CCCCXIII.—*The Alleged Thallous Thioper-rhenate.*

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IN a recent paper, Feit (*Z. angew. Chem.*, 1931, **44**, 65) states that by treating aqueous potassium per-rhenate with hydrogen sulphide and evaporating the solution, a dark brown mass was obtained, which dissolved in water to a brown solution. This solution gave with thallous sulphate a dark brown precipitate, described as thallous tetrathioper-rhenate, $TlReS_4$, which might be removed by filtration, leaving a mother-liquor from which a lighter precipitate, believed to be monothioper-rhenate, was precipitated by the addition of more thallous sulphate.

In a previous communication (this vol., p. 1439) the present authors expressed the view that the red solution formed from per-rhenate probably contained soluble thioper-rhenate. They were unable, however, to isolate either the alkali salt or any heavy-metal derivative. Concentration resulted simply in the separation of per-rhenate contaminated with rhenium sulphide, the first crop of crystals being chocolate-coloured and containing less than 1% of sulphur. In view of Feit's findings, an endeavour has been made to repeat his experiments, but such attempts have only yielded thallous per-rhenate varying in colour from golden to dark brown: the sulphur content of the lighter crystals being never greater than a trace, and the darker products being obviously mixtures of crystals of per-rhenate with particles of rhenium sulphide. The present evidence confirms the view that the thio-derivatives are present only in very small quantity, and indicates that the separation of even a moderately pure thallium derivative is extremely improbable.

EXPERIMENTAL.

Potassium per-rhenate was treated with hydrogen sulphide, and the dark brown colloidal solution so produced was filtered, yielding a clear pink solution. (Feit, who continued saturation until the sulphur added was equivalent to $KReS_4$, makes no mention of filtration, but we found this necessary, as some colloidal and some precipitated rhenium sulphide were invariably present.) To this was added a limited quantity of thallous nitrate, whereupon a dark precipitate was obtained. The precipitate was filtered off, and to the mother-liquor further thallous solution was added, giving a lighter precipitate again identical in form with thallous per-rhenate. This process was repeated several times, the products becoming lighter and lighter in colour and containing, finally, the merest trace of sulphur. When examined microscopically, the darker precipitates were evidently mixtures of thallous per-rhenate and rhenium sulphide, whilst the lighter precipitates were almost pure per-rhenate. Undoubtedly all these products were essentially thallous per-rhenate, and in view of our earlier findings (*loc. cit.*) that the solutions were virtually alkali per-rhenate, this was to be anticipated.

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