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Short Notes

THE STOICHIOMETRIC NUMBER FOR THE HYDROGEN EVOLUTION REACTION ON NICKEL IN ALKALINE SOLUTION: FURTHER COMMENTS ON THE WORK OF HORIUTI AND SUGAWARA

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A summary of this controversy to date is: (i) The present authors employed¹⁾ the normal equation to calculate a value of the stoichiometric number ν , for the hydrogen evolution reaction on nickel in alkaline solution, utilizing a statistical sample of 37 values, and applying classical probability statistics; (ii) HORIUTI and SUGAWARA²⁾ suggested an alternative method for calculating ν , and obtained a value of $\nu=1$ for the system mentioned, the statistical confidence limits of the result being unstated^{**)}; (iii) The present authors analysed¹⁾ HORIUTI and SUGAWARA's method and established that, should the measured overpotential values be subject to a bias of the order of 1 millivolt, the method used by HORIUTI and SUGAWARA (*loc. cit.*) would become grossly inaccurate; whereas values obtained by the normal method would remain unaffected.

HORIUTI has now published³⁾ the comments of the Referees of the American Journal on HORIUTI and SUGAWARA's work, and in turn their opinions of the Referees' comments, and so on. The position appears to be unchanged. There are several methods for obtaining ν , each of which involves certain inaccuracies; that used by HORIUTI and SUGAWARA is much more sensitive to small errors in the absolute value of overpotential than is our method, where the effect of a small (e. g. $\pm 1\text{mv}$) bias on the overpotential was computed and found to be insignificant.⁴⁾

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^{**)} An earlier publication by HORIUTI (Ref. 3) reported measurements of a quantity equivalent to the stoichiometric number on Ni but no distinction between the values 1 and 2 could be made because of irreproducibility of the electrode surface.

1) J. O'M. BOCKRIS and E. C. POTTER, *J. Chem. Phys.* **20**, 614 (1952).

2) J. HORIUTI and H. SUGAWARA, *this Journal* **4**, 1 (1956).

3) J. HORIUTI, *Sci. Pap. Inst. Phys. Chem. Res.* **37**, 274 (1940).

4) J. O'M. BOCKRIS and E. C. POTTER, *this Journal* **4**, 55 (1956).

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It appears sufficient to state here only certain details of our experimental results, relevant to the validity of the confidence limits which we have calculated for ν . General theoretical matters which HORIUTI and SUGAWARA raise have been discussed extensively elsewhere.^{5),6)}

(i) The experimental results contained a bias of the order of 1 mv. Their *reproducibility* is expressed with ordinary probability statistics in terms of i_0 .

(ii) Correspondingly, at zero current density, an apparent overpotential of ± 1 -2 mv was sometimes observed.

(iii) HORIUTI and SUGAWARA's indication (*loc. cit.*, p. 43) that a small bias in overpotential would lead to an infinite value of $(\partial i_c / \partial \eta)_{\eta=0}$ is incorrect. The overpotential η and the cathode current density i_c are linearly related when η is between zero and -20 mv. Hence,

$$\left[\frac{\partial}{\partial i_c} (\eta + x) \right]_{\eta=0} = \left[\frac{\partial \eta}{\partial i_c} \right]_{\eta=0},$$

when $x > -20$ mv. Let x be a bias much less than 20 mv, e. g., a bias of -1 mv. Then, $\left[\frac{\partial}{\partial i_c} (\eta + x) \right]_{\eta=0} = \left[\frac{\partial \eta}{\partial i_c} \right]_{\eta=0}$ and the polarization resistance, to which ν in the normal method of calculation is proportional, remains unchanged.

(iv) The 95% confidence limits of one estimate of $\log i_0$ have been misread from our paper as -0.3 and $+0.5$. These limits refer to an estimate of the stoichiometric number based upon one particular experiment whereas the results quoted in our paper for the stoichiometric number referred to the statistically computed value from many determinations. Since there is no way of estimating the confidence limits of one estimate of $\log i_0$ from the information given in our original paper, the statistically calculated data for the two Tafel lines already

TABLE I. Certain statistical data.

(With 95% confidence limits)

Concn. NaOH	Temp. °C	$-a$ volt	b volt	$\log i_0$ amp/cm ²	$\left(\frac{\partial \eta}{\partial i_c} \right)_{\eta \rightarrow 0}$ ohms/cm ²	$(\eta)_{i_c=0}$ volts	ν
0.18 N	18	0.638	0.094	- 6.77	12.2×10^1	± 0.0025	1.7
		± 0.007	± 0.001	± 0.03	$\pm 0.7 \times 10^1$	± 0.0007	+0.3, -0.2
0.06 N	1	0.755	0.110	- 6.88	20.4×10^1	± 0.0002	2.3
		± 0.007	± 0.001	± 0.02	$\pm 1.5 \times 10^1$	± 0.0006	+0.5, -0.4
0.006 N	3	0.596	0.084	- 7.12	24.7×10^1	± 0.0000	1.6
		± 0.013	± 0.001	± 0.04	$\pm 1.9 \times 10^1$	± 0.0007	+0.6, -0.5

5) *Ibid.*, p. 9.

6) J. O'M. BOCKRIS, *Modern Aspects of Electrochemistry*, Chapter IV, New York, 1954.

illustrated in Fig. 7 of that paper and for one other line chosen at random from those in Table V of the same paper are here given.

These data show that the 95% confidence limits for one estimate of $\log i_0$ were near ± 0.03 for our alkaline solution work, and that the 95% confidence limits, e. g., for one estimate of ν were $+0.5$ and -0.4 . Consequently, one estimate of ν could not be relied upon to differentiate $\nu=1$ from $\nu=2$. Replication of the measurements, however, increases the precision of the mean. Thirty-seven separate estimates of ν were reported and the 95% confidence limits of the mean become $+0.5/\sqrt{37}$ and $-0.4/\sqrt{37}$, i. e., ± 0.1 , as already published.

It appears that HORIUTI and SUGAWARA must find some significant invalidity in the statistical analysis or accept the results reported.*)

*) The same method has now been used by PENTLAND, BOCKRIS and SHELDON (Ref. 7) for the calculation of the stoichiometric number. It allows unambiguous evaluation of ν , for some ten metals in acid and alkaline solution, so long as proper statistical procedures are used.

We take this opportunity of pointing out that the equation of BOCKRIS and AZZAM (Ref. 8), claimed by HORIUTI (Ref. 9) to be dimensionally incorrect, is in fact dimensionally correct, as can easily be discerned by recalling that the expression $K = \exp(-\Delta F^*/RT)$ has the tacit dimensions of the equilibrium constant appropriate to the equilibrium between the initial and activated state for the given rate determining step (Ref. 10).

- 7) N. PENTLAND, J. O'M. BOCKRIS and E. SHELDON, in press.
- 8) J. O'M. BOCKRIS and A. M. AZZAM, *Trans. Faraday Soc.* **48**, 145 (1952).
- 9) J. HORIUTI, *this Journal* **4**, 55 (1956).
- 10) J. O'M. BOCKRIS and R. PARSONS, *J. Chem. Phys.* **21**, 569 (1953).