

117. The Action of Sodium Silicate on Manganous Salts in Solution.

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The action of sodium silicates on manganous salts in aqueous solution has been studied. This is not a simple double decomposition, *e.g.*, $\text{MnSO}_4 + \text{Na}_2\text{SiO}_3 = \text{MnSiO}_3 + \text{Na}_2\text{SO}_4$, but owing to hydrolysis of the sodium silicate the manganous salt reacts with the sodium hydroxide, so the precipitate consists of manganous hydroxide and silica.

WALCKER stated (*Quart. J. Sci.*, 1828, **25**, 371) that when a solution of sodium silicate is added to one of manganous sulphate a white precipitate is obtained. This was not closely examined, and it does not appear to have been further investigated.

An attempt has been made to prepare hydrated manganous ortho- and meta-silicates by this method. The manganous salts used were the chloride, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, and sulphate, $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$. The sodium ortho- and meta-silicates were prepared by fusing together the appropriate amounts of silica and sodium carbonate. A solution of $\text{Na}_2\text{O} \cdot 4\text{SiO}_2$ was also prepared by adding silica portionwise to a hot solution of sodium hydroxide to saturation, and filtering the solution. When this was evaporated to dryness, and the residue dried at 242° and fused, it contained SiO_2 , 79.84%, and therefore corresponded closely to $\text{Na}_2\text{O} \cdot 4\text{SiO}_2$.

The precipitation was carried out with solutions of concentration varying from *M* to 0.02*M*, and at temperatures ranging from that of the room to the b. p. s of the solutions. Some of the precipitations were carried out with the manganous salt in excess, and others with an excess of sodium silicate. In all cases a white, flocculent precipitate was obtained which gradually became pink, and finally dark brown when exposed to air. When the precipitation and filtration were carried out in a non-oxidising atmosphere a white gelatinous mass was obtained which rapidly became dark brown on exposure to air, yielding a mixture of manganese oxides and silica. When this mass was dried at room temperature in a non-oxidising atmosphere a whitish friable mass was obtained. This remained unchanged on exposure to air at room temperature, but rapidly darkened when heated, becoming black at 250° . No precipitation takes place in slightly acid solution.

As it was evident that the precipitate contained manganous hydroxide, the freshly precipitated mixture was treated with hot boric acid solution in order to dissolve out this hydroxide. The dried precipitate was also treated in the same manner. In both cases the white, insoluble portion was filtered off, washed, dried, and examined. It consisted entirely of silica, without any trace of manganese. As the precipitate had not been baked, a variable proportion of the silica also passed into solution.

As the precipitates contained varying amounts of water, determinations of MnO and SiO_2 gave very variable results. The ratio should be constant if the samples consisted of manganous silicate, but it varied from 0.509 to 2.668 when precipitation was carried out with sodium orthosilicate, from 0.428 to 1.109 when with sodium metasilicate, and from 0.098 to 0.302 when $\text{Na}_2\text{O} \cdot 4\text{SiO}_2$ was employed. The ratios should be 2.359, 1.0179, and 0.2948, respectively. The precipitate therefore appears to consist of manganous hydroxide and silica, and hydrated manganous silicates cannot be prepared by this method. Sodium silicate is hydrolysed in aqueous solution, and the manganous salts evidently react with the sodium hydroxide thus produced, the reaction continuing until the whole of the sodium silicate has been hydrolysed.

When the dried precipitate is heated to red heat in a reducing atmosphere, manganous silicate is obtained just as it would be if the appropriate amounts of manganous hydroxide and sodium silicate were mixed and so treated.

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