the alkaline earth iodides and bromides is greater than the difference between the activity coefficients of the bromides and chlorides.

In Table I it can be seen that C_m decreases sharply at higher concentrations of NaBr. When the activity coefficients are applied to calculate the concentration quotient, K_m increases slightly at higher (NaBr). $K\gamma$ decreases slightly as (NaBr) is increased. Consequently, when the activity coefficients are utilized, the calculated equilibrium constant, K_a, does remain constant (within experimental error) over a range of concentrations.

Fluoride Solutions.—Cerous fluoride is very sparingly soluble even in acid solution. However, preliminary tests showed that when the concentration of cerous ion was reduced to less than 10^{-5} molal, and when the hydrogen fluoride concentration was less than 7×10^{-3} molal in solutions at *p*H 1.41, the precipitation of cerium was negligible, and about one-fifth of the cerium was associated with fluoride ion. Because of the limitations on the concentration of HF which are imposed by the insolubility of CeF_3, no high degree of accuracy can be claimed for the measurement of the association constant.

In accordance with the observed behavior of cerous ion with other univalent anions when the fraction of complexed cerium is small, CeF^{+2} was considered to be the complex formed. Equation (7) was considered to represent the net reaction inasmuch as the charge of Ce^{+3} should make the momentarily-formed acid $HCeF^{+3}$ completely strong.[6] The product of the equilibrium constant for the reaction of Equation (7) and the equilibrium constant for the association of H^+ with F^- equals K_a for the ion-pair formation

$$Ce^{+3} + F^- = CeF^{+2} \qquad (10)$$

The value of 1.0×10^4 agrees qualitatively with the value for the association of ferric ion and fluoride.[14]

Summary

The distribution of cerous ion between cation exchange resin and solutions of sodium iodide, bromide, fluoride and perchlorate has been measured. The constants for ion-pair formation between Ce^{+3} and the halides have been calculated.

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(14) H. W. Dodgen and G. K. Rollefson, THIS JOURNAL, **71**, 2600 (1949).

SAN FRANCISCO 24, CALIF. RECEIVED APRIL 11, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE ROYAL INSTITUTE OF SCIENCE]

The Behavior of Solutions of Titanium Dioxide in Sulfuric Acid in the Presence of Metallic Sulfates

BY S. M. MEHTA AND S. R. PATEL

A systematic study of the behavior of solutions of titania in sulfuric acid in the presence of different amounts of alkali sulfate has not been made so far. This paper reports results of such a study.

When titanium dioxide (0.1 g.) is heated alone with sulfuric acid (40 cc., sp. gr. 1.8) to 230°, a clear solution results which on further heating to about 285° gives a white precipitate. This precipitate when washed free from sulfate with absolute alcohol and then dried at 350–400° (yield about 84%), corresponds to the formula $TiOSO_4$[1] as reported by the majority of previous investigators.[2]

When the heating is carried out as before but in the presence of ammonium, sodium or potassium sulfate, in weight ten times that of titanium dioxide, the yield of $TiOSO_4$ obtained is 39, 13 and 50%, respectively. When, however, the weight of the alkali sulfate is one hundred times that of the titanium dioxide, the solution remains clear even on boiling for 10–15 minutes. Sodium sulfate is thus better than the other sulfates in promoting the solution of titanium dioxide in sulfuric acid.

In trial experiments it was noticed that bivalent metallic sulfates showed a different behavior from that observed in the case of monovalent metallic sulfates. The effect of the sulfates of zinc, manganese, cobalt, copper and ferrous ammonium sulfate has been studied and the results obtained are described below. The experimental procedure followed in conducting these experiments was similar to that described for the monovalent metallic sulfates.

When $ZnSO_4 \cdot 7H_2O$ was used in place of the alkali sulfate, in weights varying from one-fourth to six times the weight of titanium dioxide, it was observed that with a weight of zinc sulfate greater than that of titanium dioxide, the precipitate when dried at 220° has the formula $ZnSO_4 \cdot Ti(SO_4)_2$. When, however, the weight of zinc sulfate so taken was equal or less than the weight of titanium dioxide, the precipitate obtained appeared to be a mixture of $ZnSO_4 \cdot Ti(SO_4)_2$ and $TiOSO_4$. The data obtained for these precipitates are given in Table I.

TABLE I

TiO_2, g.	$ZnSO_4 \cdot 7H_2O$, g.	H_2SO_4, cc.	Ti, %	Zn, %	SO_4, %	Formula
0.1134	0.0289	40	16.92	7.76	66.32	....
.1022	.0767	40	17.70	9.00	66.00	....
.1267	.1267	60	15.11	11.25	67.64	....
.1000	.2000	60	12.03	17.12	71.76	$ZnSO_4 \cdot Ti(SO_4)_2$
.1000	.2500	60	12.11	16.42	71.80	
.0980	.7840	125	12.14	16.44	72.01	

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(1) Titanium was estimated according to the method of Hope, Moran and Ploetz, *Ind. Eng. Chem., Anal. Ed.*, **8**, 48 (1936).

(2) Merz in Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. **7**, p. 93 (1927); Blondel, *J. Chem. Soc.*, (ii)**76**, 556 (1899); Spence and Sons, Ltd., British Patent, 263,886 (1925), *C. A.*, **22**, 143 (1928); Rosenheim and Schütte, *Z. anorg. Chem.*, **26**, 250 (1901); Berzelius and Rose, Mellor, *op. cit.*, p. 94; Boguslavskaya, *C. A.*, **33**, 8135 (1939); Boguslavskaya and Ottamanovskaya, *ibid.*, **35**, 2432 (1941); Hixson and Frederickson, *ibid.*, **39**, 3720 (1945).

The compound $ZnSO_4 \cdot Ti(SO_4)_2$ is white in color, hygroscopic, soluble in mineral acids and decomposed by water to give metatitanic acid.

Using the sulfates of manganese, cobalt, magnesium and copper it was found that they behave in a manner similar to zinc sulfate and the compounds of the type $RSO_4 \cdot Ti(SO_4)_2$ (where R = a bivalent metal) are obtained. The properties of these compounds were found to be similar to those of $ZnSO_4 \cdot Ti(SO_4)_2$ except that the compounds containing manganese and cobalt were colored yellow and pink, respectively. The behavior of copper sulfate was slightly different in the sense that the compound $CuSO_4 \cdot Ti(SO_4)_2$ was obtained only when the quantities of copper sulfate were four to six times the quantity of titanium dioxide.

In the case of ferrous ammonium sulfate (or ferrous sulfate) it was observed that steel-gray precipitates were obtained with weights of ferrous ammonium sulfate greater than that of titanium dioxide. These precipitates appeared to be of ferric sulfate with adsorbed titanium but were not compounds of the type $RSO_4 \cdot Ti(SO_4)_2$.

The compounds $RSO_4 \cdot Ti(SO_4)_2$ (where R = zinc, manganese, copper and cobalt) prepared as described above were further examined by a study of their thermal decomposition. This was done by heating a known weight (0.5 to 1 g.) of the compound in a platinum boat which was placed in an electric furnace and passing air free from moisture and carbon dioxide from one end of the furnace tube to drive out the gaseous products of decomposition. The percentage decomposition of the substance was calculated from the amount of the residue left behind. The time required to attain a given temperature was kept nearly constant (one hour) and the desired temperature was maintained for two hours in each experiment at the end of which no more gases were evolved. It was noticed that the temperature at which the thermal decomposition of the compounds $RSO_4 \cdot Ti(SO_4)_2$ commences are 375° for $CuSO_4 \cdot Ti(SO_4)_2$, 400° for $ZnSO_4.Ti(SO_4)_2$, 400° for $CoSO_4 \cdot Ti(SO_4)_2$ and 450° for $MnSO_4 \cdot Ti(SO_4)_2$. It was also noticed that the main product in the gaseous products of decomposition is sulfur trioxide with traces of sulfur dioxide at temperatures above 700°.

The percentage decomposition of the different compounds—$RSO_4 \cdot Ti(SO_4)_2$—at various temperatures is given in Table II.

TABLE II

% decompn. of	600°	650°	700°	750°	800°	850°
$ZnSO_4 \cdot Ti(SO_4)_2$	58.3	62.3	70.6	88.0	92.6	93.3
$CuSO_4 \cdot Ti(SO_4)_2$	66.7	78.3	91.4	95.0	98.2	100.0
$MnSO_4 \cdot Ti(SO_4)_2$	65.1	67.8	70.2	73.0	88.3	98.7
$CoSO_4 \cdot Ti(SO_4)_2$	67.9	80.6	97.1	99.5	99.8	100.0

The curves obtained by plotting the values of the percentage decomposition against temperature have S-shape for all the four compounds. The curve obtained in the case of $ZnSO_4 \cdot Ti(SO_4)_2$ is given in Fig. 1 for illustration. The S-shape of these curves indicates that the decomposition of all these sulfates is relatively slow in the beginning, then becomes very rapid and finally slows down again with rise of temperature. Since the temperatures of decomposition of the bivalent metallic sulfates are beyond 650°[3] and they decompose energetically at temperatures above 700° (with the exception of copper sulfate) it may be concluded that more than 50% decomposition up to 650° corresponds to the decomposition of $Ti(SO_4)_2$ in the molecule. The steep portions of the curves correspond with the energetic decomposition of the bivalent metallic sulfates. Since the temperatures of energetic decomposition of $MnSO_4$ and $CoSO_4$ are much higher than 650° the residues left at 650 and 600°, respectively, were extracted with water and the aqueous extract was found to contain the same quantity of the bivalent metallic sulfate which would be expected from the weight of the double sulfate taken.

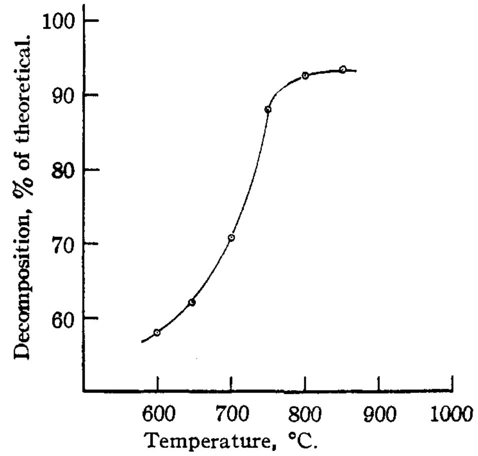

Fig. 1.—Thermal decomposition of $ZnSO_4 \cdot Ti(SO_4)_2$.

It is noticed from Table II that the sulfates $RSO_4 \cdot Ti(SO_4)_2$ decompose almost completely at 850° and the residues are found to be mixtures of titania and the metallic oxide with a small amount of undecomposed sulfate in cases where the observed decomposition is not 100%. These residues of thermal decomposition of $ZnSO_4 \cdot Ti(SO_4)_2$, $CoSO_4 \cdot Ti(SO_4)_2$, $CuSO_4 \cdot Ti(SO_4)_2$ and $MnSO_4 \cdot Ti(SO_4)_2$ possess characteristic colors, *viz.*, pale yellow, green, gray and grayish-brown, respectively. In view of the fact that these colored residues are mixtures of titanium dioxide with other metallic oxides with characteristic colors, it appears that they may be found useful as paint materials.

Summary

A solution of titanium dioxide in sulfuric acid gives a precipitate of $TiOSO_4$ when heated to 285°. The presence of alkali sulfates retards this precipitation and sodium sulfate is found better in this respect.

In the presence of bivalent metallic sulfates, the compounds of the type $RSO_4 \cdot Ti(SO_4)_2$ are obtained having different colors depending on the nature of the bivalent metal present in the compound. A similar compound is not obtained

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(3) "Handbook of Chemistry and Physics," Chemical Rubber Publishing Co., Cleveland, Ohio, 1940, p. 1491.

when ferrous ammonium sulfate (or ferrous sulfate) is used.

The thermal decomposition of $RSO_4 \cdot Ti(SO_4)_2$ has been studied and found to be almost complete at 850°. The colored residues left at this temperature are intimate mixtures of titania and bivalent metallic oxides with or without a small amount of undecomposed substance and may be useful as paint materials.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE ROYAL INSTITUTE OF SCIENCE]

Recovery of Titania from the Bauxite Sludge

BY S. M. MEHTA AND S. R. PATEL

This paper deals with the amount of titania which may be recovered from its sulfuric acid solution in the form of $RSO_4 \cdot Ti(SO_4)_2$ by taking advantage of the formation of such compounds.[1] The following table contains data obtained with 0.1 g. titanium dioxide and the different bivalent metallic sulfate.

TABLE I

RECOVERY OF TiO_2 FROM H_2SO_4 SOLUTIONS OF $RSO_4 \cdot Ti(SO_4)_2$

R	RSO_4, g.	H_2SO_4, cc.	Recov., %
Zn	0.3	60	59.71
	.4	100	93.69
	.8	125	99.00
Cu	.4	100	90.33
	.6	100	97.40
	.8	125	99.04
Mn	.2	60	85.09
	.4	100	99.28
	.6	100	99.65
Co	.3	50	62.66
	.4	75	98.58
	.6	80	99.47
Mg	.3	50	67.98
	.4	60	99.19
	.6	80	99.74

The percentage recovery of titanium dioxide given in Table I was calculated from the weight of the precipitate of $RSO_4 \cdot Ti(SO_4)_2$ which was analyzed for its titanium contents. This was further checked from the estimation of titanium in the filtrate.

It will be observed from Table I that the recovery of titania increases as the amount of the bivalent metallic sulfate is increased and it reaches about 100% with the highest amount of the bivalent metallic sulfate used.

As titanium occurs together with a large proportion of aluminum in the bauxite sludge, the effect of aluminum sulfate on solutions of titania in sulfuric acid was studied, by following the general procedure outlined before.[1] With amounts of $Al_2(SO_4)_3 \cdot 18H_2O$ less than that of titania, the precipitates obtained are of titanyl sulfate containing only about 1% of aluminum, but when the amount of aluminum sulfate is increased to six or ten times, the precipitate obtained consists of anhydrous aluminum sulfate with about 2 to 3% of titanium. However with amounts of aluminum sulfate equal to or double that of titania, the precipitates appear to be mixtures of titanyl sulfate and anhydrous aluminum sulfate.

The bauxite sludge also contains silica and iron together with a certain proportion of the sulfate ions. In order to determine the conditions for the quantitative extraction of titania from such a material, experiments were carried out with artificial mixtures ultimately approaching the proportions present in the bauxite sludge. In the first instance, a mixture containing TiO_2 (0.1 g.) and $Al_2(SO_4)_3 \cdot 18H_2O$ (1.2 g.) was prepared and was treated with concd. sulfuric acid (sp. gr. 1.79, 180 cc.). This was heated to 230° for about an hour. The precipitate was separated from the liquid and was found to be aluminum sulfate containing 2.17% of titanium. When this experiment was repeated adding $Fe_2(SO_4)_3 \cdot 9H_2O$ (0.2 g.), the precipitate contained ferric iron as might be expected. The filtrate contained nearly 50% of titania which was precipitated quantitatively in the form of $ZnSO_4 \cdot Ti(SO_4)_2$ by heating the filtrate to boiling with the addition of $ZnSO_4 \cdot 7H_2O$ (0.4 g.).

It may be observed from what is stated above that a sample of bauxite sludge may be treated by this process for the recovery of titania. In the following paragraphs the analysis and the treatment of a sample of bauxite sludge have been given and in conclusion an outline of a modification of the process has been suggested.

TABLE II

ANALYTICAL DATA OF BAUXITE SLUDGE

Total loss on strong heating, %	51.65
Moisture, %	9.22
Sulfate, %	27.61
Titania, %	13.60
Ferric oxide, %	9.62
Alumina, %	18.82
Silica, %	5.65

Finely powdered (180-mesh) bauxite sludge (25 g.) was digested with concd. sulfuric acid (400 cc.) and heated until fumes of sulfuric acid were evolved. At the end of one hour the liquid was allowed to cool and separated from the solid by decantation.

Solid Residue.—This was treated with such quantity of water (about 100 cc.) that titanium, aluminum and iron were brought into solution leaving behind an insoluble residue of siliceous material. The clear liquid was separated from the insoluble residue and was reduced with zinc dust. At this stage the solution was partially neutralized with soda ash until it contained 1% free sulfuric acid. This liquid was diluted to about five times and heated so as to get the precipitate of metatitanic acid. This pre-

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(1) Mehta and Patel, THIS JOURNAL, 73, 224 (1951).