by titration 51.9, 51.82 and 50.8 per cent. of acetic acid; and by precipitation 15.99 per cent. of chromium. Calculated for $(Cr(H_2O)_5)(C_2H_3O_2)_3$: Cr, 16.33; $C_2H_3O_2$, 55.4; for $(Cr.(H_2O)_6)(C_2H_3O_2)_3$: Cr, 15.4; $C_2H_3O_2$, 52.5.

These results are not conclusive. The salt had evidently lost acetic acid. The chromium was thus brought too high. The results, however, indicate that this acetate has 6 instead of 5 molecules of water.

Numerous attempts were subsequently made to prepare this substance, in part using lead acetate and violet sulphate, and later silver acetate and violet chloride; in only one instance did sufficient crystals separate for an analysis, and these were lost in the following manner: Acetate crystals, to the weight of about 1 gram, separated from the solution at +2° C. To increase the yield, the flask was surrounded with crushed ice and allowed to stand in the ice-chest for some hours; when it was again examined it was found that most of the crystals had disappeared. The explanation of their disappearance is probably this: The original solution was, of course, at first, supersaturated with the normal salt at the temperature of the experiment; however, the concentration of this salt was continually diminishing, owing to the somewhat rapid formation of the abnormal salts described by Recoura; the solution finally reached the state of unsaturation with respect to the normal salt and the crystals began to dissolve.

All succeeding attempts to prepare this salt in quantity have been unsuccessful; it is hoped, however, that the substance may again be obtained and further investigated.

The writer desires to acknowledge his indebtedness to Prof. A. Werner for his active interest in this work.

UNIVERSITY OF MICHIGAN,
ANN ARBOR, MICH.,
February 24, 1904.

ON THE NON-EXISTENCE OF ARSENIC PENTACHLORIDE.

BY WARREN RUFUS SMITH AND JOSEPH E. HORA.

Received April 6, 1904.

BY PASSING an excess of chlorine into arsenic trichloride cooled at —34°, and then allowing the temperature to rise to —30°, Baskerville and Bennett[1] obtained a substance which contained

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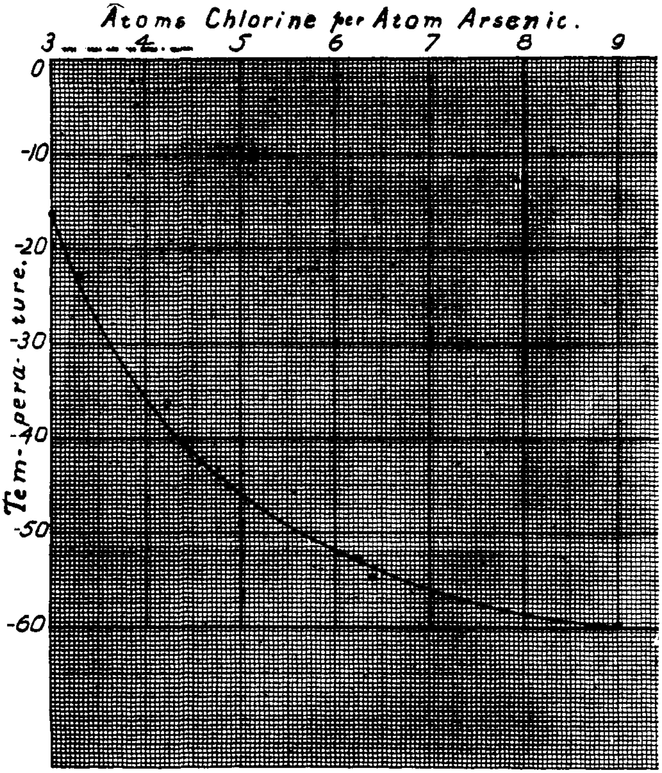
[1] This Journal, 24, 1070.

approximately 5 atoms of chlorine to 1 of arsenic, and which they assumed to be arsenic pentachloride. We have determined the freezing-points of mixtures of chlorine and arsenic trichloride and find that there is no reason for assuming that the substance containing arsenic and chlorine, in the above ratio, is anything other than a solution of chlorine in arsenic trichloride.

The freezing-points of solutions of chlorine in arsenic trichloride fall regularly up to a solution containing 9 atoms of chlorine to 1 of arsenic. From a solution containing 1 molecule of chlorine to 1 molecule of arsenic trichloride solid begins to separate at —48°, but the substance does not freeze as a whole, liquid still remaining at —70°. The solid which separates from all mixtures which we have studied seem to be arsenic trichloride; so we conclude that arsenic pentachloride is not formed by bringing together arsenic trichloride and chlorine in the required proportions at low temperatures under atmospheric pressure.

The method employed was to place a quantity of carefully purified arsenic trichloride in a large test-tube, fitted with a cork carrying two tubes. This was cooled in a bath of ether and carbon dioxide while dry chlorine was passed into the arsenic trichloride. At intervals the test-tube was removed from the bath, the cork and delivery tubes replaced by a thermometer and a small pipette, and the tube placed in a colder bath of ether and carbon dioxide. As soon as a moderate quantity of solid had separated the tube was taken out of the bath and its contents stirred continually with the thermometer while the temperature rose till all solid had disappeared. The temperature at which the last crystals disappeared was taken as the freezing-point of the mixture. The procedure was varied in some cases by allowing chlorine to boil off from a solution containing an excess, and then determining the freezing-point as above. As soon as the freezing-point had been determined, a small amount of the liquid was removed by means of the pipette and allowed to flow into an excess of normal sodium hydroxide solution contained in a liter bottle, which was stoppered as soon as possible after the solution was added. There seemed to be no considerable loss of chlorine during this addition except in the case of the solution containing the most chlorine. Here the figures are probably slightly inaccurate. To a measured portion of the alkaline solution sulphur dioxide was added and the arsenic determined by titration with iodine after acidifying with sulphuric acid and boiling off the sulphur dioxide. Another measured portion was added to an excess of standard silver nitrate solution, strongly acidified with nitric acid. This was boiled, filtered, and the excess of silver titrated with standard potassium thiocyanate. Several samples were checked by gravimetric determinations of silver and arsenic. A rough control of the ratio of arsenic to chlorine was kept, in some cases, by means of the total weights.



Results.—

	Freezing-points.	Ratio of As. to Cl.
1	—16.2°	1 : 3.00
2	—22.8	1 : 3.31
3	—36.4	1 : 4.23
4	—42.5	1 : 4.57
5	—45.4	1 : 4.91
6	—48.0	1 : 5.00
7	—53.0	1 : 6.24
8	—54.5	1 : 6.40
9	—59.5	1 : 8.99

A solution, containing more chlorine than No. 9, was cooled to —72° with no separation of solid. Several samples, including No. 6, were cooled to —70° and in no case was there complete solidification. From Nos. 4 and 8 a portion of solid was removed by means of a glass scoop, rinsed with petroleum ether cooled to —70°, transferred to alkali, and the ratio As : Cl determined. In the material obtained from No. 4 it was 1 : 3.3; from No. 8, 1 : 4. The outside of the mass of crystals was white after rinsing in each case and, in our opinion, they were arsenic trichloride contaminated by mother-liquor containing an excess of chlorine.

LEWIS INSTITUTE. CHICAGO,
March, 1904.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY NO. 95.]

ON THE COMBINATION OF A SOLVENT WITH THE IONS.

(PRELIMINARY PAPER.)

BY J. LIVINGSTON R. MORGAN AND C. W. KANOLT.

Received April 1, 1904.

As a result of the electrolysis of a solution of silver nitrate and pyridine in water, a loss of pyridine has been observed at the anode and a corresponding gain of pyridine at the cathode. By similar experiments with cupric nitrate and water, dissolved in alcohol (which, owing to experimental difficulties, are to be regarded only as preliminary) the quantity of water has been found to decrease at the anode and to increase at the cathode.

These experiments indicate that in such mixed solutions some of the ions combine with one of the solvents to form complex ions, which go through the solution and break up at the electrodes. The silver is accompanied by pyridine; the copper by water. If the negative ions are also so combined, the changes in concentration observed give only the differences between the amounts carried by the positive and by the negative ions.

The formation of such ionic complexes in mixed solvents leads to the conclusion that they also exist in solutions in one solvent; or, in other words, *when a substance ionizes in going into solution, the ions, one or both, attract a certain amount of the solvent and form complex ions with it.*