CCCLXXVII.—*Germanium. Part III. Salts of Germanic Acid.*

By William Pugh.

It is well known that germanium dioxide is soluble both in acids and in alkalis (Winkler, *J. pr. Chem.*, 1886, **34**, 177; van Bemmelen, *Rec. trav. chim.*, 1887, **6**, 205), but whilst a considerable amount of information has been published recently on the salts of germanium dioxide with acids, chiefly by Dennis and his co-workers (*J. Amer. Chem. Soc.*, 1921—1925), comparatively little is known about its salts with bases. The preparation and some of the characteristics of the germanates of sodium, potassium, lithium, barium, lead, and silver are now described.

Sodium Germanate.—In common with other weakly acidic oxides (*e.g.*, silica and tin dioxide) germanium dioxide displaces carbon dioxide from sodium carbonate at its melting point. Pure anhydrous sodium carbonate (0·4884 g.; 1 mol.) and germanium dioxide (0·4819 g.; 1 mol.) were fused together in a platinum crucible over a blast lamp; vigorous effervescence of carbon dioxide occurred and the melt gradually became more viscous. After 5 minutes the melt had become homogeneous and the loss in weight was 0·2025 g. (Calc. for $Na_2CO_3 + GeO_2 = Na_2GeO_3 + CO_2$: 0·2028 g.). By the use of an excess of sodium carbonate only $1\frac{1}{3}$ equivalents of carbon dioxide could be displaced, with the formation of the orthogermanate. Sodium carbonate itself loses carbon dioxide at its melting point; according to Mallard (*Ann. Chim.*, 1873, **28**, 86), the loss is 1·75% of the total weight. Table I gives the observed loss in weight with time of fusion of a mixture of sodium carbonate (0·7495 g.; 2 mols.) and germanium dioxide (0·3695 g.; 1 mol.). The data for sodium carbonate alone (0·9200 g.) are added for comparison. Col. *a* gives the loss in weight in grams, col. *b* that in mols. of carbon dioxide per mol. of sodium carbonate, and col. *c* the loss in mols. of carbon dioxide per mol. of germanium dioxide.

Table I.

Time (mins.).	$Na_2CO_3 + GeO_2$.			Na_2CO_3.	
	a.	*b.*	*c.*	*a.*	*b.*
2	0·2060	0·662	1·324	0·0130	0·0340
4	0·2100	0·675	1·350	0·0130	0·0340
7	0·2110	0·678	1·356	0·0135	0·0353
15	0·2120	0·681	1·362	0·0145	0·0379
25	0·2130	0·684	1·368	0·0160	0·0418

These figures show that the mixture loses two-thirds of its carbon dioxide immediately on fusion and that the subsequent loss is small and comparable with the loss sustained by sodium carbonate when heated alone. There is therefore a clear indication that 4 mols. of carbon dioxide are displaced by 3 mols. of germanium dioxide. The composition of the product corresponds either to a true compound of the formula $4Na_2O,3GeO_2$ or to a mixture of the ortho- and meta-germanates in the proportion 1 : 2. It is significant that Niggli (*J. Amer. Chem. Soc.*, 1913, **35**, 1693) and Morey (*ibid.*, 1914, **36**, 215) have shown that in the system Na_2O–SiO_2 the only stable silicates are the ortho- and the meta-silicates.

Sodium metagermanate, prepared by fusing molecular proportions of sodium carbonate and germanium dioxide, is a white, crystalline substance which is very hygroscopic and absorbs carbon dioxide from the air. It is very soluble, but the solution, which has an intensely alkaline reaction, is rapidly hydrolysed and hydrated germanium dioxide separates. When this solution is evaporated in an atmosphere free from carbon dioxide, it thickens to the consistency of water-glass without crystallising. This viscous solution is highly supersaturated, for on the introduction of a minute nucleus it solidifies completely with evolution of much heat. If, however, the solution be inoculated as it evaporates at the ordinary temperature, the heptahydrate crystallises readily. The best method of preparing this hydrate consists in fusing germanium dioxide with about 10% more than the theoretical quantity of sodium hydroxide, extracting the melt with water, and evaporating the solution over concentrated sulphuric acid. Fusion proceeds much more readily in this case than in the former and, moreover, the excess of sodium hydroxide prevents the undesirable separation of germanium dioxide as the solution becomes concentrated. The crystals were washed with ice-cold water and dried on filter-paper in the air (Found : Na_2O, 21·2 ; GeO_2, 35·7 ; H_2O, 43·0. $Na_2GeO_3,7H_2O$ requires Na_2O, 21·2 ; GeO_2, 35·7 ; H_2O, 43·1%).

The heptahydrate crystallises from water in the rhombic system. Its complete crystallography is being investigated. On standing in air the crystals lose their transparency owing to the absorption of carbon dioxide, but in its absence they retain their transparency indefinitely. They do not absorb moisture from the air, neither do they effloresce. The aqueous vapour pressure, as determined with a tensimeter, is 4 mm. at 20° and 5·5 mm. at 25°. The crystals melt in their own water of crystallisation at about 83°. When freshly prepared, the heptahydrate dissolves completely in water, the solution being strongly alkaline, but the partly dehydrated or carbonated hydrate does not dissolve completely. Its solubility, expressed in g. of anhydrous sodium germanate per 100 g. of water, is 14 at 0° and 25·9 at 25°. Owing to the weakness of germanic acid, this salt gives excellent results on direct titration with *N*- or *N*/10-sulphuric acid and a suitable indicator: with methyl-orange the end-point is sharply defined, but with phenolphthalein the pink colour fades gradually and disappears long before the true end-point is reached.

Potassium Germanate.—All attempts to prepare potassium germanate in the wet way have failed. In one experiment 10 g. of germanium dioxide were fused with 14 g. of potassium hydroxide and the melt was extracted with water and filtered. The solution was concentrated over a free flame and finally over concentrated sulphuric acid. A small nucleus of fused potassium germanate was added from time to time, but the solution merely dried to a thick syrup. In another experiment, the solution obtained after extracting the melt with water was poured into alcohol; the liquid slowly separated into two layers. The denser solution of potassium germanate was repeatedly shaken with absolute alcohol in order to remove the excess of potash and then a small nucleus was added, but even on standing over phosphoric oxide it merely dried to a gummy mass. Both these methods can be used for the preparation of the sodium salt, the heptahydrate being obtained in each case. It appears, therefore, that potassium germanate is too soluble to be crystallised from solution.

Not much better success attended the fusion of germanium dioxide with potassium carbonate: observations were made of the rate of displacement of carbon dioxide. The results are in Table II for an equimolecular mixture of potassium carbonate (0·8438 g.) and germanium dioxide (0·6390 g.), fusion being carried out at the temperature of a Méker burner.

TABLE II.

Time (mins.).	Loss in wt. (g.).	Ratio $CO_2 : GeO_2$.
3	0·2002	0·745
5	0·2076	0·772
13	0·2292	0·855
26	0·2362	0·878
60	0·2366	0·879

These results show that germanium dioxide displaces 0·75 equiv. of carbon dioxide immediately on fusion, whilst the remainder of the carbon dioxide is only slowly displaced on prolonged fusion. It is conceivable that the whole of the carbon dioxide would be displaced at a higher temperature. Potassium carbonate when heated alone under the same conditions loses only 0·25% of its weight. Niggli (*loc. cit.*) has shown that in the system K_2O–SiO_2 the only stable silicates are the meta- and the di-silicate, and that when potassium carbonate is fused with silica the following equilibrium is set up: $K_2Si_2O_5 + K_2CO_3 \rightleftharpoons 2K_2SiO_3 + CO_2$. From a consideration of the results in Table II, it appears that the system K_2O–GeO_2 is analogous. In order to elucidate the constitution of the fused germanates of sodium and potassium further work is necessary under definite conditions of temperature and pressure.

Lithium Germanate.—Lithium metagermanate is readily obtained, as in the case of the sodium salt, by fusing together molar proportions of lithium carbonate and germanium dioxide. The displacement of carbon dioxide is quantitative. Lithium orthogermanate is also obtained, just as readily, by fusing 2 mols. of lithium carbonate with 1 mol. of germanium dioxide. This again brings germanium dioxide into line with silica, for corresponding silicates have been described by Niggli (*loc. cit.*) and by Hautefeuille and Margottet (*Compt. rend.*, 1881, **93**, 686).

A hydrated lithium metagermanate is formed on mixing fairly strong solutions of sodium metagermanate and a lithium salt. In the cold, it forms a gelatinous precipitate, but on boiling this becomes granular and increases in bulk. The substance was analysed after being washed and dried to constant weight over sulphuric acid (Found: Li_2O, 21·3; GeO_2, 74·4; H_2O, 4·3. $Li_2GeO_3,\frac{1}{3}H_2O$ requires Li_2O, 21·35; GeO_2, 74·4; H_2O, 4·3%).

Hydrated lithium metagermanate is a white, floury substance which does not lose weight when kept over phosphoric oxide for a week. In the air, it slowly absorbs carbon dioxide. Its solubility in water at 25° is 0·85 g. of the anhydrous salt per 100 g. of water. The aqueous solution is strongly alkaline and may be titrated with standard acid. It is readily soluble in dilute mineral acids.

Barium Germanate.—When aqueous solutions of sodium metagermanate and barium chloride are mixed, a pure white, granular precipitate is formed; its composition is variable, however, being dependent on the concentration of the solutions and on the time of washing. One specimen gave: BaO, 35·3; GeO_2, 43·5; H_2O, 21·1%; this analysis corresponds to a very complex formula, the molecular ratios being approximately 3 : 5 : 15. With prolonged washing, the barium content decreased, thus suggesting that the normal germanate, $BaGeO_3$, is hydrolysed progressively. A similar behaviour in regard to barium silicate is described by Le Chatelier in his classical work on the constitution of hydraulic mortars. When the precipitation was carried out in the presence of an excess of baryta or caustic soda, trihydrated barium metagermanate was formed; it was washed rapidly in a Gooch crucible with water, alcohol, and ether (Found: BaO, 48·5; GeO_2, 34·0; H_2O, 17·5. $BaGeO_3,3H_2O$ requires BaO, 49·2; GeO_2, 33·5; H_2O, 17·3%). The discrepancy is due to slight hydrolysis during washing. Barium metagermanate is a white powder which is slowly decomposed by water. It is insoluble in alcohol and in ether, but readily soluble in dilute acids.

Lead Germanate.—When solutions of sodium metagermanate and lead acetate were mixed, lead metagermanate was formed as a bulky, white, gelatinous precipitate which became granular on heating. It was washed and dried in the air or over calcium chloride (Found: PbO, 65·7; GeO_2, 30·8; H_2O, 3·5. $3PbGeO_3,2H_2O$ requires PbO, 65·7; GeO_2, 30·8; H_2O, 3·5%). It is a white powder practically insoluble in water and insoluble in alcohol and ether, but soluble in dilute mineral acids. At a red heat, it melts to a red, oily liquid and on cooling again it solidifies to a pale yellow solid. It does not decompose on fusion.

Silver Germanate.—Anhydrous silver metagermanate is precipitated when solutions of silver nitrate and sodium metagermanate are mixed (Found: Ag, 64·15; GeO_2, 31·1. Ag_2GeO_3 requires Ag, 64·2; GeO_2, 31·05%). It is a light brown powder which is practically insoluble in water but soluble in acids. It is sensitive to light, being rapidly turned almost jet black in sunlight. On heating, it darkens, melts to a dark liquid, and decomposes with evolution of oxygen. The loss in weight at a red heat is 4·7%. The residue consists of metallic silver and germanium dioxide. Silver germanate is completely soluble in aqueous ammonia.

Summary.

(1) Observations have been made of the rate of displacement of carbon dioxide from the carbonates of lithium, sodium, and potassium by germanium dioxide. The extent and rate of displacement are parallel with the extent to which the various carbonates lose carbon dioxide by dissociation.

(2) Heptahydrated sodium metagermanate has been crystallised from solution. Potassium germanate is too soluble to be crystallised.

(3) Metagermanates of lithium, barium, lead, and silver have been prepared by precipitation with sodium metagermanate.

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