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**STOICHIOMETRIC NUMBER OF HYDROGEN  
ELECTRODE REACTION ON NICKEL :  
REPLY TO COMMENT OF HORIUTI AND SUGAWARA**

By

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In a recent contribution to this journal<sup>1)</sup> HORIUTI and SUGAWARA have sought to show some internal inconsistency in those of our experimental data<sup>2)</sup> which lead to a value of  $2.0 \pm 0.1$  for the stoichiometric number of the hydrogen electrode reaction at nickel cathodes in alkaline solution. The main purpose of this note is to demonstrate rigorously that our data are consistent within the experimental error and to confirm that our measurements, particularly of the stoichiometric number, are accurate and precise to the statistically computed limits which we have already published. Further, we shall show that the particular technique used by us for estimating the stoichiometric number is more accurate than that preferred by HORIUTI and his associates. We affirm also that our conclusion as to the mechanism of the electrode process in question is unchanged; that is, the process consists of a rate-determining discharge step from a water molecule followed by catalytic combination of adsorbed hydrogen atoms. These two steps may be written (where M represents the metal surface and  $e^-$  the electron),



Our values of the stoichiometric number have been calculated using the already accepted equation (6) in HORIUTI and SUGAWARA'S communication, that is,

$$\nu(r) = -2i_0F \left/ \left\{ RT \left( \frac{di_c}{d\eta} \right)_{\eta=0} \right\} \right. , \quad (\text{HS } 6)$$

where  $\nu(r)$  is the stoichiometric number,  $\eta$  is the activation overpotential,  $i_c$  is the cathodic current density,  $i_0$  is the exchange current density, and  $F$ ,  $R$ , and  $T$  have their usual significance. Using the values of  $i_c$

and  $\eta$  taken from Figure 7 of our paper<sup>2)</sup>, HORIUTI and SUGAWARA have calculated  $\bar{i}$ , the current density for the forward direction of the electrode reaction from their equation (5),

$$i_0 = \bar{i} \left\{ 1 - \exp \left[ \frac{2F\eta}{\nu(r)RT} \right] \right\}, \quad (\text{HS } 5)$$

in which  $\nu(r)$  is given our mean experimental value, 2.0. When the calculated values of  $\log \bar{i}$  are plotted against  $\eta$ , a relationship is found which deviates from linearity at overpotentials numerically less than about 20 millivolts. As a result of this deviation the relationship does not form an intercept on the  $\log \bar{i}$ -axis at the experimental value of  $\log i_0$ . HORIUTI and SUGAWARA argue that, since the value of  $i_0$  used in equation (HS 6) is found by a linear extrapolation to zero overpotential of the  $\log i_c, \eta$  relationship observed at relatively great overpotentials, the experimental data are inconsistent in themselves. We do not dispute that this inconsistency exists, but, as we shall now show, its magnitude is too small to make any significant difference to our estimates of the stoichiometric number.

In order to avoid confusion with the abstraction of numerical data from Figure 7 of our paper, we shall take a general example in which convenient and reasonable values are used. It will be assumed that a TAFEL line relevant to the present discussion is obtained by using equation (9) of our paper, thus,

$$i_c = i_0 \left\{ \exp \left[ -2\beta\eta F / \nu(r)RT \right] - \exp \left[ 2(1-\beta)\eta F / \nu(r)RT \right] \right\} \quad (\text{BP } 9)$$

and substituting the following values:  $i_0 = 10^{-7.0000}$  amp/cm<sup>2</sup>,  $\beta = 0.50$ ,  $F = 96,500$  coulombs/g. equivalent,  $\nu(r) = 2.00$ ,  $R = 8.3144$  joules/°Cmole,  $T = 293.15$  °A, and  $\ln 10 = 2.3026$ . On substituting corresponding values of  $i_c$  and  $\eta$  calculated from equation (BP 9) in equation (HS 5),  $\bar{i}$  is obtained. The results of this calculation must conform to a linear relation between  $\log \bar{i}$  and  $\eta$  since equation (BP 9) is derived on this basis; the actual line obtained is shown in Figure 1 as the central straight line through the intercept  $-7.0$  on the vertical axis.

We now assess the effect on the above calculations of superposing an assumed value for the experimental error. Let all the  $\eta$  values previously used in equations (HS 5) and (BP 9) be subject in turn to a positive and a negative bias of one millivolt. It will be appreciated that a bias of this order (positive or negative) can reasonably arise in practical measurements of electrode potential in overpotential studies.

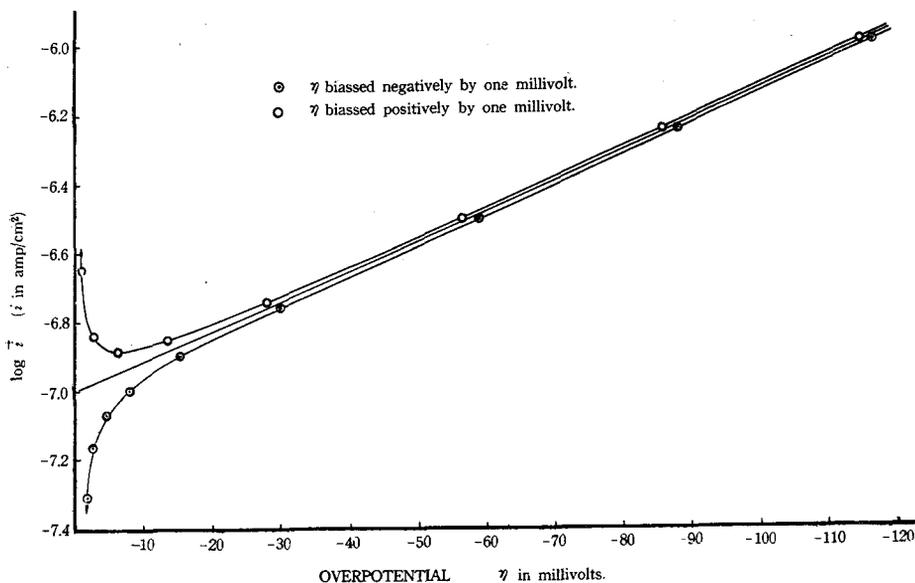


Fig. 1.

Effect of Bias in Measured Overpotential on Calculated Values of  $\log \bar{i}$

The causes of such inaccuracy derive from (for example): liquid-junction potentials, thermo-e.m.f.'s, personal errors in adjusting and reading instruments, etc.\*) The effect of numerically lowering all the relevant  $\eta$  values by one millivolt in equation (BP 9) is to alter  $i_0$  from  $10^{-7.0000}$  to  $10^{-6.9914}$ , but it is important to note that  $\left(\frac{di_c}{d\eta}\right)_{\eta=0}$  in equation (HS 6) remains unchanged. As a result of the change in  $i_0$  the value of  $\nu(r)$  calculated from equation (HS 6) becomes 2.04 instead of 2.00. On the other hand, if the  $\eta$  values are all numerically raised by one millivolt,  $i_0$  is changed to  $10^{-7.0086}$  and  $\nu(r)$  to 1.96. In both instances the bias has no meaningful effect on the values of  $i_0$  and  $\nu(r)$ , and is, therefore, without relevance to our measured values.

The effect of the same bias in  $\eta$  on the calculated values of  $\bar{i}$  is interesting, particularly at the small values of  $\eta$ . Assuming in turn positive biases of one millivolt in  $\eta$ , the upper and lower lines in

\*) We believe that no worker would yet claim to have made overpotential measurements accurate to one millivolt. A very few might justifiably claim a reproducibility of one millivolt.

Figure 1 have been calculated respectively using equation (HS 5). It is obvious from this figure that at overpotentials numerically less than about ten millivolts the biased overpotentials have caused a marked distortion of the central straight line, which refers to unbiased overpotentials. It follows, therefore, that the occurrence of a non-linear relation between  $\log \bar{i}$  and  $\eta$  at low current densities as a result of substituting practical measurements in equation (HS 5) is not evidence that an invalid estimate of  $i_0$  is obtained by the conventional extrapolation of the practical TAFEL line back to zero overpotential. Rather is such an occurrence evidence for a small bias in the practical measurements, which, as shown above, does not significantly alter the value of  $\nu(r)$  calculated from equation (HS 6), the equation always used by us.

In the particular case of the calculations made by HORIUTI and SUGAWARA using the data in Figure 7 of our paper and plotted in Figures 1 and 2 of their communication, the similarity will easily be observed between the positions of the solid black dots in these figures and the shape of the upper curve in the attached Figure 1. Apparently, HORIUTI and SUGAWARA have detected a positive bias of about one millivolt in our overpotential measurements. We need hardly remark that such a bias has no effect whatever on the numerical data on the conclusions given in our paper. Indeed, considering the remarkable sensitivity of the calculated  $\log \bar{i}$ ,  $\eta$  relation to bias in  $\eta$  it would be exceptional to find no inconsistency of the kind pointed out by HORIUTI and SUGAWARA.

There is, however, an important conclusion arising from the above discussion which we would stress strongly here. This concerns the preferable equation to be used for estimating the stoichiometric number from practical measurements. The choice lies between equations (HS 5) and (HS 6). It has been demonstrated above that a reasonable bias in the measured values of  $\eta$  has no significant effect on the value of  $\nu(r)$  calculated using equation (HS 6). With equation (HS 5), however, (which has been used exclusively by HORIUTI and his associates for estimating the stoichiometric number), knowledge of accurate values of the overpotential to an accuracy of greater than 1 mv. appears to be required before  $\nu(r)$  can be accurately calculated. In view of the known difficulty in accurately measuring small overpotentials at low current density, not only is equation (HS 6) by far the superior from the practical aspect, but equation (HS 5) used by HORIUTI can hardly ever give accurate estimates of the stoichiometric number.

We repeat that for nickel cathodes in aqueous sodium hydroxide the value of the stoichiometric number is two.

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