

porcelain tube and in the test-tube, in the latter case the vapor being practically at atmospheric pressure.

The cause of the different colors applied to sulphur vapor is doubtless due to three causes :

1. The general difficulty of describing the colors of vapors, the relative intensity of which is so much less than that of our ordinary standards.

2. The fact that the color of sulphur vapor varies with the temperature.

3. Sulphur vapor condenses so readily that when boiled in a test-tube the sides of the tube are covered with a layer of the brownish red liquid, which has doubtless sometimes been mistaken for the vapor. Similarly, when sulphur fumes escape from a hot covered crucible into which sulphur has been thrown, it is the condensing sulphur mist, very deep red in color, which one sees, and not the true vapor of sulphur.

The conclusions of this paper are that the color of sulphur vapor varies with the temperature, being of an orange tint just above its boiling-point, deepening to a red which is strongest at 500°, and then becoming rapidly lighter with increasing temperature. The color at the boiling-point is that of a normal solution of potassium bichromate; that of the deepest red is that of a rather dilute solution of ferric thiocyanate.

It is hoped it may be possible to carry these experiments further, but no reservations are made of the subject if others are interested.

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## THE FORMATION OF ALUMS BY ELECTROLYSIS.<sup>1</sup>

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THE work herein described had for its special end the formation of alums of manganese, and while, in this particular, success was not attained, it is felt that it is well to place the work on record, especially as phases of it are capable of further development, from which interesting results may be hoped.

Manganese salts in which the metal is trivalent, are not very satisfactorily known. Potassium and ammonium manganic

<sup>1</sup> Read at the Boston meeting of the American Chemical Society, August, 1898.

alums have been described by Mitscherlich, but to manganic sulphate,  $Mn_2(SO_4)_3$ , Franke, who has most thoroughly studied

it, gives the formula  $Mn \begin{matrix} \text{SO}_4 \\ \text{SO}_4 \end{matrix} Mn$ .<sup>1</sup> A salt of this consti-

tution could hardly give an alum, and the literature of the manganese alums is very unsatisfactory. It was hoped by using the oxidizing action of the electric current on a solution of manganous sulphate in the presence of an alkaline sulphate, manganic alum might crystallize out, and the reaction was studied with other metals for the sake of familiarity with the method and for comparison. Incidentally several alums were obtained and analyzed which have not been previously described.

*a. Iron Alums.*—Apparatus: Positive electrode, a platinum dish of about 250 cc. capacity resting on a coil of heavy copper wire; negative electrode, a coil of heavy platinum wire; diaphragm, the lower portion of the porous cup of a Bunsen cell. In different experiments different batteries were used, but Bunsen or crowfoot cells were generally used.

The following is a specimen experiment: Inner solution, ferrous sulphate strongly acidified with sulphuric acid; outer solution, saturated with ferrous sulphate and ammonium sulphate, and also strongly acidified with sulphuric acid; six crowfoot cells; current, 0.04 ampère. In forty-eight hours a large crop of beautiful iron-ammonium alum crystals, of perfect octahedral form, were produced. In one experiment with solutions as above and apparatus also, except that Bunsen cells were used, with current 0.02 ampères, forty-one grams of iron ammonium alum were obtained in twenty-four hours. This method is probably applicable to the formation of this alum on a commercial scale, having as its advantages the ease with which it is conducted and the fine quality of the product. Owing to the lesser solubility of potassium sulphate, the method, while successful, does not give such good results in the formation of iron potassium alum.

The formation of iron sodium alum was tried, using solutions as above, with sodium sulphate substituted for ammonium sulphate. Current, four Bunsen cells. After twelve hours the

<sup>1</sup> *J. prakt. Chem.* [2], 36, 451.

outer solution (+) was pink and in twenty-four hours had become dark purple, resembling almost a solution of potassium permanganate, while oxygen bubbles were given off at the positive pole. A little ferrous sulphate solution was added, at which the color at once disappeared, but after several hours with the current, it again became dark purple. The color disappeared at once with reducing agents. The color was that of ferrates, but the presence of ferric acid is hardly probable, and the solution being strongly acid, ferrates could not be present. It seems more probable that the compound was one of persulphuric acid. No crystals could be obtained even by using a freezing mixture. Some of the solution set aside for several weeks left, on evaporation, a hard, dirty, violet crystalline mass, containing crystals somewhat triangular in form, which were very insoluble in both water and hydrochloric acid. This substance was not pure and was not further investigated.

*Iron Rubidium Alum and Iron Cesium Alum*,  $\text{RbFe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  and  $\text{CsFe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ .—As no description of these alums was found in chemical literature, they were both formed and analyzed. In working with rubidium and cesium salts, a smaller form of apparatus was used, the positive pole being a platinum crucible of eleven cc. capacity, the negative pole a coil of heavy platinum wire, and the diaphragm an unglazed porcelain annealing cup. The cup was filled as above with a solution of ferrous sulphate and the platinum crucible, which rested in a ring of heavy copper wire, with a solution of ferrous sulphate and rubidium sulphate or cesium sulphate. Both solutions were strongly acid with sulphuric acid. Very considerable crops of both the rubidium and cesium alums were obtained in the form of small octahedra. They are of a delicate violet color, turning slightly greenish on exposure to the air. They resemble potassium alum in every respect except that the rubidium alum is very slightly soluble and the cesium alum almost insoluble in water.

Analysis :

	Calculated for $\text{RbFe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ .	I.	Found. II.
$\text{H}_2\text{O}$ .....	39.3	39.1	38.9
$\text{SO}_4$ .....	34.9	35.2	...
Fe .....	10.2	11.0	..

	Calculated for $\text{CsFe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ .	Found.	
		I.	II.
$\text{H}_2\text{O}$ .....	36.2	36.1	36.3
$\text{SO}_4$ .....	32.2	33.3	...
Fe .....	9.4	10.4	...

*b. Cobalt Alums.*—The cobalt, potassium, and ammonium alums were discovered by Marshall, whose work was the incentive to that described in this paper. The rubidium and cesium alums were made by us and have not been hitherto described. The apparatus used was the smaller form, as for the iron rubidium alum, and the experiments conducted similarly. The outer (positive) solution was kept quite strongly acid with concentrated sulphuric acid. Four Bunsen cells were used; current 0.16 to 0.19 ampère. At first it was found that in some experiments beautiful crystals were obtained in considerable quantity, in others no crystals at all. This was soon found to be due to the temperature. On nights when the laboratory was cool the crystals formed readily. By keeping the crucible with its support immersed in a beaker of water, ill effects from heating by the current were avoided and the alums readily obtained.

It is thus seen that the rubidium and cesium alums are much more readily formed than the potassium and ammonium, as would be expected. These alums are minute, deep blue octahedra, stable in dry air, but gradually decomposing in moist air with formation of cobalt sulphate; the cesium alum showed occasional cube faces. In water the alums are quickly decomposed with evolution of oxygen and reduction to cobalt sulphate. In dilute hydrochloric acid and in dilute sulphuric acid the crystals dissolve to a blue solution. In concentrated hydrochloric acid and concentrated sulphuric acid they are decomposed, giving in the latter case a brown solution.

Several methods of analysis were tried. On heating to  $200^\circ$  the salt becomes whitish pink, and apparently contains free sulphuric acid from its decomposition into cobalt sulphate, more or less water being thus retained. The best method of analysis was found to be the following: The salt is mixed with anhydrous sodium carbonate in a platinum boat, and heated in a combustion tube in an oxygen stream. The water is absorbed in a calcium chloride tube. The residue is treated with hot

water. The filtrate contains the Cs (or Rb) and the  $\text{SO}_4$ , which are estimated as cesium chloroplatinate and barium sulphate. The insoluble residue, cobalt oxide, is heated in a hydrogen stream and weighed as metallic cobalt.

	Calculated for $\text{RbCo}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ .	I.	Found. II.
Rb .....	15.5	15.9	...
Co .....	10.7	11.9 <sup>1</sup>	...
$\text{SO}_4$ .....	34.8	35.4	...
$\text{H}_2\text{O}$ .....	39.1	37.9	38.2 <sup>2</sup>
	Calculated for $\text{CsCo}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ .		Found. <sup>3</sup>
Cs .....	22.1		22.5
Co .....	9.8		10.2
$\text{SO}_4$ .....	32.0		32.2
$\text{H}_2\text{O}$ .....	36.0		36.7

*c. Chromium Alums.*—An experiment was tried using a solution of potassium chromate strongly acidified with sulphuric acid as electrolyte for the negative pole, and dilute sulphuric acid for the positive. After thirty-six hours no chrome alum was obtained, but considerable potassium sulphate was deposited, strongly colored green by the chromic solution present. On substituting ammonium chromate for the potassium chromate a considerable crop of chromium ammonium alum crystals was obtained at the negative pole. These crystals were very small. Four Bunsen cells were used in these experiments. This method of electrical reduction has been used by Piccini for the formation of vanadium<sup>4</sup> and titanium<sup>5</sup> alums.

*d. Experiments with Manganese.*—These experiments were carried out in both the large and small apparatus; with manganese sulphate and ammonium, rubidium, and cesium sulphates; with varying quantities of free sulphuric acid in the electrolytes; with different strengths of current; and at various temperatures. The solution at the positive pole in every case became deep wine color, and the higher oxide of manganese was deposited. In one case only were a few minute octahedral crystals found in a rubidium manganese solution. These were deep wine color and qualitatively contained manganese. It is not, however,

<sup>1</sup> As  $\text{CoSO}_4$  after removal of Rb as  $\text{Rb}_2\text{PtCl}_6$ .

<sup>2</sup> By loss at  $200^\circ$ .

<sup>3</sup> By method described above.

<sup>4</sup> *Gazz. chim. ital.* 25, [2], 451.

<sup>5</sup> *Ibid.*, 25, [2], 542.

improbable that these were crystals of common alum colored by manganese. In an experiment with ruthenium such crystals were obtained, the aluminum being probably derived from the porcelain diaphragm. In a number of cases the black precipitate at the positive pole, supposed to be manganese dioxide, when allowed to stand with concentrated sulphuric acid, showed itself under the microscope to be made up of flat, transparent, pale, wine-colored crystals, resembling elongated hexagonal plates. These are not readily soluble in water or acids. They were not further investigated.

The electrolytical method does not seem to be applicable to the formation of manganese alums from manganous salts.<sup>1</sup> It is hoped later to try the electrolytic reduction of manganates and permanganates.

*e. Experiments with Ruthenium.*—No crystallized oxy-salts of ruthenium are known. As the double salts of the trichloride crystallize well, an effort was made to obtain an alum by the electrolytic reduction of the nitrosochloride. The small apparatus was used. The solution at the negative pole was a solution of cesium ruthenium nitrosochloride,  $\text{Cs}_2\text{RuCl}_5\text{NO}$ , which had been boiled some time with sulphuric acid, and which might be supposed to contain the nitrososulphate. It was hoped to reduce the nitroso group and split it off as ammonia, leaving trivalent ruthenium in the presence of sulphuric acid and cesium sulphate, the most favorable condition for alum formation. No sign of alum was found, nor did the electrolyzed solution show reaction for trivalent ruthenium. A considerable quantity of ruthenium tetroxide,  $\text{RuO}_4$ , was given off. This was probably owing to oxidation at the positive pole, some of the ruthenium solution having penetrated the diaphragm into the sulphuric acid which surrounded the positive pole. The formation of ruthenium tetroxide by electrolytic oxidation has not been pre-

<sup>1</sup> Since the above was in type, a further article by Piccini has appeared in the *Zeitschrift für anorganische Chemie*, 17, 361, describing the formation of the cesium manganese alum by electrolytic oxidation, in a method apparently like that described in this paper. No particulars regarding current, etc., are given. This would seemingly settle the question of the trivalence of manganese in manganic salts. Attention is called, as in our paper, to the advantage in using rubidium and cesium compounds where it is desired to obtain difficultly crystallizable compounds. Piccini's result renders it probable that the few octahedra obtained in our rubidium manganese experiment were really rubidium manganese alum; he also found his alum contaminated by aluminum from the diaphragm.

viously noticed. Further experiments with other ruthenium compounds are being carried on.

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## ON THE DETERMINATION OF UNDIGESTED FAT AND CASEIN IN INFANT FECES.<sup>1</sup>

BY HERMAN POOLE.

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LAST summer I had the honor of presenting to the Society a paper on "Methods of Determining Fat and Casein in Feces."<sup>2</sup> In that paper I mentioned the method I had adopted in the investigation I was then engaged in, and stated why the methods previously used did not give me satisfactory results. This paper may be considered as a sequel to that one, or perhaps more correctly, a résumé of the work I have done on the subject to this time. The methods given in the paper cited were used substantially as there given throughout all the cases, no better one having been suggested; in fact, my requests for other methods met with no response at all, showing that but little work had been done directly on this line.

The methods of analysis used may be briefly stated as follows: The feces were carefully removed from the containers as well as possible and thoroughly mixed, if practicable. A portion of this was then weighed out and dried in an air-bath at 90° C. for one hour, and afterwards at 105° to 110° C. for two or three hours or until of constant weight. A portion of this dried residue was then treated with ether in a Soxhlet extraction apparatus to extract the fat and other substances soluble in ether. The extract so obtained was evaporated at 100° till dry and usually weighed. This weighing was not done in every case as it had no important bearing on the aim of the investigation, which concerned the undigested fat and casein only. After drying, the extract was saponified with alcoholic potash, a small portion generally remaining undissolved. Water was then added and the whole boiled till the alcohol had been expelled. Practically this was carried on until the mass was nearly dry, water having

<sup>1</sup> Read at the Boston Meeting of the American Chemical Society, August, 1898.

<sup>2</sup> This Journal, 19, 877.