

## DISCUSSION.

(Tuesday, December, 11, 1906, DR. T. M. LOWRY in the Chair.)

**Mr. N. T. M. Wilsmore** said that the author's work was of considerable interest in connection with the theory of the lead accumulator. Dolezalek's theoretical investigations were based in great part on the hypothesis of Liebenow, that lead dioxide gave off bi-valent negative  $\text{PbO}_2''$  ions—a somewhat unlikely reaction. It had been shown, however, by Abel that Dolezalek's results could be reached equally well from Le Blanc's assumption of the formation of quadrivalent positive  $\text{Pb}^{++++}$  ions; hence the author's measurements might have further theoretical applications.

**Mr. H. L. Joly** remarked that Prof. J. N. Collie had found a long time ago that oxygen behaved as a tetravalent element in some compounds. He hoped that somebody mathematically inclined would work out the accumulator problem afresh on Dr. Cumming's new assumption.

The **Chairman** said it would have been a great advantage if the solubility of lead peroxide in sulphuric acid had been determined by experiment rather than by calculation; such an experiment might easily have been made, whilst the calculation could only lead to very uncertain results.

**Dr. A. C. Cumming** (*communicated*): The theory for the accumulator on the assumption of tetrad lead has been worked out mathematically by Abel (*Zeit. für Electroch.* 7, p. 731).

Dr. Lowry is of opinion that the estimation of the solubility of  $\text{PbO}_2$  in sulphuric acid is an easy matter. I cannot agree with him at all. Obviously no precipitation method could be used, so that one must evaporate the solution and weigh the lead sulphate. The evaporation of half a litre of 7 or 8N sulphuric acid to obtain a few milligrams of lead sulphate is a process which requires much time and attention. I had hoped to have estimated this solubility experimentally, but a few experiments convinced me that it would require more time than I could give. It seemed better, therefore, to give a calculated value, which did not profess to be more than an approximation, than to do a hurried experiment. Since the reading of this paper, a research by Dolezalek and Finckh (*Zeit. anorg. Ch.* 51, 1906, p. 320), has appeared on the same subject. Their investigation was carried out with

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solutions in sulphuric acid, and it may be mentioned that they regard the estimation of  $\text{PbO}_2$  in sulphuric acid of less than 20 N as impracticable. It may be of some interest to compare their results with my calculation. The calculation led to the value .3 milligram. molecules per litre in 7.5 N sulphuric acid. The most dilute solution in which they were able to analytically estimate the  $\text{PbO}_2$  was 20.7 N, which dissolved 1.8 millimols per litre, so that the value obtained by calculation was of the right order of magnitude, and nothing more was claimed for it.

The experiments with sulphuric acid were, however, only an incidental part of the research, since I was mainly concerned with the determination of the value for  $\text{Pb}^{\cdot\cdot\cdot\cdot} \longrightarrow \text{Pb}^{\cdot\cdot}$ . The mean value found was 1.83 volt, and it is satisfactory to notice that, working with the sulphate, Dolezalek and Finckh obtained values varying between 1.85 and 1.90 volt.