182. *The Nature of the Ceric Sulphates.*

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The existence of the stable sulphate, $Ce(SO_4)_2$ (Meyer and Aufrecht, *Ber.*, 1904, **37**, 140; Brauner, *Z. anorg. Chem.*, 1904, **39**, 261), is largely responsible for the accepted belief in an electro-positive ceric ion. The normal nitrate has not been isolated, but only a red ceric hydroxynitrate, $Ce(OH)(NO_3)_3,H_2O$ (Meyer and Jacoby, *Ber.*, 1900, **33**, 2135). Moreover, the cerium in the " double " nitrates, $M_2Ce(NO_3)_6$, was shown (*Z. anorg. Chem.*, 1901, **27**, 359) to exist as an anion. Similarly, ceric chloride has not been isolated, but probably exists in solution as the complex acid, H_2CeCl_6, corresponding to the known series of salts, M_2CeCl_6. Brauner (*loc. cit.*) regards the complex ceroso-ceric sulphate as the cerous salt of sulphatoceric acid, $H_4Ce(SO_4)_4$, and writes its formula as $Ce^{III}HCe(SO_4)_4,12H_2O$. Praseodymium, neodymium, and lanthanum can replace the cerous atom and form analogous salts.

Brauner's formula for the ceroso-ceric sulphate suggests that ceric sulphate might be of analogous constitution, *i.e.*, $Ce^{IV}Ce(SO_4)_4$, the cerium existing partly as positive and partly as negative ions. Transport experiments have now been carried out which disprove this. The cerium in ceric sulphate solutions and in solutions of the double sulphates, $M_2Ce(SO_4)_4$, has been found always to exist as an anion. No evidence for any positive ceric ions in these sulphate solutions has been obtained. The ionisation of the solid of formula, $Ce(SO_4)_2$, must therefore be of complex character.

The usual method of preparation of this sulphate is by the action of hot concentrated sulphuric acid on ceric oxide. The sulphate does not dissolve and no reduction takes place to the cerous state (Meyer and Aufrecht, *loc. cit.*). When it is freed from sulphuric acid by washing with glacial acetic acid, its colour (Ridgeway's " Colour Standards and Colour Nomenclature," Washington, 1912) is primuline-yellow. This anhydrous sulphate is very soluble in water, and the solution on standing deposits the tetrahydrate, $Ce(SO_4)_2,4H_2O$ (Meyer and Aufrecht; Brauner, *locc. cit.*), which is sulphur- or strontium-yellow in colour (Ridgeway, *op. cit.*). From solutions of ceric sulphate in dilute sulphuric acid, a further ceric sulphate is precipitated as a pale yellow (barium-yellow) solid, and has been characterised by Spencer (J., 1915, **107**, 1265) by a phase-rule method as $CeO_2,SO_3,2H_2O$. This salt was shown by Spencer to be free from cerium in the cerous condition.

The existence of these salts, coupled with the fact that cerium in solution is present only as a complex anion, suggests that cerium sulphate exists as the complex sulphatoceric acid, $H_4Ce(SO_4)_4$, or as a product of hydrolysis of this acid, $H_4[CeO_x(SO_4)_{4-x}]$. The tetrahydrate may then be represented as $H_4[Ce(OH)_4(SO_4)_2]$, and Spencer's basic salt as $H[Ce(OH)_3SO_4]$.

In the present investigation the limits of stability of the anhydrous salt and of the tetrahydrate have been examined. The latter, if dissolved in 75—100% sulphuric acid, forms a metastable solution and deposits the anhydrous salt. On the other hand, the anhydrous salt forms metastable solutions in water with evolution of heat, and such solutions, on pouring into or addition of concentrated sulphuric acid, give rise to two new sulphates, which have been characterised by Schreinemakers's method as $H_4Ce(SO_4)_4$ (English-red) and $H_2Ce(SO_4)_3$ (orange). These higher sulphates are metastable, and gradually pass into $Ce(SO_4)_2$. This conversion is rapid if the solids are washed with glacial acetic acid, in an attempt to free them from adhering sulphuric acid. The anhydrous sulphate, $Ce(SO_4)_2$, was found to be stable in contact with concentrated sulphuric acid for 3 months.

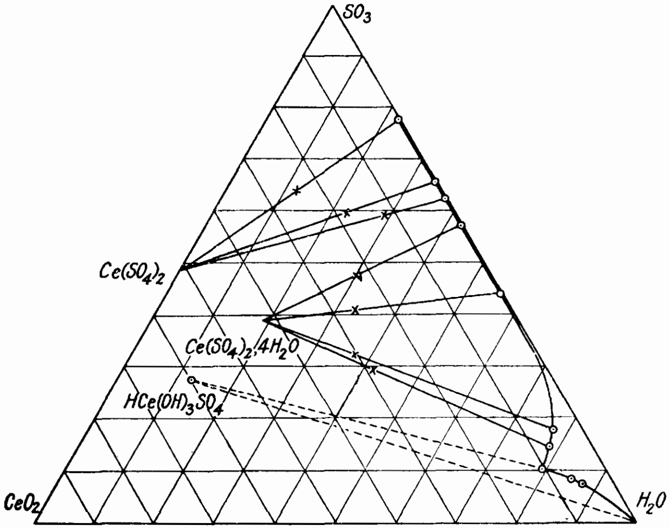
A glass-electrode titration of ceric sulphate solutions indicates that the salt, in approx. N-sulphuric acid solution, exists largely in the partially hydrolysed state as $H_3Ce(OH)(SO_4)_3$. The relative intensity of colour of the solution has been measured as a function of the sulphuric acid concentration, a Leitz colorimeter being used. The intensity increases rapidly from 0·1 to 0·4N-sulphuric acid and then remains practically constant. Temperature has a marked effect and must be carefully controlled. The diminution of colour in dilute sulphuric acid solution is probably connected with the progressive hydrolysis of the sulphatocerate anion, which results ultimately in the precipitation of the sparingly soluble basic salt $HCe(OH)_3SO_4$.

EXPERIMENTAL.

Methods of Analysis.—Ceric sulphate was prepared from the oxide (B.D.H., specially purified). It was freed from cerous sulphate by oxidation with sodium bismuthate (Metzger, *J. Amer. Chem. Soc.*, **1909**, **31**, 523). A typical analysis of 10 c.c. of the resulting solution for CeO_2, (*a*) by ignition to the oxide and (*b*) by addition of excess ferrous sulphate solution and back-titration with permanganate, gave 0·1397 g. and 0·1402 g. CeO_2 respectively, showing that the amount of cerium present in the cerous condition was negligible. It was found that concentrated solutions of the sulphate did not yield the oxide readily on ignition, and it was best to convert the cerium into cerous oxalate (Meyer and Aufrecht, *loc. cit.*), which yields the oxide easily.

Sulphate was estimated by addition of barium chloride to a solution of the ceric compound in hydrochloric acid. Mixed crystals containing cerous and barium chlorides (Zambonini, *A.*, **1916**, ii, 249) also separate, but may be removed by washing 3 times with *N*-hydrochloric acid. An analysis for sulphate by this method (10 c.c. gave 0·4723 g. SO_4) agreed with that obtained volumetrically by addition of excess of sodium hydroxide to the solution, thereby converting the cerium into ceric hydroxide, which was filtered off and washed, and the filtrate containing the excess of hydroxide was back-titrated with standard acid (10 c.c. gave 0·4732 g. SO_4).

FIG. 1.



Limits of Stability of Sulphates.—Direct experiments showed that above 75% sulphuric acid, the sulphur-yellow variety of ceric sulphate, obtained by crystallisation from solution, had enhanced solubility, and deposited the primuline-yellow variety. These two types of solid were placed in stoppered bottles with sulphuric acid of different concentrations and rotated in a thermostat at 18° for 24—72 hours. The moist solids and solutions were then analysed for CeO_2 and SO_3, and the analyses plotted on the triangular diagram (Fig. 1). This characterises the sulphur-yellow solid as the tetrahydrate, and the primuline-yellow solid as the anhydrous salt. The composition of the solution in equilibrium with the basic salt, $HCe(OH)_3SO_4$, and the tetrahydrate, $H_4Ce(OH)_4(SO_4)_2$, was determined by using excess of both solid phases, and analysis of the equilibrium composition of the solution. It was not possible definitely to fix the composition of the solution in which the tetrahydrate and the anhydrous salt coexist, for equilibrium is attained only slowly at the higher acid concentrations. The composition lies, however, between 57 and 62% SO_3.

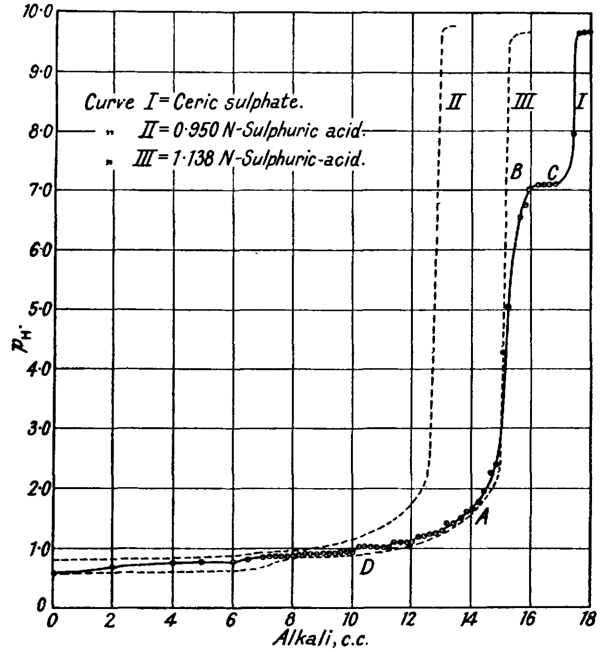
Analysis of the English-red and of the Orange Ceric Sulphates.—Addition of a concentrated solution of the metastable anhydrous salt in water to 80% sulphuric acid caused the precipitation of an orange-coloured solid. Another solid, English-red in colour, was obtained by adding concentrated sulphuric acid to the ceric sulphate solution. Of the two, the red is the more metastable, gradually passing into the orange variety before changing into the anhydrous salt. Attamps to isolate these salts, by washing with glacial acetic acid, resulted in their decomposition into the yellow anhydrous salt. The analyses of the moist solids and of their equilibrium solutions are given below :

Analysis of orange solid.				*Analysis of red solid.*			
Moist solid.		Solution.		Moist solid.		Solution.	
CeO_2, %.	SO_3, %.	CeO_2, %.	SO_3, %.	CeO_2, %.	SO_3, %.	CeO_2, %.	SO_3, %.
22·82	63·62	0·06	74·98	24·88	62·47	0·26	71·60
23·52	61·34	0·08	70·69	24·12	63·97	0·25	75·60

For the orange solid, the resulting lines intersect at CeO_2, 40·2 ; SO_3, 55·0% [Calc. for $H_2Ce(SO_4)_3$: CeO_2, 39·9 ; SO_3, 55·8%]. For the red solid, the intersection is at CeO_2, 32·5 ; SO_3, 60·0% [Calc. for $H_4Ce(SO_4)_4$: CeO_2, 32·6 ; SO_3, 59·24%].

Electro-titration of Ceric Sulphate.—25 C.c. of a solution of ceric sulphate in sulphuric acid ($Ce^{IV} = 0{\cdot}0940M$; $SO_4'' = 0{\cdot}663M$) were titrated by 1·876N-sodium hydroxide with a standardised glass electrode. The valve potentiometer used was similar to that described by Harrison (J., 1930, 1528). Contact was made with a calomel electrode through an agar salt bridge. The results of the titration, converted into p_H units, are shown in Fig. 2, in which is included, for comparison, the titration of 25 c.c. of 0·950 and of 1·138N-sulphuric acid by the same alkali. The curves show that the hydrogen-ion concentration during the neutralisation of the solution of ceric sulphate conforms closely to that of 1·138N-sulphuric acid, requiring approximately 15·1 c.c. of alkali. If the ceric sulphate is completely and easily hydrolysed to $Ce(OH)_4$, the alkali required would be 17·4 c.c., but if it is partially hydrolysed to form $HCe(OH)_3SO_4$, the amount required would be 15·1 c.c. Actually, this salt begins to be precipitated at A, and the break BC corresponds to the conversion of the solid $HCe(OH)_3SO_4$ into $Ce(OH)_4$ (alkali required, 2·5 c.c.). The composition of the solid at A, B, and C was determined by analysis in duplicate experiments.

FIG. 2.



There is a slight break in the ceric sulphate curve at D, when 10·1 c.c. alkali have been added. If the ceric sulphate exists as $H_4Ce(SO_4)_4$, the free sulphuric acid in solution is 0·287M, since each cerium atom is associated with four sulphate radicals, whilst the sulphatoceric acid would be 0·376N, making the solution 0·970N in all (cf. the sulphuric acid curve). If, however, the ceric sulphate exists as $H_3Ce(OH)(SO_4)_3$, the free sulphuric acid is 0·762N, corresponding to 10·15 c.c. of alkali, and the sulphatoceric acid is 0·282N, making the solution 1·044N in all. In agreement with this calculation, the first portion of the ceric sulphate curve is intermediate between the curves for 0·970 and for 1·138*N*-acid. The slight break at *D* coincides with the end-point of the titration of the free sulphuric acid, the partially hydrolysed sulphatoceric acid, $H_3Ce(OH)(SO_4)_3$, being assumed to be present, and may indicate that the sulphatoceric acid is a weaker acid than sulphuric. The conversion of $H_3Ce(OH)(SO_4)_3$ into $H_2Ce(OH)_2(SO_4)_2$ would require 1·25 c.c. of alkali, and there is a small but significant break on further addition of this quantity.

Intensity of Colour of Ceric Sulphate Solutions.—The relative colour intensities of solutions at 15° containing 0·0051*M*-ceric sulphate, $Ce(SO_4)_2$, and various concentrations of sulphuric acid are shown below :

Sulphuric acid, *N*	0·123	0·226	0·329	0·432	0·535	0·892
Relative intensity	0·51	0·71	0·92	1·00	1·07	1·07

Ionic-migration Experiments.—These were carried out by using a U-tube fitted with taps of bore similar to that of the tube, the bottom portion and the taps being filled with the ceric sulphate solution, and the upper portions with sulphuric acid. Solutions containing sulphuric acid from 0·5 to 20*N* and $Ce(SO_4)_2$ from 0·01 to 0·13*M* were examined over periods of 12 hours, a potential gradient of 1 volt/cm. and a current of 0·02 amp. being used. The potassium and the sodium double ceric sulphate and a mixture of ceric sulphate with lithium sulphate were also examined. In all cases, the coloured cerium ions migrated to the anode, and no evidence of any migration to the cathode was obtained.

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