65. Thiosulphate Complexes of the Tervalent Metals, Iron, Aluminium, and Chromium.

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It has been demonstrated for the first time that there exist complex compounds of Al^{+++} and Cr^{+++} with $S_2O_3^{--}$. These complexes have the general composition $[M^{III}(S_2O_3)]^+$. Furthermore it has been shown that the violet intermediate compound in the reaction of $S_2O_3^{--}$ with Fe^{+++} is the complex anion $[Fe(S_2O_3)_2]^-$

THE existence of complex thiosulphates of Al^{+++} and Cr^{+++} has not previously been demonstrated. Attempts to isolate such compounds have invariably failed owing to hydrolysis, leading to the precipitation of the hydroxides, and even in solution their existence has not been proved. By the choice of suitable conditions (low temperature and high concentration of ethyl alcohol) the degree of hydrolysis could be lowered to such an extent that it became possible to prove that thiosulphate complexes of the above metals indeed exist in solution. We also investigated the violet thiosulphate complex of Fe^{+++} whose composition has been disputed. Holluta and Martini (*Z. anorg. Chem.*, 1924, **140**, 206) studied the kinetics of the reaction between Fe^{+++} and thiosulphate and concluded that as the first stage an anion-complex $[Fe(S_2O_3)_2]^-$ is formed immediately, which later reacts slowly with a further Fe^{+++} ion to give Fe^{++} and $S_4O_6^{--}$. Schmid (*Z. physikal. Chem.*, 1930, *A*, **148**, 321) on the other hand investigated the problem by potentiometric measurements in flowing solutions and inferred that the intermediate compound consisted of a cation complex $[Fe(S_2O_3)]^+$. Our results support the former view.

EXPERIMENTAL.

The conductometric method was used to prove the existence and composition of the complex compounds. The measurements were carried out by using a lyograph ("Lautenschläger") : full detail

FIG. 1.	FIG. 2.
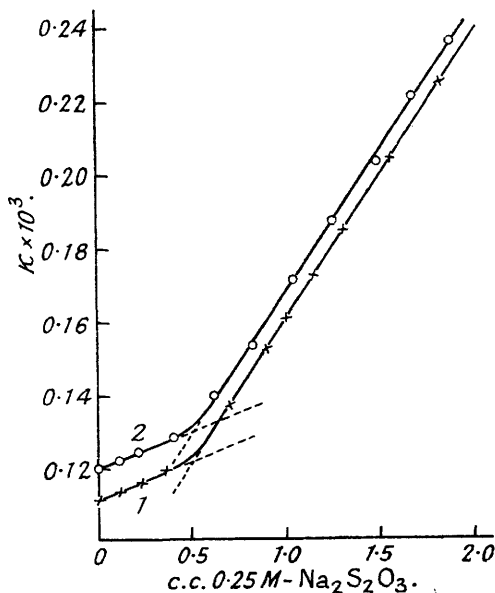
Curve 1 : Titration of 50 c.c. of 0·0025M-Al(NO₃)₃ in 70% (vol.) ethyl alcohol at 0° with an aqueous solution of 0·25M-Na₂S₂O₃. Curve 2 : Titration of 50 c.c. of 0·0025M-Cr(NO₃)₃ in 70% (vol.) ethyl alcohol at 0° with an aqueous solution of 0·25M-Na₂S₂O₃.
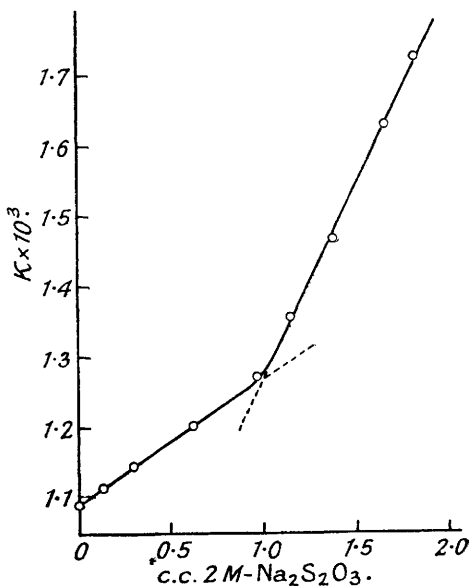
Titration of 50 c.c. of 0·02M-Fe(NO₃)₃ in 50% (vol.) ethyl alcohol at 0° with an aqueous solution of 2M-Na₂S₂O₃. Duration of titration : 2 mins.

are given by Bobtelsky and Simchen (*J. Amer. Chem. Soc.*, 1942, **64**, 454). After a number of titrations, the optimum working conditions were found to be a temperature of 0° and an ethyl alcohol concentration of 70% by volume. Higher concentrations of alcohol lower the solubility of sodium thiosulphate to such an extent that the difficulty of carrying out accurate measurements becomes excessive. The

conductometric titration curves shown in Fig. 1 (curves 1 and 2) establish the complete analogy between Cr^{+++} and Al^{+++}. In both cases we have distinct breaks corresponding to a ratio 1 M^{+++} : 1 $S_2O_3^{--}$.

The situation is somewhat different in the case of Fe^{+++}. It is well known that in the reaction between Fe^{+++} and $S_2O_3^{--}$ an unstable violet intermediate compound is formed at once and quickly decomposes to give the final products Fe^{++} and $S_4O_6^{--}$. The main difficulty in the investigation of this intermediate compound by conductometric titration lies in its very short life at room temperature. By the addition of ethyl alcohol and by lowering the temperature, the stability of the intermediate compound could be increased considerably, but nevertheless it was essential to use an apparatus which enabled titrations to be carried out within 2 minutes. To make sure that no appreciable decomposition had occurred within these 2 minutes, a few isolated points on the titration curves were checked by the rapid addition of the requisite quantity of reagent from the burette. Excellent agreement was invariably obtained between these values (whose measurement occupied only 30 secs.) and those obtained in the actual titration. The titration curves (Figs. 2 and 3) show distinct breaks corresponding to a ratio 1 Fe^{+++} : 2 $S_2O_3^{--}$. Back titrations (with the thiosulphate in the conductivity cell and the ferric salt solution in the burette) led to analogous results. This confirms Hollutta and Martini's view that an anion complex $[Fe(S_2O_3)_2]^-$ is formed as an intermediate compound.

FIG. 3.
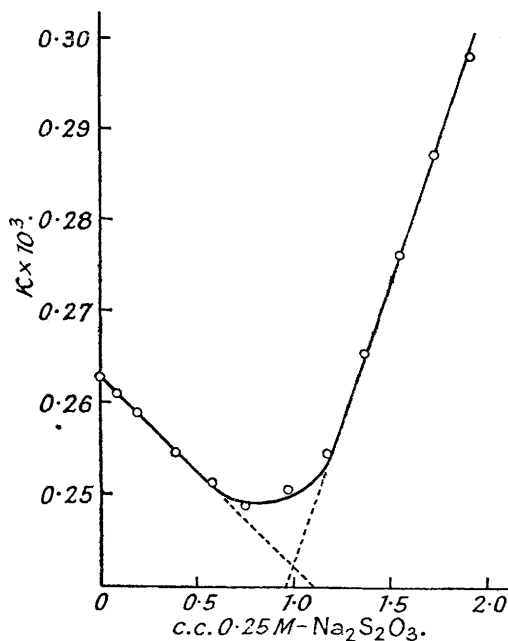
Titration of 50 c.c. of 0·0025M-Fe(NO₃)₃ *in* 70% *(vol.) ethyl alcohol at* 0° *with an aqueous solution of* 0·25M-Na₂S₂O₃. *Duration of titration :* 2 *mins.*

The above-mentioned break is most marked in Fig. 3. This is due to an anomalous effect in the conductivity of ferric ions at different concentrations of ethyl alcohol observed by the author in the course of this work. It is hoped to investigate this point later. At a concentration of about 70% of alcohol the conductivity of ferric nitrate passes through a maximum and thus it can be easily understood that in consequence of the exchange of Fe^{+++} ions by Na^+ ions, which do not show such anomalous behaviour, the titration curve falls off steeply and a very distinct break is obtained.

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