272. *Hydrothermal Reactions involving Thallium.*

By H. F. W. Taylor.

Mixtures of thallous aluminate, silicate, and aluminosilicate compositions have been subjected to hydrothermal treatment at temperatures of 200—350°. Analytical, optical, and *X*-ray powder examinations of the insoluble products have shown that several crystalline species can be obtained in a reproducible manner. Analyses of one species approximated to $TlAlSiO_4$, analogous to kaliophilite and kalsilite ($KAlSiO_4$), but the *X*-ray powder spacings differed considerably from those of either of the potassium minerals. α-Cristobalite and α-quartz were obtained from the silica-rich mixtures, but only in the absence of alumina. A species $TlAlSi_2O_6$, obtained in good yield from mixtures of approximately its own composition, readily underwent base exchange and showed a close structural similarity to leucite ($KAlSi_2O_6$) or analcite ($NaAlSi_2O_6,H_2O$), into which it could readily be converted. Thus univalent thallium can at least to a limited extent form aluminosilicates in which its rôle resembles closely that of sodium or potassium.

Univalent thallium shows a considerable likeness to the alkali metals, and it might therefore be expected to form crystalline aluminosilicates comparable with the zeolites, sodalites, or other groups of minerals containing alkali metals. However, no natural aluminosilicates are known which contain more than a trace of thallium, and although the literature contains isolated references to laboratory preparations of silicates (Fleming, *Jena Zeit.*, 1868, **4**, 33; Wyrouboff, *Bull. Soc. min.*, 1889, **12**, 536) and an aluminate (Hawley, *J. Amer. Chem. Soc.*, 1907, **29**, 300) and to the introduction of thallium into zeolites by base exchange (Steiger, *Amer. J. Sci.*, 1902, **14**, 31), no attempts to obtain crystalline thallium aluminosilicates by synthesis appear to have been recorded. In the case of the alkali metals, on the other hand, a variety of aluminosilicates have been obtained synthetically under hydrothermal conditions (*e.g.*, Morey and Ingerson, *Econ. Geol.*, 1937, **32**, 607), reactions in alkaline media at temperatures below 350° often having yielded zeolites or similar minerals (see, *e.g.*, Barrer, *J.*, 1948, 127, 2158). The possibilities of preparing thallous aluminosilicates by similar methods have therefore been partly explored in the present investigation.

Treatment of a mixture of composition Tl_2O,Al_2O_3 with either water or excess of thallous hydroxide solution yielded no crystalline products either at 200° or at 300°. Mixtures of composition $Tl_2O,nSiO_2$ or $Tl_2O,Al_2O_3,nSiO_2$, on the other hand, yielded the crystalline species described below. Each species could be obtained reproducibly under the conditions defined in the table.

Species A. Spheroidal particles showing no definite faces; diameter about 15μ; isotropic or nearly so; $n = 1{\cdot}490$. Subsequently identified as α-cristobalite.

Species B. Rods or prisms, up to 10μ in length, occurring singly, in bundles, or rosettes; positive elongation and straight extinction; apparently uniaxial, with $\omega = 1{\cdot}755$, $\varepsilon = 1{\cdot}78$. Readily gelatinised by acids.

Species C. Spheroidal particles showing no definite faces; diameter up to 35μ; usually isotropic or nearly so; $n = 1{\cdot}645$. Sometimes fringed with crystals, apparently of species B; stable to cold acids. Subsequently identified as the thallium analogue or near-analogue of analcite or leucite.

Species D. Ill-formed rods; extinction straight or nearly so, with positive elongation; birefringent; mean refractive index 1·64.

Species E. Birefringent plates of mean refractive index 1·70. Tends to form multiple twins. Species D and E were never obtained in major yields.

Discussion.—The mixtures of thallous silicate composition yielded, at temperatures up to 300°, no crystalline products other than A, which was identified by its optical properties and *X*-ray powder photographs as α(low)-cristobalite. This was formed in the highest yield when $n = 8$ or 10 and $T = 300°$; at 350°, however, a mixture of composition $Tl_2O,10SiO_2$ gave α-quartz. These results are in general accordance with those of Wyart (*Bull. Soc. franç. Min.*, 1943, 479), who investigated the hydrothermal crystallisation of silica from water or potassium hydroxide solutions. It also seems probable from the foregoing observations that neither aluminates nor silicates of thallium are likely to be formed under the conditions of the present investigations.

*Crystalline products of hydrothermal reactions.**

Composition of mixture :	$Tl_2O,nSiO_2$.	$Tl_2O,Al_2O_3,nSiO_2$.			
Medium :	Water.	Water.	Water.	TlOH, aq.	TlOH, aq.
Temp. :	300°	220°	300° or 310°	220°	310°
n.					
1	Poor crystn. (9·5) †	Good B (9·8)	Moderate B (9·5)	Good B; trace D (10·5)	Poor xtal'n. (10·5)
2	Rare A (10·0)	Mod. B; trace C (7·8)	Good B; trace C (7·8)	V. good B; fair C & D (10·5)	Good B; traces C & D (10·5)
3	Rare A (9·5)	Mod. B; poor C (7·0)	Mod. B; poor C (7·2)	V. good B; poor C & mod. D (10·5)	Good B; poor C & D (10·5)
4	Rare A (9·5)	Rare B; good C (8·0)	Poor B; v. good C (7·0—8·0)	Good B & C; mod. D (10·5)	Mod. B, C; poor D (10·5)
5	Rare A (9·5)	Rare B; good C (8·5—9·5)	Poor B & D; v. good C (7·0—8·0)	Good C; poor B & D (10·5)	Mod. B & C; poor D & E (9·8)
6	Mod. A (9·5)	Mod. C (9·0—9·5)	Mod. C (7·0—8·0)	Good C (10·5)	Good C, poor D, Rare B & E (9·8—10)
8	Good A ‡ (9·5)	Poor C—nil (8·5—9·0)	Poor—mod. C (6·5—7·5)	Poor C (10·0)	Rare B & D, mod. C (9·8—10·0)
10	Good A ‡ (9·5)	Nil (8·5)	Nil (7·5)	V. poor C (10·0)	V. poor C (10·0)
Ref. : §	*a*	*b*	*c*	*d*	*e*

* Where crystallisation is described as poor, nil, etc., considerable amorphous matter was present in the product.

† Figures in parentheses denote pH values of the cold mother-liquors after reaction.

‡ At 200° little or no crystallisation took place from these mixtures.

§ Used subsequently, with *n* to denote the product of a given experiment; thus that obtained from a mixture of composition $Tl_2O,Al_2O_3,5SiO_2$ treated with water at 300° would be 5*c*.

Mixtures of the general composition $Tl_2O,Al_2O_3,nSiO_2$ yielded, on hydrothermal treatment with water at 300°, B as the major product at the lower values of *n*, and C at intermediate values. At the highest values studied (*i.e.*, up to $n = 10$), optical and *X*-ray examination showed that, in contrast to the results obtained in the absence of alumina, little or no crystallisation had occurred. In particular, no quartz or cristobalite was ever formed in these experiments from the mixtures containing alumina. Reduction of the temperature to 220° has only a minor effect on these results.

Attempts to obtain B entirely free from amorphous matter and traces of C were unsuccessful, although microscopic examination showed that the products obtained when $n = 2$ contained a high proportion of this species. Chemical analyses of these materials gave results not incompatible with the empirical formula $TlAlSiO_4$ for B, and the 1 : 1 ratio of Tl to Al received some further support from the fact that the composition of the product, and the high yield of *B*, were substantially unaltered if a mixture of appropriate composition was crystallised, not from water, but from an excess of aqueous thallous hydroxide. Two potassium compounds of the corresponding formula ($KAlSiO_4$) have been prepared hydrothermally from mixtures of analogous composition, kaliophilite by Thugutt (*Arch. Min. Soc. Varsovie*, 1937, **13**, 109) and others, and kalsilite by Wyart (*Compt. rend.*, 1947, **225**, 944). Comparison of the *X*-ray powder data did not, however, reveal any striking similarities in spacing as between B and any of the three known forms of $KAlSiO_4$ (cf. Bannister and Hey, *Min. Mag.*, 1942, **26**, 218, and private communication; Rigby and Richardson, *ibid.*, 1947, **28**, 75) except for the spacing close to 3·10 A. which is well marked in all four cases. There is thus as yet an inadequate basis for speculation regarding the structural type of B.

Identity of C with the product obtained by base exchange of analcite with thallous nitrate is indicated by analytical, optical, and *X*-ray data. Species C could be obtained in a fairly pure condition, and analysis indicated the composition $Tl_2O,Al_2O_3,4SiO_2$. Steiger (*loc. cit.*) found that virtually complete replacement of the sodium in analcite could be brought about by treatment in a sealed tube with thallous nitrate at 220°; this was confirmed by the author, and the crystal form, refractive index, and powder photograph of the product were identical with those of C. Furthermore, three successive treatments of the latter with 20% sodium nitrate solution at 250° leached out a total of about 70% of the thallium present, and the refractive indices of the crystals fell gradually to a minimum value close to that of natural or synthetic analcite. *X*-Ray powder photographs and chemical analysis confirmed the view that this product contained a high proportion of analcite.

The fact that C forms mixed crystals with analcite, together with the apparent coincidence of its spacings with those of analcite, shows that there must be a considerable similarity in structure. On the other hand, as Steiger (*loc. cit.*) pointed out, its anhydrous character may indicate an even closer similarity to leucite.

Replacement of water by thallous hydroxide in the hydrothermal treatment of thallous aluminosilicate mixtures extends the range of formation of B to higher values of *n*, while yields of the minor products D and E are increased. *X*-Ray powder photographs of the products richest in these species showed, however, no lines that could not be attributed to either B or C. It is likely that neither D nor E was ever present in sufficient proportion to be apparent in a powder photograph, although it is possible that their strongest spacings may have coincided with spacings of B or C. The nature of D and E is obscure.

EXPERIMENTAL.

Materials.—Thallous oxide was used in the form of aqueous hydroxide, freshly prepared from thallous sulphate and barium hydroxide, moderate precautions being taken to exclude carbon dioxide. Alumina ($Al_2O_3,3H_2O$) was obtained by the action of cold water on amalgamated aluminium (Wislicenus, *Z. angew. Chem.*, 1904, **17**, 805; Weiser and Milligan, *Chem. Reviews*, 1939, **25**, 1); after washing with alcohol and ether and air-drying, ignition loss = 34·5% (theoretical). *X*-Ray powder photographs showed only a few diffuse arcs, very weak when filtered radiation was used; these were not observed on subsequent photographs. The silica was a moist gel, supplied by Messrs. B.D.H., Ltd., containing approximately 15% of SiO_2; extraction with water at 220° yielded a neutral solution free from common inorganic ions. *X*-Ray powder photographs gave no indication of crystalline character.

Preparative Methods.—Each mixture for hydrothermal treatment was prepared from appropriate quantities of the constituents by careful evaporation in a current of carbon dioxide-free air until a white powder was obtained which was sufficiently dry to be ground in a mortar; the product was weighed and kept in a well-stoppered bottle.

Hydrothermal reactions were carried out in stainless-steel autoclaves of approximately 18 c.c. capacity, similar to those described by Barrer (*loc. cit.*). In each case a quantity of mixture containing the equivalent of 2 millimols. of Tl_2O was treated with 10 ml. of water or 0·233N-TlOH. An electric oven thermostatically controlled to ±1° was used for most of the reactions, the duration of which was 36—60 hours; no significant influence on the results could be traced to variations in the time of heating within these limits.

After heating, each autoclave was cooled and opened, and the approximate pH value of the liquor determined colorimetrically as one factor governing reproducibility. The solid residue was filtered off and washed thoroughly with water, alcohol, and ether.

Optical and X-*Ray Examination*.—Optical investigations were made with a Leitz polarising microscope. Refractive indices, which were measured in white light and at room temperature, are accurate to about ±0·005. *X*-Ray data were obtained by means of a Hilger HRX diffraction unit with a 9-cm. powder camera, filtered Cu-$K\alpha$ radiation and 2—4 hour exposures being used throughout. Heavy background intensities and errors in spacing, due to the strong absorption of thallium towards *X*-rays, could be appreciably reduced by dilution of the specimen with gum arabic. Intensities were estimated visually.

Chemical Analysis.—This presents certain difficulties in the case of silicates containing thallium, which are, however, minimised when, as in the present case, acids can be used to effect decomposition. Silica, alumina, thallous oxide, and, where present, sodium oxide were determined on one sample of 0·5—1·0 g. as follows. The sample was decomposed on the water-bath with 70% nitric acid. This presented no difficulty with species B, but C required preliminary grinding followed by prolonged treatment (8—12 hours) with nitric acid. Silica was determined by the standard method, two evaporations being carried out; it should, however, be noted that thallium, as well as silica, may be volatilised by treatment with hydrofluoric and nitric acid. The solution was again evaporated, and the residue taken up in a minimum quantity of dilute nitric acid, reduced by passage of sulphur dioxide, and thallium precipitated as iodide followed by alumina as such. When sodium had to be determined, a freshly prepared solution of ammonium iodide was used to precipitate the thallium, and the sodium was afterwards weighed as sulphate. All analytical results are expressed in terms of the dry weight at 110°.

Species A. Two preparations of 10*a* gave almost identical *X*-ray data, *viz.*, 4·16s, 3·56w, 3·27w, 2·85vw, 2·52w, 2·17w, 2·06w, 1·95w, 1·89vw, 1·62w. Except for the weak spacing 3·56, these agree with data quoted by Hanawalt, Rinn, and Frevel (*Ind. Eng. Chem. Anal.*, 1938, **10**, 457) for α-cristobalite. A similar growth of α-cristobalite was observed when thallous carbonate replaced thallous hydroxide. The preparation of quartz obtained at a higher temperature showed 43 spacings all in agreement with published values (*loc. cit.*).

Species B. Analyses of specimens 2*b*, 2*c*, and 2*e* gave respectively the following results : Tl_2O, 60·0, 62·9, 63·4; Al_2O_3, 18·8, 16·7, 14·5; SiO_2, 20·9, 20·1, 23·1; totals 99·7, 99·7, 101·0 (Calc. for $Tl_2O,Al_2O_3,2SiO_2$ and $Tl_2O,Al_2O_3,3SiO_2$, respectively : Tl_2O, 65·7, 60·1; Al_2O_3, 15·7, 14·4; SiO_2, 18·6, 25·5%). Since all specimens contained traces of C, the analyses may be considered to support the former rather than the latter formula. *X*-Ray powder photographs of specimens 2*b* (two preparations) and 2*e* showed no significant discrepancies and gave the following mean data : (6·50vw), 4·81ms, 4·24vw, 3·31ms, 3·11s, 2·96mw, 2·71m, 2·36vw, 2·28w, 2·19vw, 2·09m, 1·985mw, 1·890mw, 1·840w, 1·780vvw, 1·705mw, 1·645mw, 1·625vw, 1·555vw, 1·520vw, (1·500vvw), 1·465vvw, 1·415vvw, 1·355vw, 1·340vw, 1·285vw, 1·270vw, 1·240vw, 1·225vw, 1·130vw, 1·100vvw. Prolonged and repeated washing of specimen 2*b* with a large quantity of hot water had no sensible effect on the pattern and only a slight effect on the analysis (Tl_2O, 59·6; Al_2O_3, 19·7; SiO_2, 20·1; total 99·4%), thereby indicating that no appreciable thallous carbonate was present.

Specimen C.—Treatment of products 5*c* or 6*c* with cold 10% nitric acid rendered them almost free from other species and the purified material yielded the following *X*-ray powder data : 5·44ms, 3·65s, 3·37s, 2·89m, 2·41mw, 2·195w, 1·965vw, 1·825w, 1·700w, 1·610vw. Analysis : Tl_2O, 53·7; Al_2O_3, 13·5, SiO_2 32·8; H_2O, negligible; total 100·0 (Calc. for $Tl_2O,Al_2O_3,4SiO_2$: Tl_2O, 55·3; Al_2O_3, 13·3; SiO_2, 31·4%).

Base Exchange of Analcite with Thallium.—The analcite was a synthetic sample prepared by Messrs. I.C.I. Ltd. and kindly supplied by Professor Barrer (Found : Al_2O_3, 23·1; SiO_2, 54·3; H_2O, 7·9. Calc. for $Na_2O,Al_2O_3,4SiO_2,2H_2O$: Al_2O_3, 23·1; SiO_2, 54·6; H_2O, 8·2%). *X*-Ray powder photographs showed 37 arcs in satisfactory agreement with published data (W. H. Taylor, *Z. Krist.*, 1932, **83**, 405). 2 G. of this material were treated with 8 g. of thallous nitrate in a sealed glass tube for 6 days at 250°, after which soluble salts were washed out with hot water, and the residue washed with alcohol and ether (Found : Tl_2O, 53·8; Al_2O_3, 14·2; SiO_2, 31·4; Na_2O, 0·7; H_2O, not determined; total, 100·1%). Optical properties : form unchanged (*i.e.*, isotropic spheroids showing few distinct faces), $n = 1·642$. *X*-Ray powder data: 5·66ms, 3·64s, 3·37s, 2·89m, 2·41mw, 2·20mw, 1·960vw, 1·820w, 1·705w, 1·600vw. Two preparations gave identical optical and *X*-ray data.

Base Exchange of C with Sodium.—Approximately 1 g. of the purified material was subjected to three successive treatments with 20% aqueous sodium nitrate for 2 days at 250°. These extracted approximately 45%, 16%, and 10%, respectively, of the thallium present; total 71%. After the third treatment the refractive indices of the crystals of the washed and dried material tended to a lower limit of 1·485 (refractive index of analcite = 1·486) [Found : Tl_2O, 18·3; Al_2O_3, 17·4; SiO_2, 50·5; Na_2O, 7·3; H_2O (by diff.), 6·5. Calc. for a mixture or solid solution of 67% analcite, 33% C : Tl_2O, 18·2; Al_2O_3, 20·0; SiO_2, 46·9; Na_2O, 9·4; H_2O, 5·5%]. *X*-Ray powder data : 5·72s, 4·90m, 3·65w, 3·45vs, 2·94vs, 2·82vw, 2·72m, 2·54w, 2·42m, 2·24m, 1·91mw, 1·87mw, 1·74m, 1·72vvw, 1·69vw, 1·61w, 1·59w, 1·485vw, 1·480vw, 1·410mw, 1·355mw, 1·305vw, 1·280vw, 1·260vw, 1·215m, 1·175vvw, 1·165vw, 1·015vw, 1·005vw. These are in satisfactory agreement with published data for analcite (W. H. Taylor, *loc. cit.*).

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