

467. Germanous Oxide and Sulphide.

By DAVID A. EVEREST and HENRY TERREY.

Germanous hydroxide can be prepared in either a white or a coloured form, the difference being due to varying degrees of hydration and particle size. The acidic nature of germanous hydroxide has been investigated, but no support for the view (put forward by Hantzsch) that germanous hydroxide acts as germanoformic acid can be found. Similarly, with germanous sulphide, no acidic properties can be detected.

GERMANOUS hydroxide was first investigated by Winkler (*J. pr. Chem.*, 1886, **34**, 177) and its preparation has been more recently described by Bardet and Tchakarian (*Compt. rend.*, 1928, **186**, 637) and by Dennis and Hulse (*J. Amer. Chem. Soc.*, 1930, **52**, 3553). The latter authors observed the ease with which germanous hydroxide was oxidised by air; they also showed that when the hydroxide was heated in a vacuum, water was continuously removed, no evidence of the formation of definite hydrates being obtained. Microscopic examination showed that the darkening in colour observed on dehydration was due to an increase in particle size.

Winkler's method of preparation consisted in the action of water on germanochloroform, a reaction also studied by Dennis and his co-workers (*J. Physical Chem.*, 1926, **30**, 1049). These authors observed that if germano-chloroform was first treated with a little water a white solid was formed, which, on standing in presence of excess water, changed to the characteristic red germanous hydroxide.

The method of preparation used in this research is that described by Dennis and Hulse (*loc. cit.*): a solution of germanium dioxide (0.25—0.5M.) in 6N-hydrochloric acid was reduced with excess of 30% hypophosphorous acid, and germanous hydroxide was then precipitated with an excess of dilute ammonia. Germanous hydroxide is very readily oxidised by air, and the precipitation and washing of the precipitate were carried out in an atmosphere of nitrogen. Thus prepared, germanous hydroxide is a yellow to red gelatinous substance, soluble in dilute hydrochloric acid. If the precipitation is carried out from a boiling solution, the product is dark brown and somewhat granular and dissolves much more slowly than does the yellow form in dilute hydrochloric acid.

If a concentrated solution (1.5—2.0M.) of germanium dioxide was reduced with excess of hypophosphorous acid, and the solution simply diluted with water, a thick white precipitate of germanous hydroxide was formed. In contact with the solution this white form of germanous hydroxide slowly darkened until the normal red modification was obtained. This change in colour was found to take place immediately on addition of alkali. The ease of solubility of the white modification in dilute hydrochloric acid was much greater than that of the coloured forms, the rate of solution falling off on going from the white to the brown modification. This white form of germanous hydroxide appears to be the white compound observed by Dennis and his co-workers (*loc. cit.*) on treating germano-chloroform with a little water.

It was not possible to analyse any of the samples of germanous hydroxide, attempts to dry them simply resulting in a continuous loss of water till germanous oxide was formed.

Germanous hydroxide in the above reactions resembles stannous hydroxide (Bury and Partington, *J.*, 1922, **121**, 1998; Straumanis and Strenk, *Z. anorg. Chem.*, 1933, **213**, 301). Stannous hydroxide when precipitated is white, but when it is warmed with a little sodium hydroxide or sodium carbonate solution, its colour darkens through yellow to reddish-brown and finally to the bluish-black of stannous oxide.

The Acidic Properties of Germanous Hydroxide.—From the position of germanium in the Periodic Table it would be expected that germanous hydroxide should show acidic properties, especially as the acidic nature of stannous hydroxide seems to have been definitely established (Scholder, *Angew. Chem.*, 1936, **49**, 255). The chief evidence for the alleged acidic nature of germanous hydroxide rests on experiments by Hantzsch (*Z. anorg. Chem.*, 1902, **30**, 316). He observed that there was a reduction in the conductivity of sodium hydroxide solutions on addition of germanous hydroxide. On the basis of his measurements he postulated that germanous hydroxide acted as a monobasic acid, germanoformic acid, $\text{H}\cdot\text{GeO}\cdot\text{OH}$. Hantzsch prepared his germanous hydroxide by Winkler's method (*loc. cit.*), *i.e.*, by passing hydrogen chloride over heated elementary germanium. However, as was observed by Dennis and his co-workers (*loc. cit.*) and by Delwaille and François (*Compt. rend.*, 1949, **228**, 1007), germanochloroform thus prepared contains up to 30% of germanium tetrachloride. Hydrolysis of such a mixture would give a product containing germanium dioxide, which has acidic properties (see Gulezian and Muller, *J. Amer. Chem. Soc.*, 1932, **54**, 3142, 3151). Hantzsch

also did not take into account any diminution in the conductivity of the sodium hydroxide solution which would have occurred if colloidal solution of the germanous hydroxide had taken place with the resultant removal of ions from solution by adsorption at the surface of the colloidal germanous hydroxide particles.

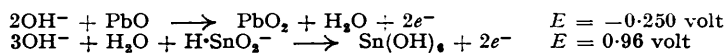
Other references to the acidic nature of germanous hydroxide have been made by Tchakarian (*Compt. rend.*, 1934, **199**, 886), Royan and Schwarz (*Z. anorg. Chem.*, 1933, **211**, 412), and Brine (M.Sc. Thesis, London Univ., 1937). Tchakarian observed that if either germanous oxide or hydroxide was heated with 50% sodium hydroxide solution, hydrogen and sodium germanate were formed. He assumed that in dilute alkali sodium germanoformate was formed, but that this decomposed when the concentration of alkali was increased. He put forward no evidence, however, for the actual formation of sodium germanoformate. Royan and Schwarz observed that if the hydride $(\text{GeH}_2)_x$ was treated with alkali a red opaque solution was obtained, which was said to contain sodium germanite Na_2GeO_2 , but they did not report any actual investigation of this solution. Brine attempted to detect the formation of germanite polarographically by using saturated solutions of germanous hydroxide in 0.1N-alkali. He did not take any precautions to ensure the absence of any quadrivalent germanium, but the only waves he obtained were due to this, for he had already studied its polarographic behaviour in acid and alkaline media. Dennis and Hulse (*loc. cit.*) observed that germanous hydroxide when freshly precipitated gave with alkali reddish opaque solutions which they thought to be colloidal.

There are clearly considerable discrepancies in the literature as to the nature of solutions of germanous hydroxide in alkali. It was hoped that information could be obtained by means of potentiometric titrations of aqueous solutions of germanous hydroxide with alkali, but its low solubility in water precluded this: we found 0.044%, whereas Robinson (*Ann. Reports*, 1944, **41**, 111) quotes 0.18%. Even our lower figure should be accepted with reserve, as it is quite possible that a large part of the germanous hydroxide was present in the colloidal form.

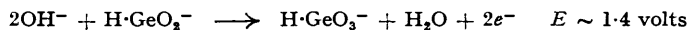
Similarly, attempts to obtain evidence from the solubility of germanous oxide in alkali solutions of different concentrations were not successful. No relation between the results could be observed, and it was uncertain if the measured solubilities were not all due to quadrivalent germanium, germanous oxide being slowly oxidised by cold alkaline solutions (Tchakarian, *loc. cit.*). The solubilities observed were considerably smaller than those found for stannous oxide in alkali by Garrett and Heiks (*J. Amer. Chem. Soc.*, 1941, **63**, 562).

The method eventually used was a variation of Hantzsch's conductometric method. Preliminary experiments on sodium hydroxide-germanous hydroxide systems showed that oxidation caused large conductivity changes owing to the formation of the acidic germanium dioxide. It was therefore very important to ensure complete absence of any quadrivalent germanium during the course of the experiments (see p. 2284). It was found that there was no reaction between germanous hydroxide and sodium hydroxide, and no acidic properties of germanous hydroxide could be detected. There is also practically no tendency for the formation of colloidal solutions if all the quadrivalent germanium is absent. It was found, however, that if these solutions were exposed to the air, and some quadrivalent germanium was formed by oxidation, colloidal solutions were readily formed; this phenomenon is also shown by germanous sulphide.

This lack of acidic properties of germanous hydroxide is at first sight somewhat surprising. However, by comparison with the potentials of the bivalent-quadrivalent couples for lead and tin, it was seen that the germanite ion would have an extremely high reduction potential in alkaline media:



Latimer ("Oxidation Potentials," p. 136) has given a rough estimate of the corresponding germanium couple:



It seems probable indeed that the fact that bivalent germanium can exist at all in alkaline media is due to the insolubility of germanous hydroxide. If the germanite ion did exist in alkaline media it would spontaneously decompose into germanate, with deposition of germanium and/or liberation of hydrogen. This conclusion is supported by Tchakarian's observations on the oxidation of bivalent germanium in alkaline media (*loc. cit.*). It is a well-known fact also that alkaline solutions of stannous hydroxide tend to decompose on standing, giving stannate and metallic tin.

Acidic Nature of Germanous Sulphide.—Germanous sulphide has been prepared by a number of workers, and observations on its solubility in alkalis have been made. The crystalline form was prepared by Dennis and Joseph (*J. Physical Chem.*, 1927, **31**, 1716) by reduction of germanium disulphide with hydrogen, and also by Pugh (*J.*, 1930, 2371) by the action of hydrogen and hydrogen sulphide on germanium dioxide at 700°; prepared in this manner, it is a dark red to black crystalline solid. The pure substance was insoluble in alkali at room temperature, but if finely divided it was soluble in hot dilute caustic alkali.

Johnson and Wheatley (*Z. anorg. Chem.*, 1934, **216**, 273) also prepared crystalline germanous sulphide by direct volatilisation out of germanite. They found the crystalline material to be somewhat soluble in caustic alkali. They also prepared amorphous germanous sulphide, as did Dennis and Hulse (*loc. cit.*); this form was found to be readily soluble in dilute caustic alkalis. None of these authors claimed that these alkaline solutions contain thiogermanites and it seems to be implied, although it is not stated, that these solutions are actually colloidal. In view of the fact that germanites do not appear to exist, the nature of these solutions was reinvestigated, especially as none of the above authors recorded any precautions to exclude air when observing the solubility of germanous sulphide in alkali.

Amorphous germanous sulphide was used throughout this work. This substance is difficult to obtain in a state of purity, a small percentage of quadrivalent germanium usually being present. It was found that when germanous sulphide contained a trace of quadrivalent germanium, it was readily soluble in caustic alkali, an opaque red solution being obtained. If these solutions were centrifuged a considerable amount of germanous sulphide could be separated. Addition of dilute hydrochloric acid precipitated germanous sulphide completely, and precipitation was also brought about if ammonium chloride, ammonium carbonate, or potassium chloride was added to the solution. These facts all point strongly to the solutions being colloidal. These colloidal germanous sulphide solutions are readily oxidised, germanium disulphide and dioxide being formed. It was also found that if great care was taken to remove all quadrivalent germanium, and if precautions were taken against oxidation, then amorphous germanous sulphide was insoluble in caustic alkalis. It therefore seems probable that colloidal solutions in caustic alkalis were only formed in presence of germanium disulphide and dioxide. Both these compounds are soluble in alkalis, giving germanate and thiogermanate ions, these ions providing the charges needed to stabilize the colloidal germanous sulphide particles. It can therefore be stated that germanous sulphide resembles the oxide in showing no observable acidic properties.

EXPERIMENTAL.

A solution of germanium dioxide (0.25—0.5M.) was reduced by $\frac{1}{2}$ hour's refluxing with excess of 30% hypophosphorous acid. The germanous hydroxide was then precipitated by addition of excess of ammonia solution, filtered off in a nitrogen atmosphere, and well washed with air-free distilled water.

The solubility of germanous hydroxide was measured by addition of excess to about 100 ml. of air-free distilled water in a 250-ml. conical flask. A vigorous stream of oxygen-free nitrogen was then bubbled through the solution for about 15 minutes, after which the flask was carefully sealed, and placed in a thermostat at 25° for 24—30 hours, the flask being shaken at regular intervals. The excess of germanous hydroxide was then allowed to settle out, and 25-ml. samples of the supernatant liquid were carefully pipetted out and oxidised by addition of two or three drops of hydrogen peroxide (30-vol.), and the germanium dioxide so formed was titrated as a monobasic acid after addition of glycerol (Tchakarian, *Compt. rend.*, 1928, **187**, 229). The results obtained, expressed as g. of germanous oxide (GeO) per 100 ml. of water, were as follows: 0.054, 0.033, 0.048, 0.033, 0.052, 0.058, 0.027, 0.051; mean, 0.044.

Acidic Properties of Germanous Hydroxide.—The conductivity experiments were carried out in a three-necked flask of about 500-ml. capacity; the two outside necks held the electrodes which were 2-cm. squares of bright platinum. Air-free distilled water (100 ml.) was then added, and a rapid stream of oxygen-free nitrogen was passed continuously through the solution, ensuring that an inert atmosphere was present and also that the contents of the flask were well stirred.

To get pure germanous hydroxide, free from any quadrivalent germanium, some of the freshly precipitated compound was dissolved in about 5—7 ml. of concentrated hydrochloric acid. This solution was then evaporated to about half its original volume, any quadrivalent germanium distilling out as germanium tetrachloride (b. p. 83°). This purified solution was then poured into the water contained in the three-necked flask, whereupon hydrolysis took place and pure germanous hydroxide was precipitated. Alkali (0.1N.) was then run into the solution, and the change in conductivity noted. The minimum of the conductivity curves was taken as the point where all the hydrochloric acid had been neutralised; any reaction between the germanous hydroxide and the alkali would then start at that point. No solution of the germanous hydroxide was observed to take place even when ten times the theoretical amount of alkali had been added. There was also no trace of a break in the conductivity curve obtained (see figure). When a very vigorous stream of nitrogen was passed into the solution, a red opaque suspension was formed, but after a few minutes' standing all the germanous hydroxide had

settled out. The amount of germanium in the supernatant liquid was shown to be negligible by oxidising the solution by bubbling a stream of air through it, adding acid to give an acidity of 6*N.*, and passing in hydrogen sulphide, but no germanium disulphide was precipitated. Subsequent experiments under the same conditions have shown that germanous hydroxide is insoluble in alkali up to 1*N.* in concentration if all quadrivalent germanium is absent; otherwise colloidal solutions tend to be formed.

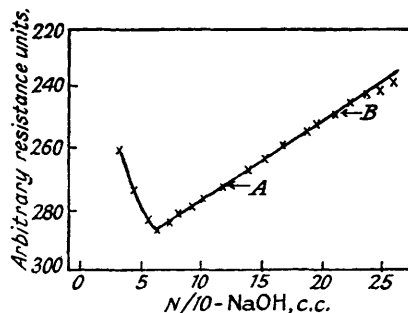
Germanous Sulphide. All the preparations were carried out by passing hydrogen sulphide into a solution of bivalent germanium in hydrochloric acid (see preparation of germanous hydroxide). In the first method this solution was first neutralised with dilute ammonia, hydrogen sulphide passed in, and the resultant precipitate of germanous sulphide filtered off in a nitrogen atmosphere and then dried in a vacuum over phosphoric oxide, the desiccator having been filled with nitrogen before evacuation. Germanium was determined by oxidation with nitric acid to germanium dioxide, followed by ignition (Found: Ge, 72.69, 74.04, 71.40, 73.03. Calc. for GeS: Ge, 69.37%). The high results were traced to co-precipitation of germanous hydroxide owing to the fact that the solution had been neutralised with ammonia before passage of hydrogen sulphide. On drying, germanous hydroxide would give germanous oxide. These samples were all soluble in caustic alkalis, even after digestion for 24 hours with a few ml. of ammonia (d 0.880) to remove germanium disulphide. It was very probable that these samples contained germanium dioxide formed by oxidation of the germanous oxide. Germanium dioxide cannot be detected in presence of germanous sulphide by determination of only germanium, as the percentage of germanium is the same in both cases.

The second method consisted of first saturating the bivalent germanium solution with hydrogen sulphide, adding dilute ammonia solution while the passage of hydrogen sulphide was continued till all the germanous sulphide had been precipitated, filtering this off, and drying it as before. Germanium was determined as before. Sulphur was determined by dissolving the germanous sulphide in alkali in presence of hydrogen peroxide; this solution was then boiled for about $\frac{1}{2}$ hour, the sulphur being oxidised to sulphate, which was then precipitated as barium sulphate and ignited (Found: Ge, 69.19; S, 30.91. Calc. for GeS: Ge, 69.37; S, 30.63%). These results indicate that a very small amount of germanium disulphide was still present; it was observed that this sample was somewhat soluble in caustic alkalis, giving a colloidal solution. When this sample was digested for 24 hours in ammonia solution (d 0.880) to remove the last traces of germanium disulphide, it was found to be quite insoluble in alkalis. This was shown by placing the sulphide in air-free *N*-sodium hydroxide solution, and bubbling in a rapid stream of nitrogen to stir the solution and to ensure an inert atmosphere. After 2 hours no solution had taken place.

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WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, LONDON.

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A and B represent the amounts of sodium hydroxide necessary to neutralise the first and the second hydrogen atom in germanous hydroxide.