

markably similar in other properties, we should not expect the spectrograph to reveal this fact to us without more complete fractionation. And the writers believe, though it may not be well founded, that this third possible solution suggests the direction which future investigations of the tellurium problem should take.

Atomic weight determinations of the various fractions of tellurium which the spectrograph has shown to be free from all known impurities are now in progress in this laboratory.

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THE PREPARATION OF FERROUS CHLORIDE BY THE ELECTROLYSIS OF AN ETHEREAL SOLUTION OF FERRIC CHLORIDE.

BY H. EARNEST WILLIAMS.

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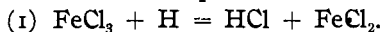
The electrolysis of ferric chloride in ether was attempted in the hope that a chlorine substitution product could be obtained. It was thought that metallic iron would separate at the cathode and that the chlorine liberated at the anode would act on the ether, producing monochlorether.

The ether used (U. S. P.) was treated with calcium chloride and sodium to remove water and alcohol, and then distilled. The ferric chloride was from Merck. It contained six molecules of water of crystallization.

The electrolytic cell was a glass bottle provided with a cork bored with three holes, one for a reflux condenser and the other two for glass tubes carrying platinum electrodes, 3 by 6 cm.

The continued electrolysis of a dilute solution of ferric chloride gave a green precipitate, separating out on the cathode, which increased in amount as more current was passed through the solution. No liquid product was observed. The solution, which was acid to litmus, was neutralized with acid sodium carbonate and distilled, but no new product, other than ferrous chloride could be detected. The green precipitate was found by analysis to contain: Cl, 34.7 and Fe, 28.5. It agreed in every respect with $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$.

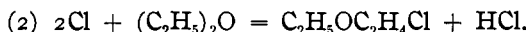
The conductivity of an ethereal solution of ferric chloride is at first slight, but rises rather gradually and at last remains fairly constant. This may be explained by the increase in the amount of the hydrochloric acid, the first molecules of which come from the slight hydrolysis of the very deliquescent ferric chloride. The amount of acid is increased, during electrolysis, in accordance with the equation



This accounts for the precipitation of ferrous chloride. The electrolysis of the hydrochloric acid formed would give hydrogen and chlorine. The latter might be expected to oxidize the ferrous chloride to ferric, but

this action is evidently prevented in some way, for there is a precipitate of the ferrous salt formed.

We may assume that the chlorine acts on the ether according to the equation:



Since monochlorether was not detected among the products of electrolysis, we may also assume that some of the hydrogen at the cathode acts upon it, reducing it to ether and hydrochloric acid, as follows:



In case the hydrogen reduces both monochlorether and ferric chloride, a certain amount of ferrous chloride will be produced. In case the ferric chloride only is reduced, the amount of hydrogen necessary will be nearly equal to the amount transported by the current, provided none is evolved. Also the amount of ferrous chloride, for the same current, will be greater than it would be if monochlorether is being reduced. To settle this point, the relation between the hydrogen transported and the ferrous chloride formed was determined.

An ethereal solution containing 1.2380 grams of ferric chloride was electrolyzed for 3 hours. Water was added to extract the ferrous chloride and the aqueous solution was made up to 250 cc. The iron was titrated with standard permanganate, using a buret with pinchcock. The amount of ferrous chloride found, 0.2256 gram, would require 0.0017 gram of hydrogen for its production, according to equation 1. The current used, 127.78 coulombs, would transport 0.0013 gram of hydrogen.

In a second determination, 1.2050 grams of ferric chloride gave 0.1952 gram ferrous chloride, requiring 0.0015 gram of hydrogen for its production. The current used, 107.00 coulombs, would transport 0.0011 gram hydrogen.

The use of the pinchcock of the buret would cause an error in reading the amount of permanganate used, thus increasing the apparent amount of ferrous chloride and of the hydrogen necessary for its production. If the amount of hydrogen necessary to produce the ferrous chloride found is less than the current would liberate, then, provided none is set free in the gaseous form and no metallic iron is deposited, the hydrogen is playing some other role than the reduction of ferric chloride. Since no monochlorether is found and, furthermore, the solution gives a strong reaction for free chlorine, it is evident from the data that the hydrogen is used only for the production of ferrous chloride.

In all probability the chlorine is prevented from oxidizing the ferrous chloride to ferric because the ferrous chloride is precipitated, on account of its slight solubility at the ordinary temperature. Hence the concentration of ferrous ion in the solution is not great. The hydrochloric acid formed (Eq. 1) takes up water with avidity and since the ether was made

as nearly anhydrous as possible with the aid of sodium, the amount of water available as an ionizing medium is very small. The six molecules of water in the ferric chloride furnish four to the ferrous chloride, and in all probability much of the remaining water is taken up by the hydrochloric acid. The slight solubility of the ferrous chloride and the removal of water by the acid formed lower to a minimum the tendency of the chlorine to oxidize the ferrous chloride, so that it is precipitated.

The electrolysis of concentrated solutions of ferric chloride, using a high current density, gives metallic iron and hydrogen at the cathode and a few bubbles of gas, probably oxygen, at the anode. Dilute solutions of ferric chloride on electrolysis with low current density yield ferrous chloride at the cathode. No chlorine or other gas is evolved. Hydrochloric acid accumulates in the solution as electrolysis continues. In general, the more rapid the electrolysis, the greater the tendency to produce hydrogen and metallic iron at the cathode. The voltage need not be greater than 4 volts.

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THE EQUILIBRIUM OF THE REACTION BETWEEN METALLIC SILVER AND FERRIC NITRATE.

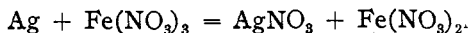
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1. Introduction and Outline.

When metallic silver is added to ferric nitrate solution, a partial reaction takes place as follows:



This reaction is of interest since it is one of the few oxidation reactions in which the substances on both sides of the equation are present in comparable amounts at equilibrium. Consequently it affords an opportunity of determining the equilibrium constant by purely chemical means and of comparing it with that determined by electromotive force measurements.

The equilibrium of this reaction does not seem to have been studied chemically, but the electromotive force of the ferrous-ferric electrode