

192. Germanium (Germanyl) Ferrocyanide.

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Ionised ferrocyanides react with acid solutions of germanium dioxide to form an insoluble white precipitate. The reaction can be used as a qualitative test for germanium and, under proper conditions, leads to a product of definite composition, namely *germanyl ferrocyanide*, $[\text{Ge}(\text{OH})_2]_2\text{Fe}(\text{CN})_6$ or $(\text{GeO})_2\text{Fe}(\text{CN})_6 \cdot 2\text{H}_2\text{O}$.

INSOLUBLE ferrocyanides of quadrivalent titanium, zirconium, thorium, and tin are well known (Gmelin, "Handbuch der Anorganischen Chemie," 8th Edn., System No. 59, Part B, 1930, p. 604), but no corresponding compound of germanium has been described hitherto. Many years ago, one of us (F. S.) observed that a white precipitate appeared when an acid solution of germanium chloride was treated with potassium ferrocyanide. The nature of this precipitate and the conditions necessary for the preparation of *germanyl ferrocyanide* are now described.

The formation of a white precipitate, or even a colloidal opalescence, on treatment with ferrocyanide may well serve as a useful qualitative test for germanium. This element is usually associated in minerals with arsenic and is separated from other metals by distillation of the volatile chloride from hydrochloric acid solutions. However, even with the utmost precautions to keep arsenic in the quinquevalent state the distillate contains some arsenic which then interferes with the simple test for germanium by precipitation as the white sulphide. Neither trivalent nor quinquevalent arsenic gives a precipitate with ferrocyanides (Gmelin, *op. cit.*, p. 607). Hence, if the distillate is treated with potassium ferrocyanide solution the appearance of a precipitate is evidence of the presence of germanium. One part of germanium in 10,000 parts of solution gives an opalescence; larger amounts give a white gelatinous precipitate.

The nature and appearance of this precipitate vary with the conditions. In slightly acid solution there may be a time lag of an hour or more before precipitation, but it is shortened by increasing the acidity of the solution and by raising the temperature; the optimum conditions appear to be an acidity at least equivalent to 4*N*-hydrochloric acid and a temperature of 50—60°. The appearance of opalescence or a precipitate, depending on the concentration of germanium, is then a matter of seconds. Sulphuric, acetic, and chloroacetic acid are much less effective in coagulating the initial sol; and if the temperature exceeds 70° the initial white precipitate becomes blue rather quickly.

This colour change is undoubtedly due to the formation of Prussian-blue by decomposition of the excess of ferrocyanide in the strongly acid solution (Gmelin, *op. cit.*, p. 584). It takes place slowly in the cold, even in the dark and in the absence of air, but rapidly if a large excess of ferrocyanide is employed. Consequently, in the early part of the work it was impossible to get a product of uniform composition. Later, it was found that if the ratio of ferrocyanide to germanium does not exceed one g.-ion per g.-atom the precipitate darkens only slowly during several days. This is fortunate because the gelatinous precipitate cannot be filtered off and, as it is highly retentive of adsorbed electrolytes, its washing by decantation and centrifugation occupies several days. Under the most favourable conditions encountered the final product had acquired a pale mauve tinge. This product was found to contain two atomic proportions of germanium for each ferrocyanide radical and its analysis corresponds with the empirical formula $(\text{GeO})_2\text{Fe}(\text{CN})_6 \cdot 2\text{H}_2\text{O}$ or $[\text{Ge}(\text{OH})_2]_2\text{Fe}(\text{CN})_6$. X-Ray structure analysis is the only means of establishing unequivocally which is the actual structure. No compound even approximating in composition to $\text{GeFe}(\text{CN})_6$ has been detected in this work, and this is in accord with the general chemistry of germanium, for there is no recorded compound of this element in which the occurrence of a simple quadrivalent germanium ion has been established.

A similar zirconyl ferrocyanide, $(\text{ZrO})_2\text{Fe}(\text{CN})_6$, has been described by Weibull (*Lunds Univ. Arsskr.*, 1881—82, II, 18, No. 5, 40), though Venable and Moehlmann (*J. Amer. Chem. Soc.*, 1922, 44, 1705) obtained products with ferrocyanide-zirconyl ratios as high as 3:4. Our

experience with the germanium ferrocyanide leads us to suspect, however, that the American authors' products were highly contaminated with Prussian-blue.

EXPERIMENTAL.

Germanyl Ferrocyanide.—Pure germanium dioxide (4 g.) was dissolved in hot 5*N*-sodium hydroxide (100 ml.). The solution was diluted to 400 ml., filtered from a trace of undissolved oxide, neutralised with hydrochloric acid, and treated with concentrated hydrochloric acid to bring the acidity to 5*N*. The temperature was adjusted to 60°. Precipitation was made with 0.2*M*-potassium ferrocyanide (200 ml.).

The only practical way of washing the pure, white, bulky, and gelatinous precipitate was by settling and decantation. Because each settling period was of the order of a day the whole process of washing was extremely tedious and led to continuous darkening of the product. After the fourth wash the precipitate was dried *in vacuo* for several days, becoming then more granular. Further washing with water was then possible in a much shorter time and without appreciable decomposition. Finally, the moist precipitate was centrifuged 10 times with small amounts of ether to ensure complete removal of adsorbed hydrochloric acid. Alcohol could not be used for this purpose, for it tended to peptise the material. The product was then dried *in vacuo*.

It was a pale mauve powder which was quite stable in air and showed no tendency to become blue after many weeks' exposure to the laboratory atmosphere. Some samples that had been less thoroughly washed did become blue on storage. A thin film of Prussian-blue could often be seen over the surface of the precipitate in the centrifuge tube.

Analysis.—Germanium was determined as Mg_2GeO_4 by a modification of Muller's method (*J. Amer. Chem. Soc.*, 1922, **44**, 2493). Modification was necessary because *germanyl ferrocyanide* is insoluble in water and in acids. It does however dissolve in caustic alkalis and in aqueous ammonia. An ammoniacal solution of the sample was therefore treated with ammonium sulphate-magnesium sulphate solution, the proportions of the reagents being carefully controlled in accordance with Muller's directions. The precipitate of magnesium ammonium germanate, after being washed, was ignited to Mg_2GeO_4 . The ferrocyanide in the filtrate from the germanium determination was determined, after acidification with sulphuric acid, by titration with standard permanganate by the method of de Haen (*Annalen*, 1854, **90**, 160) or with standard ceric sulphate using ferroin as internal indicator (Vogel, "Quantitative Inorganic Analysis," Longmans, 1947, p. 383). In a few cases too, the total iron was determined volumetrically after decomposition of a fresh sample with concentrated sulphuric acid (Kjeldahl). Excellent agreement was obtained by all methods.

In all, over 30 analyses were made of samples of 4 different preparations {Found: Ge, 34.2; $Fe(CN)_6$, 49.6; Fe, 13.0. $[Ge(OH)_2]_2Fe(CN)_6$ requires Ge, 34.2; $Fe(CN)_6$, 49.84; Fe, 13.1%}.

Confirmation that the compound contains either co-ordinated water or hydroxyl groups was obtained by pyrolysis. A weighed sample, mixed with copper oxide to decompose volatile cyanogen compounds, was heated in a combustion train in pure dry air and the water liberated was absorbed in "Anhydrone." The water absorbed amounted to 8.6% (Calc. for $2H_2O$, 8.5%).

Properties.—Pure germanyl ferrocyanide is a white solid which, like all other ferrocyanides, is slowly decomposed by strong acids with formation of Prussian-blue. It is insoluble in water and in moderately strong acids, but dissolves readily in alkalis, with decomposition, forming soluble germanates and alkali ferrocyanides. Heat decomposes it; at 130° it loses about one-third of its weight, and the vapours smell strongly of cyanogen compounds; at a red heat in air it loses half its weight and the vapours carry germanium as well, probably the result of reduction by carbon to the volatile germanous oxide. When desiccated *in vacuo* over sulphuric acid it becomes extremely hygroscopic; it will then absorb up to one-third of its own weight of water.