

THE ELECTROLYTIC METHOD AS APPLIED TO  
PALLADIUM.

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Our knowledge bearing upon the behavior of this metal towards the current is limited and rather indefinite. In 1868, Wöhler published, in the *Annalen*, **143**, 375, an article entitled, "Ueber das Verhalten einiger Metalle im elektrischen Strom," from which the following facts are taken: Palladium, as the positive pole of a battery, consisting of two Bunsen cells, was immersed in water acidulated with sulphuric acid, when the metal immediately became coated with a deposit having a bright steel-like color. This deposit is doubtless palladium dioxide, as it liberates chlorine when treated with hydrochloric acid, and carbon dioxide when warmed with oxalic acid. At the same time, black, amorphous metal separated upon the negative pole. Its quantity was slight. In the second edition of *Classen's Quantitative Electrolysis*, p. 72 (American edition), it is stated that a feeble current will deposit palladium in a beautiful metallic state from an acid solution. One Bunsen cell is given as sufficient for this purpose. A more energetic current produces a spongy deposit. Ludwig Schucht has communicated\* that from an aqueous solution of palladious nitrate, acidulated with a few drops of nitric acid, the current precipitated upon the negative pole a bronze-colored deposit, which, as it grew more dense, became darker, and finally black in color. At the positive pole there was a simultaneous deposition of oxide, showing a reddish color. In alkaline palladic solutions the precipitation of metal was much retarded; the deposition of oxide was also observed.

Our first experience in the electrolysis of palladium salts was acquired from the double cyanide in an excess of potas-

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\* Berg- und Hüttenmännische Zeitung **38**, 121; also, Zeit. für anal. Chem., **22**, 240.

sium cyanide. In such solution a current, generating one cc. oxyhydrogen gas per minute, failed to cause metallic deposition until after the expiration of thirty-six hours; in other words, not until the excess of potassium cyanide had been completely converted into alkaline carbonates. Then the deposit was black in color, but the precipitation was not at all complete. No deposition of oxide was noticed upon the positive pole. The conduct of the metal in cyanide solution led to the trial of certain separations, the results of which will be given in a later communication. The action of the current (feeble) was also tried upon a solution of palladium chloride, in the presence of a large excess of potassium sulphocyanide. In this case the deposition of metal was exceedingly rapid. Spongy spots were noticeable. The deposit was black in color. The experiment was made with this solution in the hope that possibly a separation of copper from palladium might be found; but, as these metals separate with equal rapidity from their sulphocyanides, the results are valueless for this purpose.

The next attempt was made with palladammonium chloride,  $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ , in just sufficient ammonium hydroxide to retain it in solution. The total dilution of the solution was 125 cc.; the acting current gave 0.9 cc. OH gas per minute. The poles were distant from each other about two inches. Just as soon as the circuit was completed, a yellowish-brown coating appeared upon the spiral of the positive pole; while upon the dish, in connection with the negative pole, a deposit of metal closely resembling the platinum itself in color made its appearance. After acting through the night the current was interrupted, the metal deposit carefully dried and weighed. The precipitation was incomplete. It was, however, discovered that the deposition at the positive pole, which gradually increased in mass and assumed a black color, had entirely disappeared. In all instances where the ammonium hydroxide was in decided excess, the precipitation of oxide on the positive pole was not observed. This behavior is similar to that of nickel when its ammoniacal solutions are electrolyzed. In subsequent experiments the course was somewhat modified. From solutions such as

just described, the palladium thrown out upon the platinum dish was extremely slow in dissolving, even in fuming nitric acid, so that it was deemed expedient to first coat the platinum dishes employed in the electrolysis with a layer of silver, varying in weight from 0.1 to 0.3 gram. This was done in the experiments recorded below, and was found to be decidedly advantageous. The layer of silver seemed to hasten the deposition of the palladium.

## EXPERIMENT I.

A quantity of palladammonium chloride (= 0.2228 gram Pd) was dissolved in ammonium hydroxide; to this solution were added 20 to 30 cc. of the same reagent (sp. gr. 0.935) and 75 cc. water. The current allowed to act upon this ammoniacal liquid gave 0.9 cc. oxyhydrogen gas per minute. The decomposition continued through the night. At no time was there any oxide deposition upon the anode. The palladium gradually assumed a bright metallic appearance. After drying, the deposit showed about the same appearance as is ordinarily observed with this metal in sheet form. The washing was limited to hot water, and when the deposit was perfectly dry, the dish containing it was covered with a watch glass and exposed to a temperature ranging from 110° to 115° C. This was done to expel any hydrogen that might possibly have been retained by the palladium.

$$\begin{array}{rcl}
 \text{Weight of silvered dish + Pd} & = & 61.9575 \text{ grams.} \\
 \text{" " " - Pd} & = & 68.7350 \\
 \hline
 & & 0.2225 \text{ Pd.}
 \end{array}$$

## EXPERIMENT II.

In every respect similar to Experiment I, gave

$$\begin{array}{rcl}
 \text{Weight of silvered dish + Pd} & = & 71.9540 \text{ grams.} \\
 \text{" " " - Pd} & = & 71.7315 \\
 \hline
 & & 0.2225 \text{ Pd.}
 \end{array}$$

The filtrates from these deposits were warmed for eight hours with ammonium sulphide without showing any formation whatever of palladium sulphide.

In several experiments, with conditions unlike those just described, and where consequently an incomplete precipita-

tion of metal occurred, the digestion with ammonium sulphide produced in every instance, in a very short time, a reddish-brown flocculent sulphide, carrying with it quite a considerable quantity of free sulphur.

In a second series of two experiments, in each of which there was the same amount of palladium as in the previous trials, the quantity of ammonium hydroxide in excess was made 30 cc., while the current (giving 0.8 cc. oxyhydrogen gas per minute) was allowed to act for sixteen hours. The results were quite concordant:

## EXPERIMENT III.

$$\begin{array}{rcl} \text{Weight of silvered dish + Pd} & = & 72.1055 \\ \text{" " " - Pd} & = & 71.8825 \\ \hline \end{array}$$

$$\text{Weight Pd} = 0.2230 \text{ gram.}$$

## EXPERIMENT IV.

$$\begin{array}{rcl} \text{Weight of silvered dish + Pd} & = & 62.0512 \\ \text{" " " - Pd} & = & 61.8280 \\ \hline \end{array}$$

$$\text{Weight Pd} = 0.2232$$

It may be remarked that in filling the silvered platinum dishes a rather large surface of silver was allowed to remain above the electrolyzed liquid, so that by merely adding water it was possible to ascertain when the palladium was fully precipitated. When the deposition was not finished the new silver surface soon showed streaks of metal.

A third series of two experiments, in which the added amount of palladium was double that recorded in the preceding examples, the same conditions were observed as before, with the exception that as the current was only giving 0.70 cc. oxyhydrogen gas per minute, the time of precipitation was extended to eighteen hours. The results were as follows:

## EXPERIMENT V.

$$\begin{array}{rcl} \text{Weight of silvered dish + Pd} & = & 72.3555 \\ \text{" " " - Pd} & = & 71.9100 \\ \hline \end{array}$$

$$\text{Weight Pd} = 0.4455$$

## EXPERIMENT VI.

$$\begin{array}{rcl} \text{Weight of silvered dish + Pd} & = & 62.2600 \\ \text{" " " - Pd} & = & 61.8138 \\ \hline \end{array}$$

$$\text{Weight Pd} = 0.4462$$

Curiously enough, upon warming the liquid poured off from the palladium in Experiment V, with ammonium sulphide there appeared a very slight sulphide precipitate after some hours. The liquid from Experiment VI showed no trace of unprecipitated metal.

The deposits in the experiments just recorded were bright, metallic and very dense. In none was there the slightest tendency to sponginess. To show the accuracy of the method, the results may be tabulated as follows:

<i>Experiment.</i>	<i>Found Pd.</i>	<i>Calculated Pd.</i>
I, . . . . .	0.2225	0.2228
II, . . . . .	0.2225	0.2228
III, . . . . .	0.2230	0.2228
IV, . . . . .	0.2232	0.2228
V, . . . . .	0.4455	0.4456
VI, . . . . .	0.4462	0.4456

If the percentage differences be calculated, it will be found that they are quite within the limit of error occurring in almost any ordinary gravimetric determination.

The behavior of ammoniacal palladium solutions, when exposed to the action of the electric current, will be further studied as time permits, and, if possible, the attempt will be made to re-determine the atomic weight of the metal by this method in a somewhat modified form.

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## NOTES AND COMMENTS.

### CHEMISTRY.

INDIAN INDUSTRIAL PRODUCTS—*Jour. Soc. Chem. Industry*, **9**, 670.—The following information respecting dyes and tanning materials and lac are extracted from a memorandum on Indian inland trade compiled in the Revenue and Agricultural Departments of the Government of India, and which has recently been issued from the Government central printing office at Simla.

*Dyes* and *tans* comprise indigo, myrabolans, cutch, turmeric, aniline dyes, and "others." The first is by far the most important, and stands at 323 lakhs of rupees\* in a total trade in dyes and tans valued at 442 lakhs of rupees.

\* A lakh of rupees = 100,000 rupees.