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## Short Notes

### DETERMINATION OF STOICHIOMETRIC NUMBER OF HYDROGEN ELECTRODE REACTION IN THE PRESENCE OF ISOTOPIC EFFECT

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HORIUTI and one of the authors<sup>1)</sup> have derived a fundamental equation for the stoichiometric number of the rate-determining step  $\nu(r)$  of a hydrogen electrode reaction as

$$-\frac{RT}{F} \frac{d \ln \bar{I}}{d\eta} + \frac{RT}{F} \frac{d \ln \bar{I}}{d\eta} = \frac{2}{\nu(r)}, \quad (1)$$

where  $\bar{I}$  or  $\bar{I}$  is the forward or the backward unidirectional current density,  $\eta$  the hydrogen overvoltage,  $F$  the Faraday,  $R$  the gas constant and  $T$  the absolute temperature. This equation enables us to determine  $\nu(r)$ , if  $\bar{I}$  and  $\bar{I}$  are measured at given  $\eta$ 's by means of hydrogen isotope. However,  $\bar{I}$  and  $\bar{I}$  cannot be determined experimentally unless the electrolytic separation factor of hydrogen isotope is known, inasmuch as there exists an isotopic difference between protium and deuterium or tritium in the rate of hydrogen electrode reaction. The present paper is concerned with the modification of the basic equation (1) for determination of  $\nu(r)$  in the presence of the isotopic effect in the hydrogen electrode reaction.

Let  $x$  or  $y$  be the atomic fraction of hydrogen isotope, say tritium in the present case, in hydrogen gas or in aqueous electrolyte, the electrolytic separation factor  $S_f$  or  $S_g$  in the forward or the backward direction is expressed as

$$S_f = \frac{\frac{\bar{I}_H}{1-y}}{\frac{\bar{I}_T}{y}}, \quad S_g = \frac{\frac{\bar{I}_H}{1-x}}{\frac{\bar{I}_T}{x}}, \quad (2a), (2b)$$

where  $\bar{I}_H$  or  $\bar{I}_H$  is the rate of protium transferred unidirectionally from aqueous electrolyte to hydrogen gas or reversely,  $\bar{I}_T$  or  $\bar{I}_T$  is the rate with which tritium is transferred similarly unidirectionally, each expressed in terms of current density.

On the other hand,  $\bar{I}$  or  $\bar{I}$  is expressed as

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$$\vec{I} = \vec{I}_H + \vec{I}_T, \quad \bar{I} = \bar{I}_H + \bar{I}_T. \quad (3 \text{ a}), (3 \text{ b})$$

Eliminating  $\vec{I}_H$  and  $\bar{I}_H$  from Eqs. (2) and (3), we have

$$\vec{I} = \left\{ 1 + \frac{(1-y)S_l}{y} \right\} \vec{I}_T, \quad \bar{I} = \left\{ 1 + \frac{(1-x)S_g}{x} \right\} \bar{I}_T, \quad (4 \text{ a}), (4 \text{ b})$$

When  $x$  and  $y$  are infinitesimally small, as realized in usual experimental conditions,  $\vec{I}$  and  $\bar{I}$  are simply expressed as

$$\vec{i} = \frac{S_l \vec{I}_T}{y}, \quad \bar{i} = \frac{S_g \bar{I}_T}{x}. \quad (5 \text{ a}), (5 \text{ b})$$

Introducing  $\vec{I}$  and  $\bar{I}$  into Eq. (1), we have

$$-\frac{RT}{F} \frac{d \ln \frac{\vec{I}_T}{y}}{d\eta} + \frac{RT}{F} \frac{d \ln \frac{\bar{I}_T}{x}}{d\eta} - \frac{RT}{F} \frac{d \ln \frac{S_l}{S_g}}{d\eta} = \frac{2}{\nu(r)}. \quad (6)$$

HORIUTI and FUKUDA<sup>2)</sup> have recently advanced a theorem as valid for irreversible electrolysis in case of infinitely low tritium content as

$$\frac{S_l}{S_g} = S, \quad (7)$$

where  $S$  is the partition coefficient of tritium between electrolyte and hydrogen gas under the exchange equilibrium. The  $S$  is now a constant independent of  $\eta$ . Hence we have

$$\frac{d \ln \frac{S_l}{S_g}}{d\eta} = \frac{d \ln S}{d\eta} = 0. \quad (8)$$

Introducing Eq. (8) into Eq. (6), we have

$$-\frac{RT}{F} \frac{d \ln \frac{\vec{I}_T}{y}}{d\eta} + \frac{RT}{F} \frac{d \ln \frac{\bar{I}_T}{x}}{d\eta} = \frac{2}{\nu(r)}. \quad (9)$$

The  $\vec{I}_T$  or  $\bar{I}_T$  can be experimentally determined by measuring the rate of transfer of tritium from solution into gas or in the reverse direction.

It follows that  $\nu(r)$  can be determined on the basis of Eq. (9) in the presence of the isotopic effect in the hydrogen electrode reaction under the condition of infinitely low tritium content. Experimental results of  $\nu(r)$  of platinum hydrogen electrode reaction will be published in the near future.

#### References

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- 2) J. HORIUTI and M. FUKUDA, This Journal, **10**, 73 (1962).