

The dehydration of thomsonite.

By A. E. MOURANT, M.A., D.Phil.

[Read March 23, 1933.]

THE dehydration of thomsonite has recently been studied by Mr. M. H. Hey.¹ The work here described was carried out in the Mineralogy Department at Oxford in the years 1925 and 1926. At the suggestion of Mr. Hey the results, though inconclusive by themselves, are now published for comparison with his own, which were mostly obtained by a different method.

The material used was from a specimen of thomsonite and prehnite labelled 'Kilpatrick Hills, Scotland' (Reg. No. 8660, Mineral Collection, Oxford University Museum). Its practical identity of composition and physical properties with that used in most of Hey's work shows that it almost certainly came from Bowling quarry, Old Kilpatrick, Dumbartonshire.

All the thomsonite used for quantitative work was kept in a desiccator over 20 % sulphuric acid. That used for dehydration was crushed down to cleavage prisms about 0.5 mm. in diameter. Further crushing was avoided owing to the danger of surface effects. The chemical composition and principal physical properties are given in table I. The cell-sides were kindly determined recently by Mr. F. A. Bannister and the refractive indices by Mr. M. H. Hey.

Low temperature dehydration.—Thomsonite was kept over slightly dilute sulphuric acid for several weeks and the loss of weight determined. Over 89.2 % acid 0.4611 gm. lost 0.0002 gm. in a day, and only 0.0001 gm. in the next month. The total loss amounts to 0.07 % or 0.12 mol. per unit cell. Over 95.6 % acid equilibrium was not reached in 89 days; after this period 0.31 % of water (0.55 mol. per unit cell) had been lost. The water vapour-pressure over 84.5 % sulphuric acid is 0.154 mm. Hg. That over stronger acids is unknown. Tammann² observed a loss of 0.008 % in the weight of thomsonite kept over 85.1 % sulphuric acid.

¹ M. H. Hey, *Min. Mag.*, 1932, vol. 23, p. 51.² G. Tammann, *Zeits. Physikal. Chem.*, 1897, vol. 27, p. 323.

TABLE I. Thomsonite from Kilpatrick used for dehydration experiments.

Composition.	Atoms (and molecules		
	%	H ₂ O) per unit cell, assuming O = 80.	
SiO ₂ ...	36.84	Si ... 19.76	Si + Al = 39.76 (40, theoretical).
Al ₂ O ₃ ...	31.64	Al ... 20.00	Ca + Mg + Na = 12.55 (12 in 'normal' thomsonite).
CaO ...	14.19	Ca ... 8.16	Density = 2.381.
MgO ...	0.29	Mg ... 0.23	Cell-sides in Å.: <i>a</i> 13.07, <i>b</i> 13.07, <i>c</i> 13.23 (all ± 0.05). Oxygen atoms per unit cell (from cell-sides, density, and composition) = 80.97.
Na ₂ O ...	4.00	Na ... 4.16	Refractive Indices: α 1.528, β 1.531, γ 1.543 (± 0.003).
K ₂ O ...	trace	— —	($\alpha + \beta + \gamma$)/3 = 1.534.
H ₂ O ...	13.53	H ₂ O ... 24.20	
Total ...	100.49		

High temperature dehydration.—It was possible that the measurement of the water content of considerably dehydrated thomsonite would be complicated by the material absorbing considerable quantities of air as chabazite does. A series of gravimetric experiments suggested that absorption was negligible, but since they were not conclusive another test was made. Several small clear crystals were heated to 300° C. for a few hours and cooled overnight in a stream of dry air. Some were then rapidly transferred to a small quantity of water and observed for half an hour. Since changes in birefringence showed that hydration was still proceeding, some larger pieces were put under a small inverted test-tube and left for a day, at the end of which no air had appeared. It may therefore be concluded that dehydrated thomsonite does not absorb air appreciably.

It was therefore possible to use the isobaric method of dehydration for the quantitative work. Air was slowly driven by a water-pump through a saturating worm immersed in a thermostat and then passed over thomsonite which was heated to various temperatures; its water content was determined by weighing. The heating tube was of hard glass, surrounded by a tubular sand-bath similar to that of Friedel.¹ This was heated in a gas-furnace, the temperature being controlled by a pressure regulator followed by a mercury thermostat. The range of temperature seldom exceeded 0.5° C.

The thomsonite, originally weighing 1.4342 gm., was contained in a porcelain boat which was weighed in a bottle against a similar counterpoise. During heating at a given temperature it was weighed every day or two until the weight appeared constant. At the first

¹ G. Friedel, Bull. Soc. Franç. Min., 1896, vol. 19, p. 363.

three temperatures the attainment of equilibrium was then tested by lowering the temperature of the furnace three or four degrees and weighing again. The results obtained are tabulated in table II and shown graphically in fig. 1 in comparison with some of those obtained by Hey.

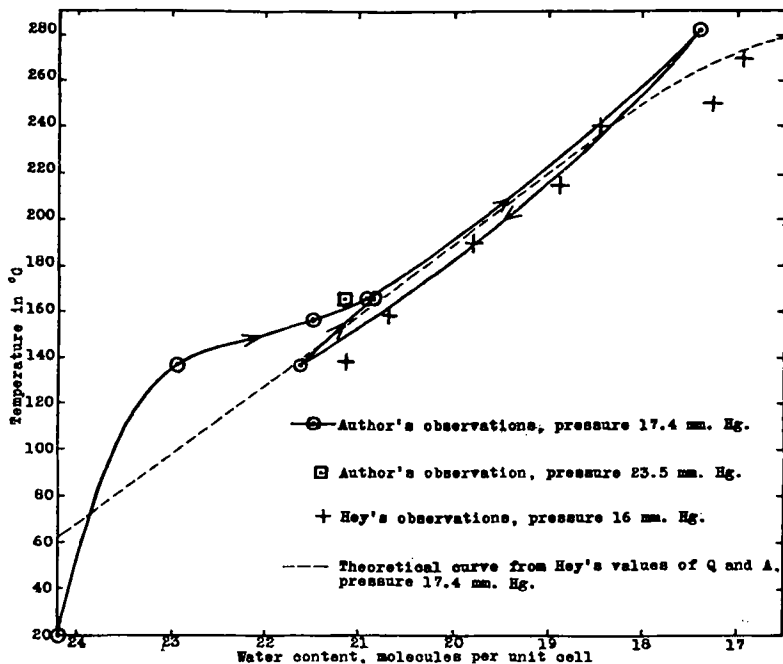


FIG. 1. Isobaric dehydration and rehydration of thomsonite. The abscissae correspond to the author's observed water contents but Hey's points are compared on the basis of water losses.

TABLE II. Observations on the dehydration of a single sample of thomsonite in the order in which they were made. Water vapour-pressure, 17.4 mm. Hg., except for the run marked *, where it was 23.5 mm. Hg.

Temperature °C.	Water content Mols. per unit cell.	Hours.	
20	24.20	—	† Equilibrium checked by lowering temperature slightly.
136.2	22.93	121†	
155.9	21.48	94‡	‡ Weight not quite steady but equilibrium shown to be practically complete by lowering temperature.
164.6	20.91	205†	
164.6*	21.14	109§	
282.3	17.38	103§	§ Weight steady; equilibrium not checked.
134.3	21.61	284§	
164.5	20.85	44	Only one weighing.

The chief features of interest in the writer's curve are the 'hysteresis' loop and the point of inflection. The failure of the material to recover its original water content at about 135° C. after heating to 282° C. agrees with the observations of other workers, but it is surprising to find that after subsequent heating at 164.5° C. the zeolite has practically returned to its original composition at that temperature.

The general run of the curve is very close to those of Hey. The high water content observed by the writer round about 150° C. might at first sight be attributed to failure to reach equilibrium, but in each case equilibrium was confirmed by observing the increase in weight produced by lowering the temperature slightly for a few hours. The rapid change of water content in the neighbourhood of 156° C. was thus made particularly clear, for on lowering the temperature 3.6° C. two-thirds of the quantity of water required by the writer's curve was reabsorbed in nine hours. At the first heating to 164.6° C. equilibrium was almost certainly complete, for on raising the vapour-pressure to 23.5 mm. Hg. the gain in weight corresponded to 0.25 molecule as compared with 0.18 calculated from Hey's values for A and Q. Imperfect internal equilibrium of the zeolite might yet have allowed the recovery of weight on reducing the temperature from 136.2° C. and thus account for the considerable discrepancy between the curves at that temperature, but the differences at higher temperatures cannot be explained thus. The general correspondence between the curves would be somewhat improved if they were compared on the basis of water content instead of water loss, by moving Hey's curve 0.40 molecule to the left. The correspondence between Hey's theoretical curve and the actual course of the second heating is close but, in view of the above considerations, the loop in the writer's curve is probably genuine and due to lattice shrinkage and recovery.

The apparent recovery from shrinkage during cooling and reheating to 164.5° C. has been tested by Mr. F. A. Bannister, who has compared the lattice dimensions of the untreated thomsonite with those of the actual material which had been used in the above experiments and had then stood over 20 % sulphuric acid for six years. Unfortunately the acid itself had reached and slightly attacked some of the material so that its water content could not be determined reliably ; but sufficient of the pure material was left for the X-ray work. The lattice dimensions of the untreated thomsonite are a 13.073, b 13.073,

c 13.23 Å., and the refractive indices α 1.528, β 1.531, γ 1.543. After the heat treatment and subsequent exposure over dilute acid, the cell-sides were a 13.048, b 13.048, c 13.23 Å., and the refractive indices α 1.524, β 1.527, γ 1.539. The probable maximum error in the cell sides is 0.05 Å., but the relative values of a and b before and after treatment are correct to ± 0.01 Å. The determinations of refractive index (made by Mr. M. H. Hey) are correct to ± 0.003 .

The immediate effect of heating a specimen of thomsonite to 270° C. was shown by Mr. Bannister (this vol., p. 103) to be a contraction of a and b from 13.09 to 12.93 Å., a difference of 0.16 Å. Such a contraction must certainly have occurred in the material heated by the writer to 282° C., but the residual contraction is now only 0.025 Å., so that the substance has nearly recovered as suggested by the loop in the isobaric curve. It is not, however, certain to what extent the recovery took place in the later stages of heating (14 days at about 150° C.) and to what extent in the subsequent six years at room-temperature. The water content has not completely recovered. The refractive indices show it to be about one molecule per unit cell less than in the untreated substance.

The writer wishes to thank Prof. H. L. Bowman for suggesting the research, for his very helpful supervision, and for designing and largely constructing the heating apparatus. The work was carried out with the aid of a King Charles I Scholarship at Exeter College, Oxford.
