DISCUSSION.

Dr. F. Mollwo Perkin said he had been extremely interested in Mr. Rhodin's Paper. He would like to ask him what was the weight of the platinum in the cathodes, and what was the effective surface, because, without knowing the surface, to be told that the current employed was 2 amperes did not convey any information as to current density. He agreed with the author that nitric acid was the most satisfactory electrolyte to use, and that it gave much better results than sulphuric acid. It would not have been possible to employ such high currents if sulphuric acid had been used. The second portion of the Paper was of interest, because it showed how the correct composition of an alloy to be used under various conditions could be arrived at from theoretical considerations.

Mr. W. R. Cooper said he was much interested in the second portion of Mr. Rhodin's Paper, but he had to confess that he did not altogether follow the reasoning of the author. For example he found some difficulty in accepting the view that the dissolving action of Muntz's alloy in sea-water was galvanic. If that were the case, he did not see how both the metals could be affected. Did the author mean that the copper and zinc formed a couple? If so there did not seem much reason why the solution of the copper should be voltaic, or that there was any object in introducing conductivity of the metals in his calculation of the best composition for Muntz's metal. On the other hand, if the metals were regarded as dissolving separately by voltaic action, would there not be a considerable interference by local action through the copper and zinc forming a couple? Mr. Cooper did not feel that the author had very conclusively proved his conclusions as to the solution of Muntz's metal.

Mr. Arnold Stevenson asked what was the difference of potential between the electrodes with each of the current densities employed. Had

the author tried adding gelatine to the electrolyte with the view of obtaining better deposits, and, if so, had he found that the copper deposited contained carbon?

The Chairman complimented Mr. Rhodin on the scope and interest of his Paper, which he was sure had been much appreciated by all present. (*Applause.*) He could not, however, agree with Mr. Rhodin in his theory of mass action as applied to this case. He had brought with him a copy of that portion of the curve recently published by Shepherd,* which referred to the copper-zinc alloys under consideration (Fig. 1). In order to obtain the curves, alloys of increasing percentages of zinc were chilled from temperatures ranging from about $1,100^{\circ}$ C. to 400° C., below which the curves were practically straight lines. The regions α and $\alpha + \beta$ are those with which we are concerned. Examined under the microscope it is at once apparent that the α and the β crystals are different in structure and colour. An alloy containing up to 36 per cent. zinc cooled very slowly from or below 400° C., would be homogeneous in appearance, and practically structureless when etched and examined under the microscope, though of course the boundaries of the α crystals might be developed. After 36 per cent. zinc is passed, we find a mixture of α and β crystals, the proportion of β increasing steadily until 46.5 per cent. zinc is reached, beyond which the α crystals disappear altogether and the alloy again becomes homogeneous, but this time consisting of β crystals. Muntz's metal is composed of α and β crystals (see Fig. 2). The α crystals in Muntz's metal, which may be assumed not to have been cooled rapidly from above 600° C., would contain 36 per cent. zinc; the β crystals would contain 46.5 per cent. zinc. When a piece of Muntz's metal is polished and slightly etched either with ammonia or with the solution used by Mr. Rhodin in his dissolution experiments, viz., HCl of 10.037 N strength, the β crystals are dissolved, leaving the α crystals in a raised pattern. This is easy to see and there can be no doubt of it whatever. If the α crystals could hold together as a continuous skeleton, all the β would eventually be dissolved out, leaving a sponge of α . But in this alloy the α crystals are surrounded with β , and when the β dissolves the α crystals, which are of microscopic fineness, fall into the solution and then themselves dissolve. An analysis of the solution might give the impression that the alloy had been uniformly dissolved, but it is not so. The surface of the alloy continues to appear smooth, except under the microscope, because the particles of α detached by the dissolution of the supporting β are so small.

The rate at which Muntz's metal dissolves is regulated by the relative proportions of the α and β crystals.

Mr. J. G. A. Rhodin in reply to Mr. Cooper said that the ultimate conclusion drawn in the appendix to the paper was that the seat of the E.M.F. was in the electrolyte. Whether the charges of the dissociated hydrogen ions were directly delivered, or some "atomic voltaic combinations" existed, was immaterial. The author hence supposed the two metals to be shunted dissolving poles. (*Vide* "Mathematical Calculation of the Composition of Muntz's Metal.")

The point raised by Professor Huntington was not in opposition to the tenor of the Paper. A structural development was admitted, but this takes place in such a way as to keep the surface approximately constant. Under the circumstances described, the wire at the end of the experiment was just as pliable and homogeneous as when it was put in, but the surface had developed a certain roughness. The α and β crystals did not concern the

* *Journal of Physical Chemistry*, June, 1904.

present problem, which dealt with total dissolution velocity. The analysis of the wire after the experiment did not support the Chairman's theory, which would also leave the question of how the α and β crystals dissolved open to inquiry.

With regard to the deposition of bright copper mentioned by Mr. Stevenson, the discovery of the action of gelatine was made originally by Sir Joseph Swan. The determination of the actual conditions necessary for *intentional* production of such deposits was made by the author in 1892 as Sir Joseph's assistant, and by his orders. On the whole the process may be described as follows. A 4 or 5 per cent. solution of best Swiss gelatine is treated with two or three drops of strong nitric acid per 100 c.c. on a water bath till it loses its gelatinising properties. Five or more c.c. of this solution are added to 1 litre of ordinary electroplater's solution (acid sulphate of copper). Deposition takes place with a current density of 150 amperes per square foot. The current must be interrupted every 10 or 15 seconds for a similar period, as otherwise slimy growths appear on the deposit. The space between the electrodes must be vigorously stirred. In this way most brilliant deposits can be obtained. The method was, on Sir Joseph Swan's suggestion, applied to the production of gold-leaf by electrolysis.