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# VELOCITY OF HYDROGEN EVOLUTION: COMMENTS ON A CALCULATION DUE TO KEII

By

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In a paper by J. HORIUTI and A. MITUYA<sup>1)</sup> the statement occurs: "J. O'M. BOCKRIS<sup>2)</sup> has recently questioned the present result for the contamination of mercury surface by the anode material, i. e. platinum." A calculation due to KEII to refute the statement follows. It is presumed here that it refers to the criticism made by the present author of the results of MITUYA<sup>3)</sup>, which appear to be the same as those now republished.

I. KEII's calculation is wrong in detail because:

(a) Expression (6) in the paper should be

$$C_{Pt^{4+}} = \frac{C_{H^+}^4}{(P_{H_2})^2} e^{-4FE_H/RT},$$

instead of that give (using the same assumptions and terminology as did KEII).

(b) KEII assumed the dissolution reaction would be  $Pt \rightarrow Pt^{4+} + 4e^-$ . Consideration of the standard potentials for this reaction and for  $Pt \rightarrow Pt^{2+} + 2e^-$  shows the latter to be more favourable for dissolution. The  $E_H$  value for the latter reaction is +1.2<sup>4)</sup> and  $z$  is 2. Recalculation shows that KEII's result for the concentration of dissolved platinum ions too small by a factor of about  $10^{21}$ .

II. KEII's calculation is wrong in concept. The platinum contamination is due to migration of small (possibly colloidal) particles of platinum which occur due to mechanical disintegration of the anode and or the reference electrode.

A criticism of MITUYA's work on similar grounds was made by

- 1) J. HORIUTI and A. MITUYA, J. Research Inst. for Catalysis Hokkaido University, 2, (1951), 85.
- 2) J. O'M BOCKRIS, Chem. Rev., 45, (1948), 525.
- 3) A. MITUYA, Bull. Inst. Phys. Chem. Research Tokyo 19, (1940), 142.
- 4) W. LATIMER, Oxidation Potentials, New York, 1938.

A. N. FRUMKIN<sup>5)</sup>.

III. MITUYA's results are compared with those of more recent authors in Table I.

TABLE I.

Worker	Conditions	$\alpha^{*)}$	$i_0$ (exchange current)
MITUYA <sup>3)</sup>	0.1N HCl, 0°C.	0.21	$2.10^{-10}$
JOFA <sup>6)</sup>	0.1N HCl, 25°C.	0.48	$9.10^{-13}$
BOCKRIS and PARSONS <sup>7)</sup>	0.1N HCl, 25°C.	0.51	$5.10^{-13}$
POST and HISKEY <sup>8)</sup>	0.1N HCl, 25°C.	0.50	$6.10^{-13}$

The suggestion that the marked difference between MITUYA and other authors is due to platinum contamination is supported by:

(a) One hundredth coverage of mercury with platinum lowers the hydrogen overpotential on Hg by 0.25 v<sup>9)</sup>. MITUYA's values are 0.1 lower than those of BOWDEN and GREW<sup>10)</sup>, who worked over the same current density range (and about 0.2 v. lower than those of the authors given in Table I).

(b) WATSON<sup>11)</sup> observed that the presence of platinum conductivity electrodes in the cell vitiated results of hydrogen evolution rates at low current densities, although the solution was in contact only during its preparation.

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5) A. N. FRUMKIN, *Acta Physicochim.*, **18**, (1943), 34.

6) Z. JOFA, quoted by FRUMKIN, ref. 5.

7) J. O'M. BOCKRIS and R. PARSONS, *Trans. Farad. Soc.*, **45**, (1949), 916.

8) B. POST and C. F. HISKEY, *J. Am. Chem. Soc.*, **73**, (1951), 161.

9) F. P. BOWDEN and E. K. RIDEAL, *Proc. Roy. Soc., A* **120**, (1928), 59, 80.

10) F. P. BOWDEN and K. E. W. GREW, *Discuss. Farad. Soc.*, (1947), 86.

11) R. G. H. WATSON, quoted by J. O'M. BOCKRIS, R. PARSONS and H. ROSENBERG, *Trans. Faraday Soc.*, **47**, (1951), 766.

\*) By  $\alpha$  is meant the term in the equation  $b = RT/\alpha F \ln i_0/i_c$ , calculated for regions where this equation applies.