ART. LIX.—*A method for the Separation of Aluminum from Iron;* by F. A. GOOCH and F. S. HAVENS.

[Contributions from the Kent Chemical Laboratory of Yale University.—LXI.]

OF the well-known methods for the separation of aluminum from iron—by the action, for example, of an alkaline hydroxide in aqueous solution or by fusion of the mixed oxide in potassium or sodium hydroxide; by reduction of the iron oxide to the metal by heating in hydrogen, with the subsequent solution of the metallic iron in hydrochloric acid; by boiling the nearly neutral solution of the salts of aluminum and iron with sodium thiosulphate either with or without sodium phosphate; by acting with hydrogen sulphide or ammonium sulphide upon solutions of the salts containing also an ammoniacal citrate or tartrate—no single process can be said to be ideal as regards directness, rapidity and accuracy of working. We have deemed it not superfluous, therefore, to attempt the utilization of a reaction which should apparently be capable of effecting directly and quickly the separation of aluminum from iron under conditions easily attainable.

It is known* that the hydrous aluminum chloride $AlCl_3.6H_2O$ is very slightly soluble in strong hydrochloric acid, while ferric chloride, on the other hand, is extremely soluble in that medium. It is this difference of relation of which we wished to take advantage.

It appeared at the outset that crude aluminum chloride could be freed from every trace of a ferric salt by dissolving it in the least possible amount of water, saturating the cooled solution with gaseous hydrochloric acid, filtering upon asbestos in a filtering crucible or cone, and washing the crystalline precipitate with the strongest hydrochloric acid. Aluminum chloride prepared in this way gave no trace of color when dissolved in water and tested with potassium sulphocyanide. The correlative question as to how much aluminum chloride goes into solution under the conditions was settled by taking a portion of the pure aluminum chloride, dissolving it in a very little water, diluting the solution with strong hydrochloric acid, saturating the cooled liquid with the gaseous acid, filtering on asbestos, precipitating by ammonia the aluminum salt in the filtrate and weighing the ignited oxide.

From 10cm³ of such a filtrate we obtained in two determinations 0·0022 grm. and 0·0024 grm. of the oxide, the mean of which corresponds to 23 parts of the oxide or 109 parts of the hydrous chloride in 100,000 parts of the strong hydrochloric acid. This degree of solubility, though inconsiderable when

* Gladysz: Ber. d. d. chem. Gesell., xvi, 447.

the objective point is the preparation of the pure salt of aluminum, is obviously incompatible with the attainment of quantitative accuracy in the retention of the aluminum. We have found, however, that various mixtures of anhydrous ether and the strongest hydrochloric acid can be used satisfactorily as solvents for the iron chloride, while the aluminum chloride is insoluble to a very high degree in a mixture of hydrochloric acid and ether taken in equal parts and thoroughly saturated with gaseous hydrochloric acid at the atmospheric temperature. We found that 50 cm^3 of the solution of aluminum chloride, obtained by mixing about 0·1 grm. of the hydrous chloride (dissolved in 2 cm^3 of water) with the mixture of pure, specially prepared aqueous hydrochloric acid and ether in equal parts and again saturating the liquid at 15° C. with gaseous hydrochloric acid, left upon evaporation and ignition 0·0004 grm. in each of two experiments—results which indicate a maximum solubility corresponding to 1 part of the oxide or approximately 5 parts of the chloride in 125,000 parts of the equal mixture of ether and aqueous hydrochloric acid of full strength.

Pure aqueous hydrochloric acid of full strength mixes perfectly with its own volume of anhydrous ether, but it is a curious fact that the addition to this mixture of any very considerable amounts of a solution of ferric chloride in strong hydrochloric acid determines the separation of a greenish oily etherial solution of the ferric salt upon the surface of the acid. The addition of more aqueous acid does not change the conditions essentially, but more ether renders the acid and the oily solution completely miscible. The ferric chloride seems to abstract ether from the ether-acid mixture and, then dissolved in the ether, remains to some extent immiscible with the aqueous acid thus left until the addition of more ether restores to the mixture that which was taken from it by the ferric chloride. Our experiments show that, while for the separation of insoluble aluminum chloride from certain small amounts of solu ble ferric chloride the mixture of the strongest aqueous hydrochloric acid and ether in equal parts serves a most excellent purpose, when larger amounts of ferric chloride are to be dissolved ether must be added proportionately in order to prevent the separation of the ethereal solution of ferric chloride from the rest of the liquid.

Great care was taken to insure the purity of the aluminum chloride used in the test experiments. The so-called pure chloride of commerce was dissolved in the least possible amount of water and this solution was treated with a large volume of strong hydrochloric acid. The chloride thus obtained, free from iron, but possibly contaminated (as we found by expe-

rience) with some alkaline chloride, was dissolved in water and converted by ammonia to the form of the hydroxide, which was thoroughly washed and dissolved in hot hydrochloric acid of half-strength. From this solution, after cooling, gaseous hydrochloric acid precipitated the hydrous chloride in pure condition. The chloride thus prepared was dissolved in water and the strength of the solution was determined by precipitating the hydroxide from definite portions, and weighing the ignited oxide in the usual manner.

TABLE I.

	Al_2O_3 taken in solution as the chloride.	Al_2O_3 found.	Final volume.	Error.
	grm.	grm.	cm^3	grm.
(1)	0·0761	0·0746	50	0·0015—
(2)	0·0761	0·0745	50	0·0016—
(3)	0·0761	0·0741	50	0·0020—
(4)	0·0761	0·0734	50	0·0027—
(5)	0·0761	0·0756	50	0·0005—
(6)	0·0157	0·0149	45	0·0008—
(7)	0·0157	0·0147	40	0·0010—
(8)	0·0157	0·0144	45	0·0013—
(9)	0·0480	0·0481	30	0·0001+
(10)	0·0960	0·0957	30	0·0003—

In the experiments recorded in Table I, measured portions of the standardized solution were submitted to the treatment with hydrochloric acid and ether. The essential thing in the process is to have at the end a mixture of the strongest aqueous hydrochloric acid with an equal volume of anhydrous ether saturated at a temperature of about 15° C. The most convenient way to secure these conditions seems to be to mix the aqueous solution of the aluminum salt with a suitable volume of the strongest aqueous hydrochloric acid—enough to make the entire volume something between 15 and 25 cm^3—to saturate this mixture with gaseous hydrochloric acid while the liquid is kept cool by immersing the receptacle containing it in a current of running water, to intermix a volume of ether equal to the volume of the liquid, and finally, to treat the ethereal mixture once more with the gaseous acid to insure saturation. The precipitated crystalline chloride was collected upon asbestos in a perforated crucible, washed with a previously prepared mixture of hydrochloric acid and ether carefully saturated with the gaseous acid at 15° C., and either ignited after careful drying at 150° or redissolved in water, converted to the hydroxide by ammonia in the usual way and weighed as the oxide after filtration, washing, and ignition. In experiments (1) to (4) the precipitated chloride was ignited directly; in

experiment (5) the ignition was made with great care in an atmosphere of superheated steam; and in experiments (6) to (10) the chloride was dissolved, precipitated as the hydroxide, and weighed as the oxide.

The experiments in which the chloride was converted to the hydroxide before ignition show upon the average an absolute loss of about 0·0006 grm.; the single experiment in which the ignition took place in steam shows about the same loss—0.0005 grm.; while in those experiments in which the chloride was dried and then ignited directly, the average loss amounts to about 0·0020 grm. The error of the process which involves the precipitation of the aluminum as the hydroxide, falls within reasonable limits, but it is plain that the direct ignition of the chloride is liable to error, which may possibly be explicable as a mechanical loss occasioned by the too rapid evolution of the hydrochloric acid and water of crystallization, or, possibly, as the result of a very slight volatilization of the aluminum still holding chlorine in spite of the decomposing action of the water upon the chloride. In either case, it would seem to be reasonable to suppose that a layer of some easily volatilizable oxidizer placed upon the aluminum chloride might serve to obviate the difficulty—in the one case, by serving as a screen to diminish mechanical transportation of the non-volatile material; and in the other, by acting as an agent to promote the exchange of chlorine for oxygen on the part of the aluminum chloride.

We have tried, therefore, the expedient of covering the aluminum chloride before ignition with a layer of mercuric oxide, which of itself left no appreciable residue when it volatilized. The hydrous chloride was collected as usual upon the asbestos in a perforated crucible, dried for a half-hour at 150° C, covered with about 1 grm. of the pure mercuric oxide, gently heated with great care under a suitable ventilating flue, and finally ignited over the blast. The results are given below:

TABLE II.

	Al_2O_3 taken in solution as the chloride.	Al_2O_3 found by ignition with HgO.	Final volume.	Error.
	grm.	grm.	cm_3	grm.
(1)	0·0761	0·0758	25	0·0003—
(2)	0·0761	0·0754	25	0·0007—
(3)	0·0761	0·0751	25	0·0010—

It is obvious, therefore, that the precipitation of the crystalline hydrous aluminum chloride from solutions of the pure salt is perfectly feasible and very complete, when effected by aqueous hydrochloric acid and ether thoroughly saturated with

the gaseous acid and kept cool; and that the conversion of the chloride into the weighable form of the oxide is best effected by ignition under a layer of mercuric oxide, or by dissolving it in water and precipitating it as the hydroxide to be afterward washed, dried, and ignited. Of the two methods the former is by far the more convenient.

The precipitation of the aluminum chloride in pure condition from solutions containing ferric chloride ought not, it would seem, to present any difficulty, providing only that the precaution is taken to have present a sufficient excess of ether. The question was put to the test of experiment with the results recorded in Table III.

Measured portions of the standardized solution of aluminum chloride were evaporated nearly to dryness in a platinum dish, an amount of pure ferric chloride equivalent to about 0·15 grm. of the oxide was added in a very little water, 15 cm³ of the mixture of strong hydrochloric acid and ether in equal parts were introduced, the liquid was saturated at 15° C. with gaseous hydrochloric acid (the dish being held in a convenient device for cooling it by running water), 5 cm³ more of ether were added to secure complete miscibility of the solutions, and more gas passed to perfect saturation. The aluminum chloride was collected upon asbestos in a perforated crucible, washed with a mixture of ether and aqueous hydrochloric acid thoroughly saturated with the gaseous acid, dried at 150° C. for a half-hour, covered with 1 grm. of pure mercuric oxide, and ignited at first gently and finally over the blast.

TABLE III.

	Al_2O_3 taken in solution as the chloride.	Al_2O_3 found by ignition with HgO.	Fe_2O_3 present as chloride.	Final volume.	Error.
	grm.	grm.	grm.	cm³	grm.
(1)	0·0761	0·0757	0·15	25–30	0·0004—
(2)	0·0761	0·0756	0·15	25–30	0·0005—
(3)	0·0761	0·0755	0·15	25–30	0·0006—
(4)	0·0761	0·0755	0·15	25–30	0·0006—

The results show plainly a very satisfactory limit of error.