

24 THE MEASUREMENT OF THE POTENTIAL OF

DISCUSSION.

The Chairman, in opening the discussion, said that the paper of Dr. Sand represented a large amount of very laborious work, which would, however, prove of great use to electrochemists. The whole question of potential was one of fundamental practical importance; for example, in oxidation or reduction process—he spoke from his own experience—slight differences in the potential often meant very great differences in the amount of energy absorbed and the course of the reaction. A further practical outcome of Dr. Sand's experiments was to insist on the importance in electrolytic processes of circulating the electrolyte, if it is desired to keep the potential constant. He was much interested in the results obtained with the partially-oxidised alcoholic solution of cuprous chloride, in which case the curves showed two breaks, one corresponding to the reduction of cupric chloride, and the other to the deposition of copper. The action was similar to that which was well known to obtain in the deposition of iron, where a longer time was necessary to precipitate the metal from a ferric than from a ferrous solution, probably on account of the reduction which had first to take place, as in the former instance.

He had much pleasure in moving that a vote of thanks be passed to Dr. Sand for his interesting, exceedingly difficult, and carefully worked-out paper.

Dr. H. Borns supposed that the experiments had been made chiefly with smooth electrodes; had platinised electrodes also been applied?

Mr. J. K. H. Inglis asked Dr. Sand whether he had tried the plan (advocated by Luther) of placing the capillary connection to the normal electrode just behind the cathode. In this way, since this capillary would not cut the lines of force between the anode and cathode, no fall of potential in the electrolyte due to Ohm's law would come into consideration, and therefore the calculation would be much easier. Probably this method, however, would not be so accurate as that adopted by Dr. Sand.

Professor R. Threlfall said he had often read Dr. Sand's earlier paper, on a similar subject, with great pleasure; he thought it contributed to a real advance in electrochemistry. The present paper might possibly yield just such a definite and finite answer, but if it did he was afraid he had not succeeded in gathering it. He considered that in this research the author had attempted something too difficult; there were too many elements of uncertainty in the phenomena studied, too many unknown changes to make a complete elucidation possible, or at least easy. Such unknown elements were of course familiar to all electrochemists. For instance, why in the electro-deposition of platinum does the presence of a minute quantity of lead make all the difference? He believed that it was in the explanation of such comparatively *simple* phenomena, stripped of all unnecessary complications, that future advances in electrolysis would be made, and not from the study of *difficult* experiments, involving innumerable chances of misapprehension, such as Dr. Sand has bravely attempted to tackle. The work that had yielded the most valuable results in the past was the constant and minute study of simple things—familiar difficulties that occurred in one's daily practice.

He would like to venture a further word of criticism on Dr. Sand's method of making his electrode-potential measurements. He thought that the method of employing a capillary tube in connection with the cathode, placed, for example, in an undercut hole beneath the cathode, was preferable to that used by Dr. Sand.

THE ELECTRODES IN STATIONARY LIQUIDS 25

Dr. Sand, in reply, said that the answer to Dr. Borns was that he had used both kinds of electrodes; the results obtained with the platinised platinum electrodes would be found in the printed paper. He quite felt the force of what Professor Threlfall had said. Although the experiments had been originally carried out with the hope of obtaining from them a considerable amount of information regarding organic electrochemical reactions, he agreed that in the meantime it would be better to confine the application of his method to simpler cases, such as Professor Threlfall had indicated. The object of the present paper, however, was to describe the method, to indicate the nature of the uses to which it might be put, and also to show the limits of its applicability. It certainly went considerably further than his previous method.

With regard to his plan of measuring the electrode-potential, he did not think that it was more accurate than the method indicated by Mr. Inglis and Professor Threlfall, but probably the reverse. For his experiments, however, these last-named methods were not applicable; for in order that convection-currents might be avoided it was essential to have a smooth working electrode, over the whole surface of which the current-density should be perfectly uniform and which must, according to the reaction, be placed horizontally either at the very top or at the very bottom of the apparatus. His experiments were essentially with stationary liquids; they were diffusion experiments, and from this fact arose the main difficulties he had to contend with.