

ART. XLI.—*The Reactions in a System of Nickel or Platinum, Mercury, and Sodium Chloride*; by CHARLES A. PETERS.

[Contributions from the Kent Chemical Laboratory of Yale Univ.—ccxxvii.]

DURING the progress of work upon the electrolysis of sodium chloride with the mercury cathode,\* it was noticed that when the outer cell containing sodium hydroxide, sodium chloride in solution over mercury, and nickel wire in contact with both liquids was allowed to stand several days a scum formed on the surface of the mercury. Upon shaking the liquids in the separatory funnel and drawing off the mercury the remaining liquid appeared turbid. Under the microscope transparent colorless crystals were easily seen mixed with air bubbles.

To study the conditions under which these crystals might be formed and to determine their identity, such systems as compose the outer cell of the electrolytic apparatus were made and allowed to stand. These consisted of Erlenmeyer beakers containing 300 grms. of mercury, sodium chloride solutions of different strengths and an inverted V-shaped piece of nickel wire.

In a day a scum was visible on the surface of the mercury which accumulated as the systems stood, seemingly more dense in the immediate vicinity of the wire, and, after several weeks showed, increasing in distinctness as the time increased, the familiar "apple-green" color. The nickel was corroded. The amount of the green precipitate increased faster when a greater surface of nickel was exposed in the salt solution.

This precipitate, crystalline under the microscope, when collected on the filter and well washed with water, gave tests for nickel but none for mercury, chlorine, or sodium. It turned black upon ignition. By these characteristics the crystalline substance was identified as nickelous hydroxide.

Tupput† has formed crystalline nickel hydroxide from nickel carbonate dissolved in ammonia. Crystals made by the hasty evaporation of such a solution appeared similar to those obtained from the mercury-nickel-salt systems.

The solution over the mercury showed a tendency to develop alkalinity very slowly. In one case a beaker with the mercury, water, nickel wire, and a piece of red litmus paper—without sodium chloride—stood 24 hours. The litmus paper was still reddish and showed no trace of blue or purple, but upon adding a cubic centimeter of saturated salt solution the litmus was decidedly bluish when observed two hours later.

\* This Journal, preceding article.

† Gmelin—Kraut, 1910, Bd. V, Abt. 1, p. 44.

Two days later another piece of red litmus was added, and this, in three minutes, was blue on the edges. After standing several months a piece of red litmus turned blue instantly upon introduction into the liquid over the mercury. It is evident that the amount of sodium hydroxide produced in a few days is extremely small and inappreciable in analysis.

In other experiments platinum wires were substituted for nickel. A scum formed slowly as before and under the microscope was found to be composed of coarse white crystals with numerous small globules of mercury between them. The crystals contained mercury and chlorine, and were very insoluble in water. Small amounts crystallized from boiling water had the characteristic "silky" appearance of calomel. The crystals consequently were identified as mercurous chloride. The platinum showed no erosion.

The liquid over the mercury showed the same tendency, in about the same degree as when the nickel was present, to develop alkalinity. A few cubic centimeters from one of the platinum-mercury-salt systems which had been standing several days developed only the faintest pink coloration with phenolphthalein.

#### *Summary.*

From the work described in this paper it is seen that when a solution of sodium chloride is allowed to stand over mercury with a nickel wire connecting both liquids, crystalline nickelous hydroxide is formed very slowly, sodium hydroxide being produced at the same time. When platinum is substituted for nickel, mercurous chloride is formed, sodium hydroxide being likewise produced.