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THE STOICHIOMETRIC NUMBER OF ZINC AMALGAM ELECTRODE REACTION

By

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V. V. LOSEV¹⁾ has recently observed by means of radioactive zinc the unidirectional anodic or cathodic current density \bar{i} or \tilde{i} and the directly measurable overall current density i simultaneously inclusive of the exchange current i_0 at zero polarization of a zinc amalgam electrode in contact with 0.1 N ZnSO₄ solution mixed with a small amount of tetrabutyl ammonium sulphate (5.10 M) which remarkably reduces the current i and in consequence the concentration polarization²⁾.

These experimental results enable us to determine the stoichiometric number $\nu(r)$ of the rate-determining step of the electrode process



as shown below. Simultaneous values of \bar{i} and \tilde{i} are determined at

different overvoltages from concurrent measurements of i and \bar{i} or \tilde{i} according to the relation

$$i = \bar{i} - \tilde{i}, \quad (2)$$

where i is positive or negative at the anodic or cathodic polarization respectively. Fig. 1 and 2 reproduce the results of Losev and Table I and II show the concurrent values of i , η , \bar{i} and \tilde{i} derived from Fig. 1 and 2 respectively, where $\varphi_{n.h.e}$ ^{**)}

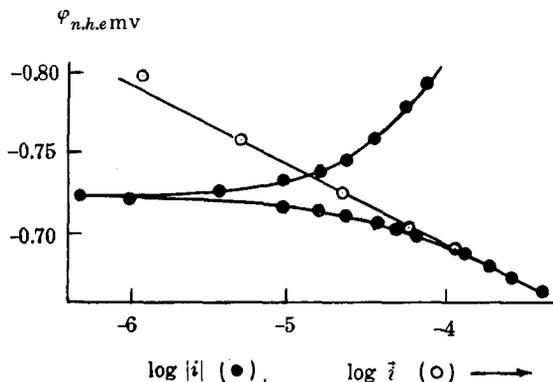


Fig. 1. Current-potential curves of zinc amalgam.

$\varphi_{n.h.e}$: potential of the electrode referred to the normal hydrogen electrode. \bar{i} : unidirectional anodic current density. i : overall current density.

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^{**)} The $\varphi_{n.h.e}$ used by LOSEV was presumed so, not being explicitly signified in the original work (Ref. 1).

is the potential of the test electrode referred to the normal hydrogen electrode and $\eta = \varphi_{n.h.e} - (\varphi_{n.h.e})_{i=0}$.

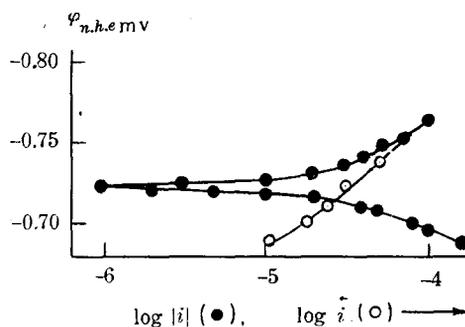


Fig. 2. Current-potential curves of zinc amalgam.
 $\varphi_{n.h.e}$: potential of the electrode referred to the normal hydrogen electrode. i_c : unidirectional cathodic current density. i : overall current density.

TABLE I.
 Concurrent values of η , i , i_c and i_c derived from LOSEV'S results in Fig. 1.

η (mv)	$i \cdot 10^5$ (a/cm ²)	$i_c \cdot 10^5$ (a/cm ²)	$i_c \cdot 10^5$ (a/cm ²)
21.8	4.82	5.72	0.90
18.9	3.80	4.78	0.98
14.5	3.03	4.10	1.07
11.4	1.95	3.39	1.44
7.3	1.13	2.88	1.75
0	0	2.14	2.14
- 0.7	- 0.10		
- 3.3	- 0.40		
- 7.3	- 0.97	1.49	2.45
- 11.2	- 1.41		
- 14.5	- 1.94	1.03	2.97
- 15.2	- 1.97		
- 21.8	- 2.68	0.77	3.45
- 29.1	- 3.44	0.55	3.99
- 36.4	- 4.27	0.40	4.67
- 43.6	- 5.22	0.28	5.50
- 50.9	- 6.24	0.20	6.44
- 58.2	- 7.11	0.15	7.26
- 65.4	- 8.14	0.10	8.24

TABLE II.
 Concurrent values of η , i , i_c and i_c derived from LOSEV'S results in Fig. 2.

η (mv)	$i \cdot 10^5$ (a/cm ²)	$i_c \cdot 10^5$ (a/cm ²)	$i_c \cdot 10^5$ (a/cm ²)
- 16.0	- 3.94		
- 11.4	- 3.02		
- 6.4	- 2.02		
- 3.6	- 1.00		
0	0	3.47	3.47
2.5	0.50		
4.6	1.02		
7.1	2.07		
8.5	2.72		
11.7	3.98	2.57	6.55
15.0	5.22	2.26	7.48
23.5	8.71	1.92	10.63
26.4	10.20	1.60	11.80
35.6	17.90	1.11	19.01

The Stoichiometric Number of Zinc Amalgam Electrode Reaction

The ratio \bar{i}/\tilde{i} derived from Table I and II is now related with the stoichiometric number $\nu(r)$ of the rate-determining step*³⁾ according to the general theory of reaction rate as³⁾

$$\bar{i}/\tilde{i} = \exp(-\Delta F'/\nu(r) RT). \quad (3)$$

$\Delta F'$ is the free energy increment of the whole system associated with the overall reaction or, particularly for (1),

$$\Delta F' = 2\mu^e + \mu^{\text{Zn}^{2+}} - \mu^{\text{Zn,am}}, \quad (4)$$

where μ^e , $\mu^{\text{Zn}^{2+}}$ and $\mu^{\text{Zn,am}}$ are the chemical potentials of metal electron e, zinc ion Zn^{2+} in the solution and amalgamated zinc Zn,am respectively. Let μ_{eq}^e be the particular value of μ^e , when (1) is in equilibrium. We have from (4) by definition

$$0 = 2\mu_{\text{eq}}^e + \mu^{\text{Zn}^{2+}} - \mu^{\text{Zn,am}},$$

so that

$$\Delta F' = 2(\mu^e - \mu_{\text{eq}}^e) \quad \text{or} \quad \Delta F' = -2F\eta, \quad (5)$$

where η is the potential of the electrode in question referred to that in equilibrium.

We have now from (3) and (5)

$$\nu(r) = \frac{2F\eta}{RT \ln \bar{i}/\tilde{i}}. \quad (6)$$

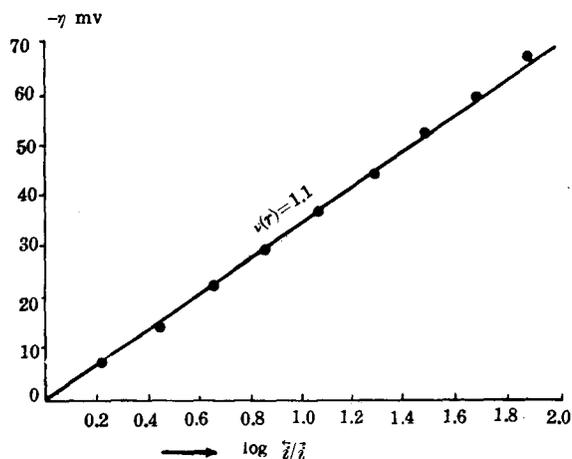


Fig. 3.

The $\eta, \log \bar{i}/\tilde{i}$ -curve at cathodic polarization ($\eta < 0$). \tilde{i} or \bar{i} : the unidirectional anodic or cathodic current density.

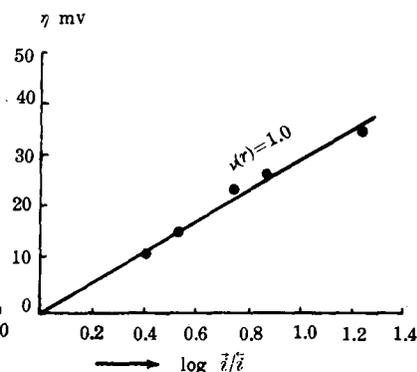


Fig. 4.

The $\eta, \log \bar{i}/\tilde{i}$ -curve at anodic polarization ($\eta > 0$). \tilde{i} or \bar{i} : the unidirectional anodic or cathodic current density.

*³⁾ The number of times of the rate-determining step to occur for every act of the overall reaction. The similar concept the "molecularity of a reaction" has been independently introduced by BORESKOW⁵⁾.

The η is plotted against $\log \vec{i}/\bar{i}$ in Fig. 3 and 4 as derived from Table I and II respectively.

Excellent straight lines through origin show that $\nu(r)$ derived from the results according to (6) is practically perfectly constant independent of η . We have from Fig. 3 and 4 $\nu(r)=1.1$ and 1.0 respectively.

The $\nu(r)$ is alternatively determined as follows from the exchange current i_0 at the electrochemical equilibrium, where $\nu(r)$ is indeterminate as expressed by (6). Expanding $\ln \vec{i}/\bar{i}$ in the latter equation with respect to i/\bar{i} referring to (2) as $\ln \vec{i}/\bar{i} = \ln (1+i/\bar{i}) = i/\bar{i} - 1/2 \cdot (i/\bar{i})^2 + \dots$, we have in the limiting case of $\eta=0^+$,

$$\nu(r) = \frac{2F i_0}{RT(\partial i/\partial \eta)_{\eta=0}}, \quad (7)$$

where $i_0 = \vec{i}_{\eta=0} = \bar{i}_{\eta=0}$. The $\nu(r)$ is determined by (7) from the values of i_0 and $(\partial i/\partial \eta)_{\eta=0}$ of the inclination of i against η at the electrochemical equilibrium. Table III shows the values of i_0

observed by LOSEV, $(\partial i/\partial \eta)_{\eta=0}$ determined from the plot in Fig. 5 of i against η in the neighbourhood of the equilibrium as derived from Fig. 1 and 2 and $\nu(r)$ calculated from these data by (7).

TABLE III. The i_0 , $(\partial i/\partial \eta)_{\eta=0}$ and $\nu(r)$.

Source of Data	i_0 a/cm ²	$\left(\frac{\partial i}{\partial \eta}\right)_{\eta=0}$ a/cm ² mv	$\nu(r)$
Fig. 1	$2.14 \cdot 10^{-5}$	$1.30 \cdot 10^{-6}$	1.3
Fig. 2	$3.47 \cdot 10^{-5}$	$2.75 \cdot 10^{-6}$	1.0

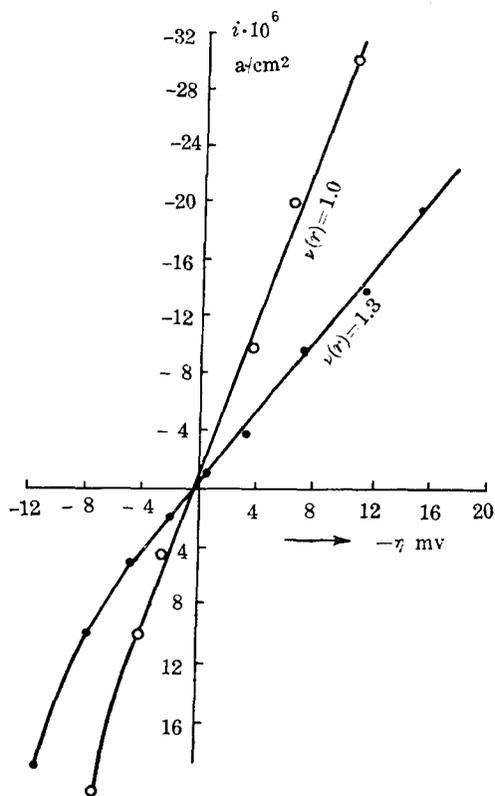


Fig. 5. The i, η -curves in the neighbourhood of electrochemical equilibrium.

● : derived from Fig. 1,
○ : derived from Fig. 2.

The stoichiometric number is further evaluated by differentiating (6) with respect to η as

$$\nu(r)(\alpha_a + \alpha_c) = 2, \quad (8)$$

where

$$\alpha_a = \frac{RT}{F} \frac{\partial \ln \bar{i}}{\partial \eta}, \quad \alpha_c = -\frac{RT}{F} \frac{\partial \ln \bar{i}}{\partial \eta},$$

are Tafel's constants for the forward and backward current and evaluated from Table I as

$$\alpha_a = 1.2, \quad \alpha_c = 0.6.$$

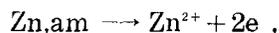
We have according to (8)

$$\nu(r) = 1.1.$$

The latter method of finding $\nu(r)$ would be expedient, when the isotopic difference of rates is pronounced as in the case of hydrogen isotopes.

It is thus concluded that $\nu(r)$ is unity.

The rate-determining step of the overall reaction (1) may be



or the overall reaction (1) may consist in the above single step in accordance with the above conclusion.

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