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THE RELATION BETWEEN FORWARD AND BACKWARD UNIDIRECTIONAL RATES OF THE HYDROGEN ELECTRODE REACTION IN THE ISOTOPICALLY MIXED SYSTEM

By

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Abstract

Validity of the well-known equation, $V_+/V_- = \exp \{-\Delta F/\nu(r) RT\}$, in the isotopically mixed system is investigated with special reference to the hydrogen electrode reaction, where V_+ or V_- is the forward or the backward unidirectional rate of the overall reaction respectively, $-\Delta F$ its affinity and $\nu(r)$ the stoichiometric number of the rate-determining step r . It is shown that the equation is formally invariantly valid for the system of any isotopic composition at any magnitude of the isotope effect, *i. e.*, the difference in specific rates between the isotopes, by replacing V_+ and V_- with the respective sums of the relevant isotopic contributions and $-\Delta F$ with $-2F\eta$, where η is the electrode potential referred to the rest potential of the same electrode in the same isotopically mixed system and F the Faraday. Applications of the equation thus verified are presented.

Introduction

It has been established¹⁾ that the forward and the backward unidirectional rates, V_+ and V_- of a chemical reaction are related to its chemical affinity, $-\Delta F$, as,

$$V_+/V_- = \exp \{-\Delta F/\nu(r) RT\}, \quad (1)$$

where $\nu(r)$ is the stoichiometric number of the rate-determining step r , here assumed to exist, of the reaction and the other notations have their usual meaning. The relation, when applied to the hydrogen electrode reaction,



assumes the form,

$$V_+/V_- = \exp \{-2F\eta/\nu(r) RT\}, \quad (3)$$

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where H^+ is a hydrogen ion in hydronium ion or in water molecule, e^- a metal electron, F the Faraday and η the overpotential*).

A number of experimental works have been reported²⁾ as based essentially on Eq. (1) on the determination of $\nu(r)$, an important criterion of the reaction mechanism. Here, the ratio V_+/V_- is very conveniently determined by means of a labelled isotope. In the cases of the hydrogen electrode reaction, however, this method is associated with a significant isotope effect, *i.e.*, the difference in specific rates between the isotopes, as indicated by large values of the deuterium separation factor (3~7) or that of tritium (~15) in the electrolysis of water.

In the special case of a sufficiently low concentration of the labelled isotope, and of an isotopically equilibrated gaseous hydrogen which takes part in an exchange reaction, an equation has been derived by Matsuda and Notoya³⁾ which determines $\nu(r)$ of the hydrogen electrode reaction without being influenced by the isotope effect. In their treatment, Eq. (3) was assumed as approximately valid under the above specified condition. However, the validity of Eq. (3) when applied to the isotopically mixed system has not so far been investigated. Especially for cases where experiments demand higher concentrations of the labelled isotope, it is necessary to derive a valid equation which is applicable to the system of any isotopic concentration, yet takes the isotope effect into account.

It will be verified below with special reference to the hydrogen electrode reaction in the isotopically mixed system that Eq. (3) holds formally invariantly for the system of any isotope content in the presence of the isotope effect, by defining η as the potential of the test electrode referred to its rest potential in the same isotopically mixed system. The only assumptions which underlie the verification are that the magnitude of the isotope effect as expressed in terms of electrolytic separation factor***) as well as $\nu(r)$ does not vary with the electrode potential.

Verification

The overall net reaction rate, V (atom/sec), of the hydrogen electrode reaction is expressed in the presence of deuterium as a tracer as,

$$V = V_+ - V_- , . \quad (4)$$

*) Potential of the test electrode referred to that of the reversible hydrogen electrode under the same conditions. In the isotopically mixed system, this is defined as the potential of the test electrode referred to its rest potential and is still a directly measurable quantity, see text.

**) As will be reported later⁴⁾, the separation factor obtained at the rest potential agrees well with literature values obtained at high cathodic polarizations, at least in the case of nickel hydrogen electrode.

Rate equation for isotopically mixed system

and,

$$V_+ = V_+(\text{P}) + V_+(\text{D}), \quad V_- = V_-(\text{P}) + V_-(\text{D}), \quad (5. a), (5. b)$$

where $V_+(\text{P})$ or $V_-(\text{P})$ is respectively the forward or the backward unidirectional rate of the protium electrode reaction only, and $V_+(\text{D})$ or $V_-(\text{D})$ that of deuterium. The isotope effect is represented in terms of the electrolytic separation factor of deuterium S_i or S_o in the forward or the backward direction, *i.e.*,

$$S_i = \left\{ \frac{V_+(\text{P})}{1-X_i} \right\} / \left\{ \frac{V_+(\text{D})}{X_i} \right\}, \quad S_o = \left\{ \frac{V_-(\text{P})}{1-X_o} \right\} / \left\{ \frac{V_-(\text{D})}{X_o} \right\}, \quad (6. a), (6. b)$$

where X_i or X_o is the atomic fraction of deuterium in the aqueous electrolyte or in the gaseous hydrogen respectively*). From Eqs. (5) and (6), we have,

$$V_+ = V_+(\text{P}) \left\{ 1 + \frac{X_i}{(1-X_i)S_i} \right\}, \quad V_- = V_-(\text{P}) \left\{ 1 + \frac{X_o}{(1-X_o)S_o} \right\}, \quad (7. a), (7. b)$$

hence from Eq. (4),

$$V = V_+(\text{P}) \left\{ 1 + \frac{X_i}{(1-X_i)S_i} \right\} - V_-(\text{P}) \left\{ 1 + \frac{X_o}{(1-X_o)S_o} \right\}. \quad (8)$$

The ratio, $V_+(\text{P})/V_-(\text{P})$, is expressed as,

$$\frac{V_+(\text{P})}{V_-(\text{P})} = \frac{2V_+(\text{P}_2) + V_+(\text{PD})}{2V_-(\text{P}_2) + V_-(\text{PD})}, \quad (9)$$

where $V_+(\text{P}_2)$ or $V_+(\text{PD})$ is the unidirectional forward rate (molecule/sec) of the reaction evolving P_2 by the reaction $2\text{P}^+ + 2\text{e}^- = \text{P}_2$, or PD by $\text{P}^+ + \text{D}^+ + 2\text{e}^- = \text{PD}$, and $V_-(\text{P}_2)$ or $V_-(\text{PD})$ that of the reverse one ionizing P_2 or PD , respectively.

Eq. (1) is applicable to a reaction in an isotopically pure system or, in isotopically mixed systems, to the individually isotopically specified reaction. Hence, for the individual hydrogen electrode reactions, $2\text{P}^+ + 2\text{e}^- = \text{P}_2$, $\text{P}^+ + \text{D}^+ + 2\text{e}^- = \text{PD}$ and $2\text{D}^+ + 2\text{e}^- = \text{D}_2$, we have respectively,

$$V_+(\text{P}_2)/V_-(\text{P}_2) = \exp \{ (2\mu^{\text{P}^+} + 2\mu^{\text{e}^-} - \mu^{\text{P}_2}) / \nu(r) RT \}, \quad (10. a)$$

$$V_+(\text{PD})/V_-(\text{PD}) = \exp \{ (\mu^{\text{P}^+} + \mu^{\text{D}^+} + 2\mu^{\text{e}^-} - \mu^{\text{PD}}) / \nu(r) RT \}, \quad (10. b)$$

and,

$$V_+(\text{D}_2)/V_-(\text{D}_2) = \exp \{ (2\mu^{\text{D}^+} + 2\mu^{\text{e}^-} - \mu^{\text{D}_2}) / \nu(r) RT \}, \quad (10. c)$$

where $-\Delta F$ was replaced by the difference in the chemical potentials, $\mu^{\text{L}} - \mu^{\text{R}}$,

*) S_i , for example, should be taken in general still as a function of X_i , in spite of this definition in terms of specific rates.

of the reactant L and the product R. Eliminating $V_+(P)$, $V_+(P_2)$ and $V_+(PD)$ from Eqs. (8), (9), (10. a) and (10. b), we have,

$$V = V_-(P) \left[Q \left\{ 1 + \frac{X_i}{(1-X_i)S_i} \right\} \exp\left(\frac{2\mu^{e-}}{\nu(r)RT}\right) - \left\{ 1 + \frac{X_g}{(1-X_g)S_g} \right\} \right], \quad (11. a)$$

where,

$$Q \equiv \left\{ \frac{2V_-(P_2)}{V_-(PD)} B_{P_2} + B_{PD} \right\} / \left\{ \frac{2V_-(P_2)}{V_-(PD)} + 1 \right\}, \quad (11. b)$$

and B_{P_2} etc. are $\exp \{ (2\mu^{P^+} - \mu^{P_2}) / \nu(r) RT \}$ etc. respectively.

V vanishes now, *i.e.*, $V=0$, at the rest potential. Assuming, as mentioned in the Introduction, that S_i and S_g as well as $\nu(r)$ remain respectively unchanged independent of the electrode potential, one can show that Q is also constant*. Hence Eq. (11. a) yields at $V=0$,

$$Q \left\{ 1 + \frac{X_i}{(1-X_i)S_i} \right\} = \left\{ 1 + \frac{X_g}{(1-X_g)S_g} \right\} \exp\left(-\frac{2\mu_0^{e-}}{\nu(r)RT}\right), \quad (12)$$

where μ_0^{e-} is the particular value of μ^{e-} at the rest potential, which depends upon $\nu(r)$ and the magnitude of S_i and S_g , and hence in general upon the material of the test electrode used.

Eliminating Q and V from Eqs. (8) and (11), we have,

$$\frac{V_+(P) \left\{ 1 + \frac{X_i}{(1-X_i)S_i} \right\}}{V_-(P) \left\{ 1 + \frac{X_g}{(1-X_g)S_g} \right\}} = \exp\left\{ \frac{2(\mu^{e-} - \mu_0^{e-})}{\nu(r)RT} \right\}, \quad (13)$$

*) Using Eq. (9) and the corresponding one for $V_+(D)/V_-(D)$, Eqs. (6. a) and (6. b) are rewritten as,

$$\frac{2V_+(P_2) + V_+(PD)}{2V_+(D_2) + V_+(PD)} = \frac{1-X_i}{X_i} S_i \equiv S'_i, \quad \frac{2V_-(P_2) + V_-(PD)}{2V_-(D_2) + V_-(PD)} = \frac{1-X_g}{X_g} S_g \equiv S'_g. \quad (i), (ii)$$

Substituting $V_+(P_2)$, $V_+(PD)$ and $V_+(D_2)$ from Eqs. (10) into Eq. (i), we have,

$$\frac{2B_{P_2}V_-(P_2) + B_{PD}V_-(PD)}{2B_{D_2}V_-(D_2) + B_{PD}V_-(PD)} = S'_i.$$

Elimination of $V_-(D_2)$ from the above equation and Eq. (ii) gives,

$$\frac{V_-(P_2)}{V_-(PD)} = \frac{S'_g B_{PD} - S'_i B_{D_2} + S'_g S'_i (B_{D_2} - B_{PD})}{2(S'_i B_{D_2} - S'_g B_{P_2})}.$$

Since B_{P_2} etc. are constant independent of the electrode potential at a definite experimental condition, the right-hand side of this equation, and hence Q is constant independent of the electrode potential.

Rate equation for isotopically mixed system

or with reference to Eqs. (7),

$$\frac{V_+}{V_-} = \exp \left\{ \frac{2(\mu^{e-} - \mu_0^{e-})}{\nu(r)RT} \right\}. \quad (14)$$

Here $\mu^{e-} - \mu_0^{e-}$ is equal to $-F\eta$ by defining η as the potential of the test electrode as referred to its rest potential in the same isotopically mixed system. This definition of η is the most desirable one as it is then directly experimentally measurable. By replacing $\mu^{e-} - \mu_0^{e-}$ with $-F\eta$ thus defined, Eq. (14) assumes the same form as Eq. (3), which is now valid for any isotopically mixed system at any magnitude of the isotope effect, provided that the magnitude as well as $\nu(r)$ does not vary with the electrode potential.

Application

The equation thus verified is applied below to the exchange reaction between light water and deuterium in the presence of a metal electrode as the catalyst. Eq. (14) gives, after replacing $\mu^{e-} - \mu_0^{e-}$ by $-F\eta$, using Eq. (4),

$$\frac{1}{V_+} \cdot \frac{\partial V_+}{\partial \eta} - \frac{1}{V_-} \cdot \frac{\partial (V_+ - V)}{\partial \eta} = - \frac{2F}{\nu(r)RT}.$$

In the limiting case of $\eta=0$, where $V=0$ or $V_+ = V_- \equiv V_0$ according to Eq. (4), we have,

$$V_0 = -\nu(r) \frac{RT}{2F} \left(\frac{\partial \eta}{\partial V} \right)_{\eta=0}^{-1}. \quad (15. a)$$

Alternatively, replacing V and V_0 by the corresponding current density i and exchange current density i_0 , using relations of the form $V = iAN_A/F$ where A is surface area of the electrode and N_A the AVOGADRO number, we have,

$$i_0 = -\nu(r) \frac{RT}{2F} \left(\frac{\partial \eta}{\partial i} \right)_{\eta=0}^{-1}, \quad (15. b)$$

which is of the same form as the hitherto used equation in the isotopically pure system. This equation indicates, as might be expected, that in any isotopically mixed systems, the exchange current density is exactly related to the reaction resistance, hence $\nu(r)$ determined from the measurements of these quantities.

Here, i_0 is the sum of contributions of the respective isotopes, *i.e.*,

$$i_0 AN_A/F = V_0 = V_-(P) + V_-(D), \quad (16)$$

and consequently its determination from the exchange reaction, which allows us to evaluate *e.g.* $V_-(D)$ only, requires in general the knowledge of S_0 specific

to the value of X_g of the system as is clear from Eq. (6. b). In the special case, however, where the deuterium concentration in the gaseous hydrogen is so high that $V_-(P)$ is negligible as compared with $V_-(D)$, i_0 is practically determined solely by $V_-(D)$ according to Eq. (16) if the value of S_g is not extremely large. Hence, firstly $\nu(r)$ is determined in this special case according to Eqs. (15. b) and (16) directly from the simultaneous measurements of $V_-(D)$ and the reaction resistance $(\partial\eta/\partial i)_{\eta=0}$ at the rest potential. When $\nu(r)$ is thus determined, then secondly i_0 in the system of hydrogen of any known deuterium content and light water is evaluated from the observation of $(\partial\eta/\partial i)_{\eta=0}$ by Eq. (15. b). Hence, the value of S_g is now determined by Eqs. (16) and (6. b) from the value of $V_-(D)$ simultaneously observed in this system. Experiments carried out along this line will be published separately⁴⁾.

Conclusion

It has been verified that the well-known equation, $V_+/V_- = \exp \{-2F\eta/\nu(r)RT\}$, where V_+ or V_- is the forward or the backward unidirectional rate of the hydrogen electrode reaction, η its overpotential and $\nu(r)$ a stoichiometric number of the rate-determining step r , holds formally invariantly for a system of any isotopic composition at any magnitude of the isotopic difference in rates, V_+ and V_- being expressed by the respective sums of the relevant isotopic contributions and η defined as the potential of the test electrode as referred to its rest potential. The equation allows us to evaluate $\nu(r)$ and magnitude of the isotope effect from the simultaneous observations of exchange rate between light water and pure deuterium or hydrogen of appropriate deuterium content and of the reaction resistance in the system.

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