to become colloidal. This prevented rapid filtration from the basic nitrate, and in order to avoid this, sodium nitrite was employed to render the liquid basic. Any precipitate which formed during this operation filtered easily.

When a concentrated solution of the nitrates is boiled with sodium nitrite, a basic nitrate results. In the case of a dilute solution, a basic nitrite separates as a granular precipitate during the boiling.

The yttrium was further purified by boiling the diluted nitrate solution with sodium nitrite. This gave a very pure product, which in solution showed no absorption of erbium.

The separation of erbium, lutecium, ytterbium, thulium and celtium was not attempted with this material.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF PITTSBURGH.]

OXIDATION AND REDUCTION WITHOUT THE ADDITION OF ACID.

II. THE REACTION BETWEEN STANNOUS CHLORIDE AND POTASSIUM DICHROMATE. A CONTRIBUTION TO COLLOID-CHEMISTRY.

BY MARKS NEIDLE AND JOSHUA C. WITT.

Received November 2, 1915.

It may be stated from the results of the first paper of this series that colloidal hydrous oxides or hydroxides are obtained in an oxidation-reduction reaction, in which acid must be added for the formation of normal salts, if the stoichiometric relation is the same without acid as with acid. If the reaction involves ions which are good precipitants of the colloids formed, precipitation takes place; otherwise, hydrosols are obtained.

The equation for the reaction between stannous chloride and potassium dichromate, with acid, is

$$3SnCl_2 + K_2Cr_2O_7 + 14HCl = 3SnCl_4 + 2CrCl_3 + 7H_2O + 2KCl,$$

where, it is seen, fourteen mols of hydrochloric acid per mol of dichromate are necessary to form the normal salts of tetravalent tin, trivalent chromium, and of potassium. The object of this investigation was to determine whether the stoichiometric relation between dichromate and stannous chloride is the same, *i. e.*, one mol of the former oxidizing three mols of the latter, and what substances are formed when no acid is added.

The Stoichiometric Relation.

Samples of commercial C. P. stannous chloride of about 0.4 g. each were rapidly transferred to beakers from a weighing bottle, dissolved in 50 cc. of water, and the solutions titrated with standard dichromate, some after adding 10 cc. of concentrated hydrochloric acid and others without the addition of any acid. Ferrous ammonium sulfate solution containing potassium thiocyanate was employed as an outside indicator.

At first the results of the titrations without acid seemed to be slightly higher than those with acid, which, as in the titrations of ferrous sulfate with dichromate without the addition of acid, would indicate that the reaction was not instantaneous. Further investigation, however, showed that the hydrochloric acid alone gave a faint pink color with the indicator, which was caused by the ferric iron in the slightly oxidized ferrous sulfate of the indicator being brought into solution by the acid. To overcome this difficulty, the titrations in which acid was used were run until a drop of the solution gave a darker tint with the indicator than acid alone. The results with and without acid were then almost identical.

Therefore the oxidizing power of dichromate towards stannous chloride is not affected if the reaction takes place without the addition of acid. Furthermore, the reaction is practically instantaneous in dilute solutions, or, in the titrations referred to above, the results should be higher without acid than with acid.[1] It is not surprising, however, that this should be the case, for the reaction may be regarded as compounded of two, each of which has a very great velocity. namely, that between ferrous salt and dichromate and that between ferrous salt and stannous salt.

When no acid is used, stannous chloride is considerably hydrolyzed in the concentrations employed in our titrations, giving milky, opalescent, solutions. The dichromate rapidly reduced the turbidity, which disappeared after a few cubic centimeters had been added. It is also interesting to note that at the end of these titrations, the solutions possessed a peculiar, faint and yet distinct, fruity odor, which was not observed in the acid titrations. We have been unable to discover the cause of this odor. In titrating the solid salt with 0.1 *N* dichromate, an olive-green solution having no turbidity is obtained immediately.

The Products of the Reaction.

The percentage of stannous tin contained in the solid chloride was estimated by titration with 0.1 *N* dichromate in the presence of an excess of hydrochloric acid, and the amount containing an equivalent weight in grams calculated. This quantity, 119.6 g., was dissolved in about 300 cc. of water contained in a liter flask. An equivalent weight of potassium dichromate (49.03 g.), enough to completely oxidize the stannous chloride, was dissolved in 200–300 cc. of water contained in a beaker. The dichromate solution was gradually added to the stannous chloride solution, the mixture being shaken vigorously to secure homogeneity. During the process of mixing, brownish and greenish blue gelatinous masses were formed and at one point the entire mixture became a jelly; but when all the dichromate had been added a perfectly clear, deep, olive-

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[1] Neidle and Witt, This Journal, 37, 2356 (1915).

green solution resulted, which in sufficient depth appeared red by transmitted light, natural or artificial. The mixture was diluted to a liter and aliquot portions removed for investigation.

Treatment with Ethyl Alcohol.—One hundred cubic centimeters were evaporated to dryness on a steam bath and dried to constant weight in an air oven. The residue was treated with 95% ethyl alcohol, which dissolved all but a white crystalline substance slightly tinged with green. This alcohol-insoluble matter was filtered off by suction through a Büchner funnel and washed with 95% alcohol, but it could not be entirely freed from the slight coloration due to an adsorbed chromium compound.

Alcohol-Insoluble Matter.—The residue from 100 cc. of the original mixture was dissolved in water and made up to 250 cc. Twenty-five cubic centimeter portions were removed for the estimation of tin, chromium and chlorine. The tin was determined by precipitation with hydrogen sulfide and ignition to stannic oxide; the chromium by addition of ammonium hydroxide to the hydrogen sulfide filtrate; and the chlorine by precipitation with silver nitrate. The potassium was obtained by subtracting the amount in the alcohol-soluble matter from the total employed in the reaction.

Alcohol-Soluble Matter.—The alcohol solution was evaporated to dryness on a steam bath, and the residue, dried to constant weight in an air oven at 120°, ground and analyzed for potassium, chlorine, chromium and tin. The methods for the tin and chlorine were the same as those above, while the potassium was determined as potassium chloride, and the chromium by fusion with sodium peroxide and titrating the resulting chromate with thiosulfate.

The results calculated to totals for the entire mixture are as follows:

	Alcohol-insoluble matter.		Alcohol-soluble matter.		Total gram equiv.
	Grams.	Gram equivalents.	Grams.	Gram equivalents.	
K	12.11	0.3097	0.92	0.0235	0.3332
Cl	11.12	0.3133	19.01	0.5361	0.8494
Cr^{III}	0.15	0.0087	17.15	0.9894	0.9981
Sn^{IV}	0.45	0.0151	60.39	2.0300	2.0451

The quantities of the elements contained in the entire mixture are: potassium, 0.3333 equivalent; chromium, 1 equivalent; chlorine and tin, 1 and 2 equivalents, respectively, provided the stannous chloride did not contain stannic tin. It will be remembered that the weight of stannous salt containing one-half the molecular weight of unoxidized chloride was employed. The results show that 0.0451 equivalent of stannic tin was present, with which 0.0226 equivalent of chlorine was associated. Thus, the total chlorine should be 1.0226 equivalents.

It is evident that the substance separated in the alcohol treatment is potassium chloride, which therefore is one of the products of the reaction.

The constituents of the alcohol-soluble matter cannot be determined from the analysis alone. It may be observed, however, that there is a deficiency of chlorine of nearly one-sixth the total. This loss was incurred when the alcohol-soluble matter was dried in the air oven, and was due to the decomposition of stannic chloride or chromic chloride, or both.

Since no tin was lost in the process of drying, hydrated stannic chloride could not have been present to any appreciable degree, for hydrated stannic chloride volatilizes considerably when heated.[1] Hydrated chromic chloride on the other hand does yield hydrochloric acid when heated to 120° C.[2] We are thus led to the conclusion that the alcohol-soluble matter consists of a mixture of the hydrous oxides of tin and chromium, and hydrated chromic chloride.

If stannic chloride were a product of the reaction, it could be extracted by means of carbon bisulfide. A portion of the original mixture was evaporated to dryness on a water bath, the residue powdered, introduced into a thimble, and extracted with carbon bisulfide for about eighteen hours, but no trace of tin could be found in the solvent. Dialysis of the reaction mixture gave further evidence that it does not contain stannic chloride.

Dialysis.

Fifty cubic centimeters of the original solution were dialyzed in a parchment paper bag suspended in a beaker filled with distilled water to the level of the solution in the bag. In a short time the external liquid was colored bluish green and considerable osmosis had taken place. Fresh water was placed in the beaker every day until it was not perceptibly colored after standing twenty-four hours. The accumulated diffusate for this period was concentrated and tested for tin, but none was found, thus proving the absence of stannic chloride in the mixture.

The dialysis was continued in order to free the hydrosol as far as possible from electrolytes. Excessive dilution by osmosis was avoided by keeping the level inside the membrane several centimeters higher than outside, which resulted in the concentration of the colloid as the osmosis diminished. In about five weeks when the diffusate was giving only a faint test for chloride ion, the contents of the bag set to a perfectly clear gel of a beautiful, emerald green in reflected light, and a deep red in transmitted light. In a second dialysis where no effort was made to keep the solution in the membrane from increasing in volume, 250 cc. increased to 1100 cc. in five weeks, giving a clear hydrosol resembling the

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[1] *Gmelin-Kraut*, 4, I, 313.

[2] *Ibid.*, 3, I, 439.

hydrogel. The hydrosol may be boiled down to a very viscous consistency and on being dehydrated over sulfuric acid becomes a firm gel.

Analysis of the gel showed that it contained all the tin, practically one-half of the chromium and a negligible quantity of chlorine. These results, together with those previously obtained, enable us to formulate the reaction as follows:

$$2K_2Cr_2O_7 + 6SnCl_2 + (6x + y)H_2O \rightleftarrows 4KCl + 6SnO_2.xH_2O + Cr_2O_3.yH_2O + 2CrCl_3 + 2HCl$$

Thus written the equation expresses the fact that dialysis yields a mixed hydrosol of hydrous stannic and chromic oxides in the molecular ration of 6 SnO_2 to 1 Cr_2O_3.

The reaction, with acid, is written ionically

$$Cr_2O_7^{=} + 3Sn^{++} + 14H^{+} \rightleftarrows 2Cr^{+++} + 3Sn^{++++} + 7H_2O. \quad (1)$$

Though no acid is added in our reaction, hydrogen ion is present, due to the hydrolytic dissociation of the dichromate and stannous chloride. Equation 1, therefore, represents the reaction when no acid is added.

Aqueous solutions contain hydroxyl ion in equilibrium with hydrogen ion according to the equation:

$$H^{+} + OH^{-} \rightleftarrows H_2O \quad (2)$$

As the hydrogen ion is removed by reaction (1) this equilibrium is disturbed, the more so as the available hydrogen is very limited and the concentration of hydroxyl ion correspondingly increases. When the latter accumulates sufficiently, the solubility products of stannic and chromic hydroxides are exceeded and the colloidal hydrous oxides are formed

$$Cr^{+++} + 3OH^{-} \rightleftarrows Cr(OH)_3;\ 2Cr(OH)_3 + (y - 3)H_2O \rightleftarrows Cr_2O_3.yH_2O.$$

$$Sn^{++++} + 4OH^{-} \rightleftarrows Sn(OH)_4;\ Sn(OH)_4 + (x - 2)H_2O \rightleftarrows SnO_2.xH_2O.$$

The formation of the hydrosols maintains the concentration of hydroxyl ion within perfectly definite limits, which insures a definite minimal concentration of hydrogen ion sufficient for reaction (1), which therefore continues to completion.

Other oxidation-reduction reactions without the addition of acid now being studied in this laboratory are those between ferrous chloride and potassium permanganate, ferrous chloride and hydrogen peroxide, and stannous chloride and hydrogen peroxide.

Conclusions.

1. The stoichiometric relations in the reaction between potassium dichromate and stannous chloride are the same with or without acid.
2. The products of the reaction are potassium and chromium chlorides, and stannic and chromic hydrous oxides in colloidal solution.
3. A clear mixed hydrosol of stannic and chromic hydrous oxides,

approximately in the molar ratio of 6 SnO_2 to 1 Cr_2O_3, may be obtained by adding an equivalent amount of dichromate solution to stannous chloride and dialyzing the mixture. The hydrosol will contain all of the tin and practically one-half of the chromium used in the reaction.

4. The equations for the reaction have been formulated.

5. The work already completed as well as that now in progress on oxidation and reduction without the addition of acid justifies the conclusion that colloidal hydrous oxides are obtained in an oxidation-reduction reaction, in which acid must be added for the formation of normal salts, if the stoichiometric relations are the same with and without acid.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY.]

THE ACTION OF HYDROGEN SULFIDE ON ARSENIC ACID.

BY WILLIAM FOSTER.

Received August 9, 1915.

I. Introduction.

Sometime ago my colleague, Professor LeRoy W. McCay, called my attention to a paper published by Usher and Travers[1] in 1905, and entitled "The Interaction of Sulfuretted Hydrogen and Arsenic Pentoxide in Presence of Hydrochloric Acid." Inasmuch as this paper contained some statements apparently not in harmony with the results obtained by McCay years before, it seemed well worth while to conduct experiments with the view of accounting for the discrepancies existing between the authors.

Ever since the days of Berzelius there has been a difference of opinion as to the chemical changes that occur when solutions of arsenic acid or acidulated solutions of arseniates are treated with hydrogen sulfide.[2]

Usher and Travers repeated and confirmed Brauner and Tomicek's work in the case of dilute hydrochloric acid solutions of arsenic acid, and also extended the investigation to solutions containing up to 32% of HCl, and obtained the results given below. The experiments were carried out at about 15°, and in every case the solution contained 0.3664% of the pentoxide.

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[1] *Trans.*, **87**, 1370 (1905).

[2] For detailed information, the reader is referred to the following literature on the subject: Berzelius, *Ann. der Phys. u. Chem.*, **7**, 2 (1826); H. Rose, *Ibid.*, **107**, 186 (1859); Wackenroder, "Dictate of Forensic Chemistry," H. Ludwig, *Archiv. der Phar., 2 te Reihe*, **97**, 32; Fuchs, *Z. anal. Chem.*, **1**, 189 (1862); Bunsen, *Ann. Chem.*, **192**, 305 (1878); McCay, *Am. Chem. J.*, **9**, 174 (1887); *Chem. News*, **54**, 287 (1886); *Am. Chem. J.*, **10**, 6 (1888); *Z. anal. Chem.*, **27**, 632 (1888); *Z. anorg. Chem.*, **29**, 36 (1901); Brauner and Tomicek, *Trans.*, **53**, 145 (1888); Neher. *Z. anal. Chem.*, **32**, 45 (1893).