols. water per unit cell.

Such an interpretation seemed possible at first, but facts have since been found which discountenance it. Careful study of the *pct*-surface seems to indicate that there is no discontinuity of gradient at any point. There appears to be a definite fall in vapour-pressure at constant temperature when the water content falls below about 0.9 mols. per unit cell.<sup>1</sup> Also X-ray photographs of natrolite dehydrated at 300–350° C. and of anhydrous ammonium natrolite have failed to reveal any marked change such as would be expected if the anhydrous substance were a different phase from natrolite (see further under

<sup>1</sup> This may in part be due to adsorptive effects; but the differences seem to the author too definite to be accounted for in that way.

metanatroilite, below). On the other hand, several cut plates, when partially dehydrated, appeared non-homogeneous, if the loss of water exceeded about 4 mols. per unit cell, opaque, porcellaneous patches appearing. But if the isothermals are really only approximately parallel to the pressure axis, such an effect is still very likely to occur, for it is quite possible that one part of the plate may lose more water than another if the difference in vapour-pressure produced by the excess loss is only very small. Such a state would not be in equilibrium, but the re-establishment of true equilibrium would take an exceedingly long time.

The peculiar course of the isobaric dehydration curves made it quite impracticable to obtain homogeneous material with water contents between 12 and 1 mols. per unit cell, so that the optical continuity between natrolite and anhydrous metanatroilite could not be tested. But a number of experiments were made with several large polished plates of the Benallt material. These were weighed, partially dehydrated, and the refractive indices determined with a total reflectometer. The results, shown in Table VII and in fig. 10, show a marked fall in the refractive index with the loss of the first four molecules of water. If, as seems probable, there is optical continuity between natrolite and anhydrous metanatroilite, this must be followed by a rise during the later stages of dehydration.

TABLE VII. Effect of dehydration on the optical properties of natrolite.

All measurements made for sodium-light.

Mols. water per unit cell.	$\alpha$ .	$\beta$ .	$\gamma$ .	2E.
16.00*	1.4784	1.4816	1.4911	100° 32'
15.88	1.4782	—	1.4900	100 12
15.90	1.4780	1.4816	1.4903	102 9
15.79	1.4777	1.4808	1.4897	101 29
15.88	1.4780	1.4810	1.4915	—
15.66	1.4768	1.4800	1.4900	100 28
15.34	1.4733	1.4768	1.4856	98 43
15.30	1.4741	1.4777	1.4865	—
15.00	1.472	—	1.485	—
14.70	1.4715	1.4746	1.4838	97 0
12.77	1.471		1.481	—
12.3	1.472		1.480	—
1.0	1.481		1.492	—

\*Assumed

The isohydric curves (fig. 8) show no intersection with the vapour-pressure curve of water, indicating that, unlike thomsonite, fully

hydrated natrolite is stable in presence of liquid water at all temperatures. But the isohydric curve of fully hydrated natrolite intersects the others, a new phenomenon not met with in thomsonite, and of some theoretical interest. The data are not sufficiently accurate to be certain of the exact intersection points, but there can be no doubt of their existence and approximate position. The temperatures ( $\theta$ ) at which the vapour-pressure curve of fully hydrated natrolite cuts the curves for natrolite with various lower degrees of hydration are included in table VI and fig. 9.

This intersection of the isohydric curves has a bearing on the theory of mixed crystals. Regarded from a purely phase-rule point of view, one would conclude that when a homogeneous natrolite crystal with, say,  $15\frac{1}{2}$  mols. water per unit cell (on the average) was heated, its vapour-pressure being continually balanced by a water vapour-pressure to prevent dehydration, nothing should happen until its vapour-pressure reaches that of fully hydrated natrolite, at about  $230^{\circ}\text{C}$ . and 1000 mm. Hg; at a higher temperature, it should break down into a mixture of two phases, fully hydrated natrolite, and natrolite of that water content which has, at the temperature in question, the same vapour-pressure as the fully hydrated material; at a suitable temperature (about  $430^{\circ}\text{C}$ .), the second phase would correspond to natrolite with  $15\text{H}_2\text{O}$ . But, regarded from a microscopic point of view, a natrolite crystal with  $15\frac{1}{2}$  mols. water per unit cell is already such a mixture, some unit cells containing 16 mols.  $\text{H}_2\text{O}$ , while others contain only 15, and possibly some even less; clearly, those forces, not as yet fully understood, which interpose to average out the vapour-pressure effects of the individual unit cells in a zeolite with a fractional average unit-cell content of water, become less effective with rise of temperature, and finally the fully hydrated unit cells exert their full effect independently of the others. Yet there seems no reason to suppose that the essential nature of the zeolitic structure, the isomorphism and formation of mixed crystals between different hydrates, should be affected, or that the optical homogeneity of natrolites with water contents less than 16 mols. per unit cell should be lost. We seem here to be finding something intermediate between the zeolitic and the 'normal' hydrate, showing the constancy of vapour-pressure during dehydration characteristic of the latter with the optical continuity characteristic of the former. It is unfortunate that the temperature and pressure at which this phenomenon would appear to occur in natrolite are so high; it is to



be hoped that further work will reveal compounds in which such behaviour occurs at more accessible temperatures and pressures, enabling a proper study of it.

It has proved possible to make a direct determination of the mean molecular heat of hydration of natrolite, thereby obtaining a check on the vapour-pressure surface. The slope of the isohydric lines at any degree of hydration, as explained in Part II of this series, gives the molecular heat of hydration for that degree of hydration, and the mean value is readily computed by the aid of fig. 9, for comparison with the direct determination. The method employed for the measurement was simple, and though not very accurate (lack of proper apparatus prevented a more accurate determination), was sufficient for the purpose. A large platinum crucible was partially filled with water, and supported with corks inside a heat-insulating arrangement of two beakers separated by cotton-wool packing. A quantity of natrolite (8.919 grams) was dehydrated at  $400^{\circ}\text{C}.$ , and after cooling and weighing emptied into the water in the crucible, which was at once covered with an insulating lid of cork and cotton-wool, bearing a thermometer. In three minutes the temperature rose  $13.2^{\circ}\text{C}.$ , remained constant for two minutes, and then began to fall. The cooling rate was observed, and the extrapolated temperature rise for perfect insulation estimated at  $14.3^{\circ}\text{C}.$  Allowing for the water-equivalents of the crucible and natrolite (the specific heat of natrolite, according to J. Joly (1887), is 0.2375), the material heated was equivalent to 30.16 grams of water, making the heat evolved 452 cal.; as the water expelled was 0.6594 gram, this gives a mean heat of hydration of 12,300 cal. per gram-molecule of water for the reaction with liquid water. Adding the molecular latent heat of water-vapour at  $20^{\circ}\text{C}.$  (10,500 cal.) we have for the directly determined mean molecular heat of hydration of natrolite by water-vapour, 22,800 cal., against 24,000 cal. calculated from the isohydric curves (both for hydration from 4 mols. water per unit cell to full hydration). These figures are all exclusive of the external work.

Considering the approximate nature of the calorimetric work, this is an excellent agreement, and forms a valuable confirmation of the accuracy of the vapour-pressure work. The calorimetric value is probably rather low, for an experiment on the cooling rate of the crucible and its contents, after replacing 5 grams of the water by practically boiling water, showed that the cooling during the first

two hours after the addition of the natrolite was abnormally slow; clearly there must have been a further evolution of heat going on. It is very difficult to estimate the amount of heat evolved in this second period, but it was probably roughly 50 cal., which would almost exactly account for the difference, leading to a value of 24,200 cal. for the calorimetric figure.

It may be mentioned that G. Friedel<sup>1</sup> appears to have been the first to compute a heat of hydration for one of the zeolites; he computed the heat of hydration of analcime at several degrees of hydration from a few isobaric dehydration curves, but could not check his results by direct measurement.

#### *Base-exchange.*

Natrolite was one of the first zeolites to receive attention from the base-exchange point of view; H. Eichhorn (1858) treated it with a 4% solution of calcium chloride, and found no appreciable reaction after ten days at the ordinary temperature. The numerous experiments of J. Lemberg (1876, 1887, 1888) are not of much use, since the products were not invariably crystalline or homogeneous, and were not optically examined. He found a fairly ready exchange with potassium carbonate solution at 100° C., but calcium chloride gave very little reaction. S. J. Thugutt (1894) worked on the same lines. K. Dalmer (1878) treated natrolite with dilute ferrous sulphate solution at room-temperature, and obtained a pale bluish-green product containing ferrous oxide, but in view of subsequent work it seems probable that there was no true base-exchange. F. W. Clarke and G. Steiger (1900) found very considerable base-exchange with 10% silver nitrate solution at 120° C., half the sodium being replaced in 18 hours. R. Gans (1905) obtained a small but appreciable base-exchange with ammonium chloride solution in two days at room-temperature. H. Kappen and B. Fischer (1928) found that ferrous, ferric, copper, and aluminium chlorides all caused decomposition rather than base-exchange. Dilute (*N*/10) hydrochloric acid they found to remove sodium and aluminium concurrently and in about equal atomic proportions.

None of these workers made any observations on the optical properties of their products except S. J. Thugutt, who obtained a compound  $K_2Al_2Si_3O_{10} \cdot 2H_2O$  by heating natrolite with 1% caustic potash solution at 200° C.; he describes the product as being in part needles

<sup>1</sup> G. Friedel, Bull. Soc. Franç. Min., 1898, vol. 21, p. 5.

with straight extinction, in part globulites and pseudomorphs after the natrolite, with weak birefringence. Much alumina and silica went into solution.

J. Koenigsberger and W. J. Müller (1921), on the other hand, made an optical study of natrolite from Böhmisches-Leipa before and after treatment with 25% KCl solution for 24 hours at 180° C., and found that although 14.96% K<sub>2</sub>O had been taken up, no effect on the refractive index or birefringence could be measured.

A quite different technique of base-exchange was discovered by E. A. Schneider and F. W. Clarke (1893), and further investigated by F. W. Clarke and G. Steiger (1900) and G. Steiger (1905). Schneider and Clarke found that when natrolite is heated with dry ammonium chloride at 350° C. till all the ammonium chloride has volatilized, the residue contains common salt, up to two-thirds of the sodium of the natrolite being removed in this way. Clarke and Steiger modified this process, heating natrolite with dry ammonium chloride in a sealed tube at 250–300° C., and found that the product is anhydrous (NH<sub>4</sub>)<sub>2</sub>Al<sub>2</sub>Si<sub>3</sub>O<sub>10</sub>. G. Steiger (1905) also heated natrolite with fusions of silver or thallos nitrate at 250–300° C., and replaced almost the whole of the sodium by silver (in 22 hours) or by thallium (in 48 hours); the thallos product was practically anhydrous, but the silver natrolite had the normal water content.

The author's experiments were directed to three main ends—the proof that the base-exchange products still retain the natrolite structure, the measurement of some of their physical properties, and an attempt (which did not succeed) to produce mesolite or scolecite by the action of calcium chloride on natrolite. It has been generally assumed, from their close similarity in angles and habit, and from J. Lemberg's indirect preparation from natrolite (via a potassium compound) of a product having the composition of scolecite, and from mesolite and scolecite of products having the composition of natrolite, that natrolite, mesolite, and scolecite are closely related in structure (at one time, indeed, they were commonly regarded as isomorphous). But this assumption rests on no secure foundation, and, while quite probably correct, requires testing by an X-ray study of all three zeolites.

Natrolite digested with a boiling solution of calcium chloride for 700 hours gave no appreciable base-exchange, and attacked the glass flask somewhat; the product retained the same optical properties as the original natrolite. Copper acetate and barium chloride solutions

also gave no appreciable base-exchange in 700 hours at the boil, while potassium chloride attacked the glass very considerably.

Natrolite digested for 4 months with cold copper acetate solution was coated with copper oxide, and showed no signs of base-exchange, but digestion with calcium and potassium chlorides and silver nitrate gave considerable base-exchange. The products were analysed and their optical properties and specific gravities determined, with the results shown in table VIII. The material treated with calcium chloride showed no trace of mesolite or scolecite under the microscope, and had about the same composition as the most calciferous natrolites known. Possibly further digestion might result in the production of some mesolite or scolecite; a digestion for a year or more is being undertaken. No effect of the calcium substitution on the refractive indices could be detected (accuracy  $\pm 0.002$ ). Nor was there any sign that calcium substitution is accompanied by an increase in the water content (several workers have assumed that this substitution is to be interpreted as a replacement of  $\text{Na}_2$  by  $\text{Ca.H}_2\text{O}$ , giving a mixed crystal of natrolite and scolecite molecules). The potassium and silver products also were homogeneous, crystalline, and orthorhombic.

The most satisfactory results, however, were obtained by Steiger's method; natrolite was heated with fusions of ammonium nitrate and potassium thiocyanate at  $170\text{--}190^\circ\text{C}$ ., and with fusions of silver nitrate, thallos nitrate, and lithium nitrate at  $230\text{--}250^\circ\text{C}$ . for 48 hours, then leached and well washed with hot water, and the air-dry products examined (see table VIII).<sup>1</sup> Nearly pure lithium, silver, potassium, ammonium, and thallos natrolites were thus obtained. As was to be expected, the substitution of potassium, silver, or thallium increases the specific gravity, while lithium and ammonium lower it. Lithium, silver, thallium, and ammonium increase the refractive index, while potassium affects it little if at all. These products also were all homogeneous and crystalline. The optic orientation is the same, and the

<sup>1</sup> For the analysis of the ammonium natrolite, the following method was used. Silica, alumina, and soda were determined on one portion in the usual way. A second portion was weighed into a dried Penfield tube, into the upper bulb of which a quantity of hydrochloric acid (15%) was then weighed. On ignition of the natrolite, both water and ammonia were expelled, and collected in the bulb containing the acid. The natrolite bulb was cut off, the tube plus acid, ammonia, and water weighed, then the ammonium chloride solution washed out, and the tube dried and weighed. The ammonia in the solution was determined as platinichloride. From these data both ammonia and water are readily calculated.

TABLE VIII. Experiments on base-exchange, with Salesl natrolite.

Treatment.	None.	Digested 4 months at room-temperature with a solution of:			Fused at 200° C. (except LiNO <sub>3</sub> and TiNO <sub>3</sub> , these at 250° C.), with: *					
		KCl.	AgNO <sub>3</sub> .	CaCl <sub>2</sub> .	LiNO <sub>3</sub> .	KCNS.	NH <sub>4</sub> NO <sub>3</sub> .	AgNO <sub>3</sub> .	TiNO <sub>3</sub> .	
Percentage composition.	SiO <sub>2</sub>	47.38	45.71	43.65	45.40	50.05	43.05	52.76	32.44	24.14
	Al <sub>2</sub> O <sub>3</sub>	27.63	26.76	28.13	27.79	30.72	25.46	31.44	18.21	15.17
	Na <sub>2</sub> O	14.96	11.71	13.54	14.28	4.68	1.94	1.36	1.31	[3.50]§
	R <sub>2</sub> O†	—	6.38	6.59	3.48	6.55	19.40	14.39	41.23	52.23
	H <sub>2</sub> O	9.58	9.14	8.56	9.35	8.82	9.88	0.32	5.44	4.96
	Total	100.50‡	99.70	100.47	100.30	100.82	99.73	100.27	98.63	[100.00]
Oxygen %	42.31	41.17	40.25	41.82	45.48	38.82	47.51	29.44	22.87	
Oxygen, atoms per unit cell.	80.94	77.70	—	78.54	79.24	79.82	79.74	80.00	79.68	
Atoms per unit cell, assuming oxygen 80.	Si	23.84	24.05	22.99	23.06	23.25	23.69	23.58	23.80	22.49
	Al	16.38	15.85	17.47	16.64	16.83	16.51	16.57	15.74	16.66
	Na	14.59¶	11.95	13.82	14.06	4.21	2.07	1.17	1.86	6.31
	R†	—	4.29	1.80	1.89	12.29	13.64	14.81	15.68	13.78
	H <sub>2</sub> O	16.08	16.00	15.04	15.83	13.66	18.13	0.48	13.32	15.40
Specific gravity	2.245	2.21(?)	Varies	2.20	2.135	2.365	2.073	3.09	3.92	
Refract. indices, Na-light.	α	1.479	1.478	Varies	1.478	1.489	1.480	1.507**	1.577	1.620**
	β	1.482	1.481	„	1.481	1.492	1.483	—	—	—
	γ	1.491	1.488	„	1.490	1.501	1.490	1.515	1.585††	1.629
Cell-sides, in Å.	a	18.31	—	—	—	17.95	—	18.0	18.59	—
	b	18.66	—	—	—	18.55	—	18.4	18.92	—
	c	6.60	—	—	—	6.47	—	6.55	6.60	—
	d††	2.92	—	—	—	—	2.95	—	—	2.98
	r	0.98	1.33	1.5?	0.98	0.68	1.33	1.44	1.5?	1.7?

\* The fusion was continued (intermittently) for 48 hours, except for the AgNO<sub>3</sub> fusion, which was continued for 96 hours, and after leaching and thorough washing the residue was digested with hot water for 12 hours, and then air-dried.

† R indicates the kation of the salt employed in the base-exchange treatment.

‡ Including 0.41 % K<sub>2</sub>O and 0.54 % CaO.

§ By difference.

|| Assuming no change in the cell-sides in the preparations of columns 2 and 4.

¶ Also 0.26 atom K and 0.29 atom Ca.

\*\* Mean of α and β.

†† Mean of β and γ.

‡‡ Spacing measured from the powder photograph (in Å.). Corresponds to the mean of the unresolved diffractions (531), (351), (222), (260), and (620).

||| Radius of the kation introduced by base-exchange, in Å. (In the case of natrolite itself, of sodium.)

birefringence approximately the same as in natrolite for all these derivatives except the silver compound. The latter has  $\alpha \perp c$  (001), whereas with all the others it is  $\gamma$  that has this direction. The silver compound is probably optically negative.

The ammonium compound was anhydrous, in agreement with Clarke and Steiger's results, but the thallos compound was found to be hydrated, although base-exchange had gone to about the same extent as in Steiger's experiments. The amount of material prepared was insufficient for a study of its vapour-pressure, but it is to be expected that this would be much higher than that of natrolite, the water being presumably only loosely held.

An X-ray study of these base-exchange products was made by Mr. F. A. Bannister. The ammonium, lithium, and silver compounds, which were coarsely crystalline, were examined by the Laue and rotating crystal methods; but the potassium and thallos derivatives were crystalline powders, only suitable for powder photographs, although their preparation had been carried out with material as coarse as that used for the other two derivatives.

The powder photographs of the potassium and thallos compounds showed a strong general resemblance to a natrolite powder photograph, and there can be little doubt of their structural correspondence, though owing to the complexity of the photographs, it was quite impossible to index them. Only in a few cases could one be certain which were corresponding lines on the photographs; but there are very distinct changes in the intensity of some of the diffractions, particularly with the thallos compound.

One line which could be identified without difficulty on the powder photographs was that given by (531), (351), (222), (260), and (620). Though really a compound line (the spacings of the five planes range from 2.846 to 2.946 Å.), these diffractions were not resolved, but gave a rather wide line, the centre of which could, however, be measured with considerable accuracy. The results are included in table VIII, and it will be seen that the introduction of potassium results in a decided increase in this group of spacings, while thallium causes a still greater increase. This is in accord with the relative sizes of the sodium, potassium, and thallos ions (see further below).

The figures given in table VIII for the oxygen atoms per unit cell for the potassium and thallos natrolites are calculated on the assumption that the introduction of these ions does not alter the  $c$  spacing,

while the  $a$  and  $b$  spacings are assumed to have increased in the same proportion as the above complex of spacings. The agreement with the theoretical figure (80) is remarkably good, even with the thallose natrolite, where the introduction of the thallium atom, much larger and nine times as heavy as sodium, has raised the density by 80 %, to 3.92, and enlarged the cell by some 4 %; although it contains 52 % thallose oxide, this compound is still a true natrolite.

The lithium, silver, and ammonium derivatives gave much coarser crystals, from which rotation photographs could be obtained. As was to be expected from the relative sizes of the sodium and lithium ions, the lithium compound has a considerably smaller unit cell than natrolite, while the silver ion, probably larger than sodium, gives rise to a compound with a larger cell.

The ammonium natrolite was anhydrous, and the loss of water counteracted the introduction of the large ammonium ion, the cell being considerably smaller than that of natrolite; the change was mainly in the  $a$ - and  $b$ -axes. A good Lauegram of ammonium natrolite, along the  $c$ -axis, was also obtained, but this furnished no additional information.

There were considerable changes in the intensity of many diffractions on these rotation photographs, but owing to their complexity but few spots could be indexed. A study of the changes consequent on the base-exchange would be of considerable interest, but would require numerous oscillation photographs to identify the diffractions, and time was not available for this.

The contraction of the unit cell consequent on the replacement of sodium by lithium is 4.7 %, while the replacements by potassium, silver, and thallium result in expansions of 1.8 %, 2.9 %, and 4.0 % respectively. There is general agreement as to the ionic radii of  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{NH}_4^+$ , which W. H. Zachariasen<sup>1</sup> gives as 0.68, 0.98, 1.33, and 1.44 Å. respectively, values which have been adopted in table VIII. But the atomic radii of  $\text{Ag}^+$  and  $\text{Tl}^+$  are in some doubt. R. W. G. Wyckoff<sup>2</sup> gives  $\text{Ag}^+$  0.97 and  $\text{Tl}^+$  1.50 Å., but L. Pauling<sup>3</sup> gives  $\text{Ag}^+$  1.26 Å. The present data go to show that this last value is probably nearer the truth. Certainly Wyckoff's radius for  $\text{Ag}^+$  is much too low, and the relative cell-sizes of potassium and silver natrolites suggest that Pauling's figure is also low.

<sup>1</sup> W. H. Zachariasen, *Zeits. Krist.*, 1931, vol. 80, p. 137.

<sup>2</sup> R. W. G. Wyckoff, *The structure of crystals*. New York, 1931, p. 192.

<sup>3</sup> L. Pauling, *Zeits. Krist.*, 1928, vol. 67, p. 377.

The mechanism of the change of cell-size is presumably by a change in the angle  $\theta$  of Pauling's natrolite structure model (1930), the silicon-aluminium chains turning about the  $c$ -axis.

A property of the zeolites which probably has some relation to base-exchange is their electrical conductivity. In so far as this is electrolytic in nature, it must be largely governed by the same forces as control the base-exchange reactions. A. Günther-Schulze (1914), indeed, has concluded that there is a direct proportionality between the electrical conductivity and the initial base-exchange velocity provided the cations are being replaced by others of the same valency. His simple equations can hardly be truly valid, for the relative sizes of replaced and replacing ions must have a considerable influence on the velocity of base-exchange. But his measurements and those of O. Weigel (1923) are in such marked disagreement that much more work is evidently necessary before valid conclusions can be drawn. The author has repeated Günther-Schulze's diffusion constant measurements, by the same method as he used, but has failed to obtain noticeable base-exchange in three weeks. Günther-Schulze's figures must therefore be in error, his conductivity and rate of base-exchange being much too high. Further experiments are in progress on the rate of base-exchange.

#### *Metanatrolite.*

In 1890 F. Rinne observed that when crystals of natrolite are heated until they become white and opaque and then cleared in oil, they show, in sections perpendicular to the elongation, a division into sectors, which extinguish at  $15^\circ$  to one another. On exposure to moist air, this metanatrolite, which is clearly monoclinic, absorbs water and is re-converted into natrolite. Its optical orientation is near that of natrolite, the positive acute bisectrix being parallel to the elongation, as in natrolite, while the obtuse bisectrix makes an angle of  $7\frac{1}{2}^\circ$  with the face (010) of the usual natrolite orientation (in natrolite it is parallel to (010)).

A. Cavinato (1927) confirmed these results, and found the optic axial angle,  $2V$ , to be about  $62^\circ$ . He also took Lauegrams of natrolite and metanatrolite, through (110), and Debyeograms, but could observe no differences. C. H. Slonim (1930) also found no differences between Debyeograms of natrolite and metanatrolite (dehydrated at  $00^\circ$  C.).

The author has repeated Rinne's experiments, and finds that de-



hydration over a bunsen burner at a temperature of about 400–600° C. produces metanatrolite, with precisely the properties described by Rinne and Cavinato. Its refractive indices are  $\alpha$  1.483,  $\beta$  1.485,  $\gamma$  1.494; the positive acute bisectrix is parallel to the elongation, with 2E about 100°; the sectors visible on cross-sections extinguish at 15° to one another; cleavage fragments give straight extinction. The cleavage of natrolite is retained in metanatrolite. On standing in air, metanatrolite crystals very soon break up into an aggregate of fibres parallel to the elongation (*c*-axis of natrolite).

Dehydration at 290–300° C., on the other hand, gave a product, still containing a little water (presumably about 1–2 mols. per unit cell), with a lower refractive index— $\alpha'$  1.481,  $\gamma$  1.492 on one preparation,  $\alpha'$  1.478,  $\gamma$  1.487 on another—and showing indeed a division into sectors on a basal section, but with an extinction difference of only 1–3°.

These data, together with the vapour-pressure measurements and X-ray work on the symmetry of natrolite, suggest that the transition natrolite  $\rightleftharpoons$  metanatrolite is a continuous one, both being really monoclinic. Mr. F. A. Bannister made an X-ray examination of several preparations. Three dehydrated at temperatures from 300 to 350° C. showed no differences from natrolite (rotation photographs about the elongation were taken); special precautions were taken in two cases to avoid re-hydration. Another specimen, dehydrated at 400–600° C. until quite opaque, was cleared in oil and examined optically; it gave the division into sectors, extinguishing at 15° to one another, and all the optical properties of the metanatrolite of Rinne. An X-ray rotation photograph of this crystal about its direction of elongation gave a rather poor photograph, owing to the tendency of the crystals to break up into a bundle of fibres; no definite differences between this photograph and one of natrolite could be observed, but there may very possibly be some slight alterations of intensity, and the cell-sides are probably slightly smaller in metanatrolite than in natrolite. The evidence is therefore decidedly in favour of the view that natrolite is isomorphous with the definitely monoclinic metanatrolite.

If this view is accepted, the 'anomalous' diffractions on the X-ray photographs of natrolite, and the peculiarities of the *pet*-surface, both mentioned above, are readily explained. Natrolite is really monoclinic, with the space-group  $C_2^3$ , the symmetry-axis being parallel to the elongation, and the angle  $\beta$  being 90° 0'; it is isomorphous with metanatrolite, which is not an independent species, but merely the

final dehydration product of natrolite, and which has the same symmetry and orientation as natrolite. But the structure shows very marked pseudo-symmetry, approaching very closely to the (orthorhombic) symmetry of the space-group  $C_{2v}^{19}$ . With the monoclinic orientation, the usual forms of natrolite become:  $a$  (100),  $b$  (001),  $m$  (101) and  $(\bar{1}01)$ ,  $D$  (110),  $e$  (011), and  $o$  (111) and  $(\bar{1}11)$ , and the axial ratio  $a:b:c = 2.773:1:2.827$ ,  $\beta = 90^\circ 0'$ , while the optical orientation becomes:  $Bx_a \perp (010)$ , positive, axial plane (001).

It cannot be said that these conclusions are definitely proved, but they appear to the author to offer the most reasonable explanation of the results so far obtained. Further work on the matter, by X-ray and vapour-pressure methods, is very desirable.

#### *Summary.*

Natrolite is shown by nine new analyses and new X-ray measurements to have a constant Si/Al-ratio and a unit-cell formula of  $Na_{16}Al_{16}Si_{24}O_{80} \cdot 16H_2O$ , in agreement with previous results.  $Na_2 \rightarrow Ca$  replacement may occur up to about 4, and  $Na \rightarrow K$  replacement up to about 2 atoms per unit cell. Natural etch-figures on natrolite from Benallt, Carnarvonshire (a new locality), show the  $c$ -axis to be polar. A detailed study of the optical properties of natrolite has been made. Some observations have been made on the effects of partial dehydration on the optical properties. The vapour-pressure has been studied at various temperatures and degrees of hydration, and several peculiarities observed. The heat of hydration has been measured and shown to be in agreement with the vapour-pressure work. Some experiments have been carried out on the base-exchange of natrolite. An X-ray study of natrolite and metanatrolite, together with the vapour-pressure observations, suggests that natrolite is really monoclinic, with space-group  $C_2^3$ , the symmetry-axis being parallel to the elongation (the usual  $c$ -axis). But there is very marked pseudo-symmetry, the symmetry very closely approaching that of the orthorhombic space-group  $C_{2v}^{19}$ , of which  $C_2^3$  is a sub-group.

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\* In the original, by a misprint, 'chaux' appears in the tabulated analysis, but it is clear from the following paragraph that soda was intended. Unfortunately, many authors have failed to notice this, and have taken the analysis for one of scolecite.

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