27. *Gallium. Part VII. Gallium Perchlorate Hydrates and a Gallium Perchlorate–Urea Complex.*

By D. J. Lloyd and W. Pugh.

Gallium is shown to conform with the other members of its group in forming hydrated and highly soluble perchlorates; a *nonahydrate* and a hexahydrate are described. The former loses $3H_2O$ readily, but the remaining $6H_2O$ are strongly co-ordinated, and attempts to dehydrate the hexahydrate lead to decomposition of the perchlorate. A 6-co-ordination *compound* of gallium perchlorate and urea is also described.

The congeners of gallium are all known to form crystalline perchlorates. No less than four hydrates of aluminium perchlorate are described, containing 15, 12, 9, and $6H_2O$ (Gmelin's "Handbuch," 8th Edn., No. 35, Part B, p. 217); one hydrate of indium perchlorate, the octahydrate (Mathers and Schleuderberg, *J. Amer. Chem. Soc.*, 1908, **30**, 212), and one of thallic perchlorate, the hexahydrate (Gewecke, *Z. anorg. Chem.*, 1912, **75**, 272), are described. No anhydrous perchlorates of these metals have yet been prepared.

Of gallium perchlorate nothing was known when the present work was commenced. Willard and Fogg (*J. Amer. Chem. Soc.*, 1937, **59**, 1197) had used solutions of gallium hydroxide in perchloric acid for the electrodeposition of gallium and, while the present work was in progress, Foster (*ibid.*, 1939, **61**, 3123) described the preparation of two hydrates containing 6 and $9\frac{1}{2}H_2O$. We had already prepared the hexahydrate and a *nonahydrate*, but we have been unable to confirm the existence of Foster's second hydrate: we are of the opinion that this was identical with our nonahydrate and that his methods of analysis were not precise enough to distinguish between the two formulæ. The differences in composition would be very small, especially as regards gallium, and it is our experience that the method, used by Foster, of estimating perchlorate as the potassium salt from alcoholic solution is not precise enough for the purpose. We have, in fact, been able to confirm our results by a determination of chloride ion after decomposition of the perchlorate. We have also shown that both hydrates decompose on strong heating to gallium oxide and that the yield of oxide is quantitative in both cases, the volatile products consisting mainly of water vapour, chlorine, and oxygen.

Determinations of loss in weight with time at different temperatures have shown that the nonahydrate is converted into the hexahydrate below 100° and into basic perchlorates of indefinite composition above 100°. At 125° the product obtained approximated closely in composition to $3Ga_2O_3,Ga(ClO_4)_3$. There was no evidence of the formation of any lower hydrates or of the anhydrous salt.

Urea and other weak organic bases form co-ordination compounds with many inorganic salts; $Al(ClO_4)_3,6CO(NH_2)_2$ has been described by Barbieri (*Atti R. Accad. Lincei*, 1915, **24**, 917). Gallium perchlorate is now shown to form a similar *compound* with urea, but all attempts to prepare co-ordination compounds with pyridine and thiourea by similar means failed. In the former case, pyridine perchlorate always separated, and in the latter case thiourea crystallised unchanged.

Experimental.

Gallium Perchlorate Nonahydrate.—Gallium metal (5 g.) was dissolved in concentrated nitric acid as described by Sebba and Pugh (J., 1937, 1376), and the solution evaporated nearly to dryness to remove the excess of acid. A small excess of 60% perchlorate acid was added, and evaporation continued until the syrupy liquid solidified on cooling. Water was then added, and the evaporation repeated in order to remove all traces of nitric acid. The crystalline mass

was dissolved in the minimum quantity of hot water and set aside to crystallise over sulphuric acid in a vacuum desiccator. Since gallium perchlorate solutions supersaturate very easily, the liquid was seeded from time to time.

Large, transparent, monoclinic crystals, several cm. long, were grown in this manner. The crystals were exceedingly soluble in water, and deliquescent; they liquefied completely after exposure to the air for a few minutes. They were also very soluble in alcohol, acetone, benzene, xylene, and light petroleums, but less soluble in ether. Hence, removal of the adhering mother-liquor and subsequent drying was best effected by centrifuging the crystals, washing them once with ice-water and once with ether, and exhausting them in a vacuum desiccator. They were then transferred to a weighing bottle and kept over sulphuric acid, being weighed at fixed intervals. In the course of a few hours, the rate of loss in weight had fallen to a low and constant value, indicating that all mechanically held water had been removed. It was necessary to confirm this because indium perchlorate is said to form an octahydrate (Mathers and Schleuderberg, *loc. cit.*) and gallium perchlorate a hydrate with $9\frac{1}{2}H_2O$ (Foster, *loc. cit.*), so in later work drying was effected over gallium perchlorate hexahydrate.

A similar product was obtained by dissolving freshly precipitated gallium hydroxide in a small excess of perchloric acid, but this was a much more tedious process because of the bulky and gelatinous nature of gallium hydroxide.

To determine the exact composition, gallium was precipitated with cupferron (Moser and Brukl, *Monatsh.*, 1929, **51**, 327) and with sodium carbonate at pH 5. Both methods gave identical results. Perchlorate was estimated by several methods; precipitation of nitron perchlorate (Loebich and Fichter, *Z. anal. Chem.*, 1926, **68**, 34, 298) and precipitation of potassium perchlorate (Arndt and Nachtwey, *Ber.*, 1926, **59**, 446, 1072) gave variable and uncertain results. Conclusive results were obtained by conversion into chloride and weighing as silver chloride (Winteler, *Chem. Ztg.*, 1897, **21**, 75; Mathers and Schleuderberg, *loc. cit.*) [Found: Ga, 13·16; ClO_4, 56·5; Cl, 19·98. $Ga(ClO_4)_3,9H_2O$ requires Ga, 13·15; ClO_4, 56·28; Cl, 20·06%].

Thermal decomposition. A weighed portion of the *hydrate* (0·1 g.) was strongly ignited in a Pyrex tube closed at one end, and the volatile products were collected in a gas-measuring burette over mercury. After removal of chlorine by combination with the mercury, the volume of oxygen remaining (25·8 ml.) agreed fairly well with the theoretical value (24·2 ml.) required for decomposition according to the equation $4Ga(ClO_4)_3,9H_2O \longrightarrow 2Ga_2O_3 + 36H_2O + 6Cl_2 + 21O_2$. That no volatile gallium compounds were lost was shown by igniting weighed portions to constant weight: theoretical yields of oxide were obtained [Found: Ga_2O_3, 17·85, 17·68. $Ga(ClO_4)_3,9H_2O$ requires Ga_2O_3, 17·67%].

A number of experiments were made in which the nonahydrate was maintained at fixed temperatures and the loss in weight determined at intervals. At 100°, the rate of loss in weight was rapid, reaching a constant value (10·6%) after a few days (Calc. for loss of $3H_2O$: 10·2%). At higher temperatures there was the same initial rapid loss, followed by slower and continuously diminishing rate of loss. On plotting the loss in weight against time, there was no evidence of the formation of lower hydrates of constant vapour pressure. At 115° the loss had reached 32% after 20 days and was still rising. At 125° the loss was 71% after 5 days and 74% after 20 days, the rate of loss after 12 days being very low. This indicates the possible formation of a stable basic perchlorate, $3Ga_2O_3,Ga(ClO_4)_3$. Foster (*loc. cit.*) also describes this compound as a possible decomposition product.

Gallium Perchlorate Hexahydrate.—This substance was readily obtained by dehydrating the powdered nonahydrate over sulphuric acid or phosphoric oxide in a vacuum. One-third of the water of hydration was removed in the course of a day, and the product maintained its weight almost unchanged for over a week when kept over sulphuric acid. The same product was obtained by dehydration at 100°. Finally, it was obtained by crystallisation from solutions containing considerable amounts of perchloric acid; thus prepared, it formed a mass of small, white, deliquescent crystals which were very soluble in water, benzene, alcohol, and acetone. They were analysed by the methods described above [Found: Ga, 14·60; ClO_4, 62·5. Calc. for $Ga(ClO_4)_3,6H_2O$: Ga, 14·64; ClO_4, 62·66%].

The water of hydration in this hydrate is very strongly co-ordinated. The substance has a very low aqueous vapour pressure as shown by the fact that, on confinement over phosphoric oxide for 6 weeks, it lost less than one-tenth of the total water of hydration. Also, on heating above 100°, it undergoes decomposition to basic perchlorates of indefinite composition.

Hexaureagallium Perchlorate, $[Ga(CON_2H_4)_6](ClO_4)_3$.—Willard and Fogg (*loc. cit.*) have shown that gallium hydroxide is precipitated when aqueous solutions of gallium salts are treated with urea. Hence, any attempts to prepare co-ordination compounds with urea must be carried out in non-aqueous solvents. Alcoholic solutions of gallium perchlorate nonahydrate (1 mol.) and urea (6 mols.) were mixed and evaporated gently to crystallisation. One recrystallisation from warm alcohol yielded bundles of small, colourless needles, melting sharply at 179° and quite stable in air. The *substance* was readily soluble in water, but with obvious decomposition; cold solutions were opalescent, and on warming they coagulated, yielding gelatinous gallium hydroxide. The crystals decomposed with violence when strongly heated. Hence, for the estimation of gallium, the substance was decomposed by evaporation with concentrated nitric acid and finally ignited. Nitrogen was estimated by the usual Kjeldahl method {Found: Ga, 9·6; Cl, 14·75; N, 23·01. $[Ga(CON_2H_4)_6](ClO_4)_3$ requires Ga, 9·6; Cl, 14·6; N, 23·05%}.

Attempts were made to prepare similar co-ordination compounds with pyridine and thiourea. When alcoholic or ethereal solutions of gallium perchlorate and pyridine were mixed, a white, crystalline precipitate was formed. Its composition, however, varied according to the conditions of precipitation, and it was eventually shown to be a mixture of pyridine perchlorate and gallium hydroxide. The proportion of gallium hydroxide was greater when 96% alcohol was used instead of absolute alcohol, and it was never possible to obtain a product free from gallium hydroxide because a small amount of water was inevitably introduced with the perchlorate. It was evident that it would not be possible to prepare a co-ordination compound except in a strictly non-aqueous medium. Attempts to prepare a pyridine complex by using the urea complex in absolute alcohol and ether were also unsuccessful.

As thiourea is an even weaker base than urea, it should be less liable to precipitate gallium hydroxide in aqueous-alcoholic solution and might be expected to co-ordinate as easily as urea, but all attempts to prepare co-ordination compounds failed. Both potentiometric and conductometric titrations of gallium perchlorate in alcohol with alcoholic thiourea gave definite indications that a compound with 6 mols. of thiourea is formed in solution.

Acknowledgment is made of a Scholarship from the National Research Grant Board and Council (S.A.) which enabled one of us (D. J. L.) to participate in the work described in this and the preceding paper.

UNIVERSITY OF CAPE TOWN. [*Received, December 14th*, 1942.]