Abstract – This review article described the electrochemical Frumkin, Langmuir, and Temkin adsorption isotherms of over-potentially deposited hydrogen (OPD H) and deuterium (OPD D) for the cathodic H2 and D2 evolution reactions (HER, DER) at Pt, Ir, Pt-Ir alloy, Pd, Au, and Re/normal (H2O) and heavy water (D2O) solution interfaces. The Frumkin, Langmuir, and Temkin adsorption isotherms of intermediates (OPD H, OPD D, etc.) at electrode/solution interfaces are determined using the phase-shift method and correlation constants, which have been suggested and developed by Chun et al. The basic procedure of the phase-shift method, the Frumkin, Langmuir, and Temkin adsorption isotherms of OPD H and OPD D and related electrode kinetic and thermodynamic parameters, i.e., the fractional surface coverage (0 ≤ θ ≤ 1) vs. potential (E) behavior (θ vs. E), equilibrium constant (K), interaction parameter (g), standard Gibbs energy (ΔG°θ) of adsorption, and rate (r) of change of ΔG°θ with θ(0 ≤ θ ≤ 1), at the interfaces are briefly interpreted and summarized. The phase-shift method and correlation constants are useful and effective techniques to determine the Frumkin, Langmuir, and Temkin adsorption isotherms and related electrode kinetic and thermodynamic parameters (θ vs. E, K, g, ΔG°θ, r) at electrode/solution interfaces.

Key words: Phase-shift method and correlation constants, Frumkin, Langmuir, Temkin adsorption isotherms, Over-potentially deposited hydrogen and deuterium, Noble metal alloy electrodes

1. Introduction

Many experimental methods have been developed and used to study the adsorption of hydrogen for the cathodic H2 evolution reaction (HER) at noble metal and alloy/aqueous solution interfaces [1-7]. The cathodic HER is one of the most extensively studied topics in electrochemistry, electrocatalysis, hydrogen technologies, and fuel cells, etc. It is well known that under-potentially deposited hydrogen (UPD H) and over-potentially deposited hydrogen (OPD H) occupy different surface adsorption sites and act as two distinguishable electroadsorbed H species, and that only OPD H can contribute to the cathodic HER [2-7]. However, there is not much reliable data on the Frumkin, Langmuir, and Temkin adsorption isotherms of OPD H for the cathodic HER and related electrode kinetic and thermodynamic parameters, i.e., the fractional surface coverage (0 ≤ θ ≤ 1) vs. potential (E) behavior (θ vs. E), equilibrium constant (K), interaction parameter (g), standard Gibbs energy (ΔG°θ) of adsorption, and rate (r) of change of ΔG°θ with θ(0 ≤ θ ≤ 1). Furthermore, there is not much reliable data on the Frumkin, Langmuir, and Temkin adsorption isotherms of over-potentially deposited deuterium (OPD D) for the cathodic D2 evolution reaction (DER) and related electrode kinetic and thermodynamic parameters. Similarly, there is not much reliable data on the Frumkin, Langmuir, and Temkin adsorption isotherms of hydroxide (OH) and deuterioxide (OD) for the anodic O2 evolution reaction (OER) and related electrode kinetic and thermodynamic parameters. Because, to the authors’ knowledge, K and g for the Frumkin adsorption isotherms of intermediates cannot be experimentally and readily determined using conventional methods [1-7]. Also, a quantitative relationship between the Temkin and Frumkin or Langmuir adsorption isotherms of intermediates has not been developed or reported to study the cathodic HER and DER or the anodic OER. Thus, there is a technological need for a useful, effective, and reliable method to determine the Frumkin, Langmuir, and Temkin adsorption isotherms of intermediates (OPD H, OPD D, OH, OD, etc.) for the sequential reactions (HER, DER, OER, etc.) and related electrode kinetic and thermodynamic parameters at the interfaces.

Although the Frumkin and Langmuir adsorption isotherms may be regarded as classical models and theories, it is preferable to consider the Frumkin and Langmuir adsorption isotherms for OPD H and OPD D rather than electrode kinetics and thermodynamics equations for OPD H and OPD D because these adsorption isotherms are associated more directly with the atomic mechanism of OPD H and OPD D. To determine the Frumkin, Langmuir, and Temkin adsorption isotherms, the phase-shift method and correlation constants have been originally suggested and developed on the basis of relevant experimental results and physical phenomena rather than mathematical
formalisms of electrochemistry and electrochemical impedance spectroscopy (EIS) [8]. The phase-shift method is a unique EIS technique for studying the linear relationship between the phase shift (90° ≥ ϕ ≥ 0°) vs. potential (E) behavior for the optimum intermediate frequency (fϕ) and the fractional surface coverage (0 ≤ θ ≤ 1) vs. potential (E) behavior of intermediates (UPD H, OPD H, OPD D, OH, OD, etc.) for sequential reactions (HER, DER, OER, etc.) at noble and highly corrosion-resistant metal and alloy/solution interfaces [9-21]. The (θ vs. E) behavior is well known as the Frumkin or Langmuir adsorption isotherm.

Many scientific phenomena have been interpreted by their behavior rather than by their nature. For example, the wave-particle duality of light and electrons, i.e., their wave and particle behaviors, is well known in science and has been applied in engineering. At first glance, it seems that there is no linear relationship between the (−ϕ vs. E) behavior for fϕ and the (θ vs. E) behavior at the interfaces. Thus, tedious experimental techniques and procedures [9-13] have been used to verify the validity and correctness of the phase-shift method. A new method must be rigorously tested, especially when it is unique, but only with pure logic and objectivity and through scientific procedures. However, the objections to the phase-shift method do not fulfill these criteria (see Text and Supporting Information in Ref. 18). The comments and replies on the phase-shift method are briefly summarized elsewhere [18-20]. In recent, the validity of the phase-shift method has been qualitatively analyzed and verified by Garcia et al. [22].

In this review article, we supplement and summarize the Frumkin, Langmuir, and Temkin adsorption isotherms of OPD H and OPD D and related electrode kinetic and thermodynamic parameters (θ vs. E, K, g, ΔGθ, r) at noble metal (Pt, Ir, Pd, Au, Re) and alloy (Pd-Ir)/normal (H2O) and heavy water (D2O) solution interfaces [9-21].

2. Theoretical and Experimental Backgrounds of the Phase-Shift Method

2-1. The equivalent circuit for the adsorption and sequential reactions

The equivalent circuit for the adsorption of OPD H and OPD D for the cathodic HER and DER at the Pt, Ir, Pt-Ir alloy, Pd, Au, and Re/H2O and D2O solution interfaces can be expressed as shown in Fig. 1a [18-20,23-25]. In Fig. 1a, Rs is the real solution resistance; Rf is the real resistance due to the faradaic resistance (Rp) for the discharge step and superposition of various effects; Rp is the real resistance due to the faradaic resistance (Rp) for the recombination step and superposition of various effects; Cϕ is the real capacitance due to the adsorption pseudocapacitance (Cq) for the discharge step and superposition of various effects; and C0 is the real double-layer capacitance. Correspondingly, neither Rs nor Cϕ is constant; both Rϕ and Cϕ depend on E and θ and can be measured. Note that both Rs and Cq also depend on E and θ but cannot be measured.

The numerical derivation of Cq from the Frumkin and Langmuir adsorption isotherms is described elsewhere, and Rq depends on Cq [23-25]. They attain maximum values at θ = 0.5 and intermediate E, decrease symmetrically with E at other values of θ, and approach minimum values or 0 at θ = 0 and low E and θ = 1 and high E. This behavior is well known in interfacial electrochemistry, electrode kinetics, and EIS. The unique feature and combination of Rq and Cq vs. E, i.e., (−ϕ and θ vs. E, imply that the normalized rate of change of −ϕ with respect to E, i.e., Δ(−ϕ)/ΔE, corresponds to that of θ with respect to E, i.e., Δθ/ΔE, and vice versa (see Footnotes c and d in Table 1). This is a typical characteristic of the Gaussian profiles of Δ(−ϕ)/ΔE and Δθ/ΔE, i.e., the Frumkin and Langmuir adsorption isotherms. Note that ϕ depends on both E and frequency (f) but θ depends on only E [25]. The linear relationship between the Gaussian profiles of Δ(−ϕ)/ΔE and Δθ/ΔE most clearly appears at the specified intermediate frequency. We refer to it as the optimum intermediate frequency (fϕ). The value of fϕ is experimentally and graphically evaluated on the basis of Δ(−ϕ)/ΔE and Δθ/ΔE for intermediate and other frequencies (see Fig. 9).

2-2. The frequency response of the equivalent circuit for the adsorption

The frequency responses of the equivalent circuit for all f that is shown in Fig. 1a are essential for understanding the unique feature and combination of (Rs, Rϕ) and (Cϕ, C0) vs. f for fϕ, i.e., the linear relationship between the (−ϕ vs. E) behavior for fϕ and the (θ vs. E) behavior. At low frequencies, the equivalent circuit for all f can be expressed as a series circuit of Rs, Rϕ, and Rp. At high frequencies, the equivalent circuit for all f can be expressed as a series circuit of Rs and Cϕ. Both the low and high frequency responses are meaning-
less for studying the adsorption of OPD H and OPD D. Note that \( R_{p} \) and \( C_{p} \) include \( R_{a} \) and \( C_{a} \), i.e., the adsorption of OPD H and OPD D, respectively. At intermediate frequencies, one finds regions in which the equivalent circuit for all \( f \) behaves as a series circuit of \( R_{a} \) and \( C_{a} \) or a series and parallel circuit of \( R_{F} \), \( C_{F} \), and \( C_{P} \), as shown in Fig. 1b. However, the simplified equivalent circuit shown in Fig. 1b does not represent the change of the cathodic HER and DER themselves but only the intermediate-frequency response.

At intermediate frequencies, the impedance (\( Z \)) and lagged phase-shift (\( -\phi \)) are given by [16-20,23,25]

\[
Z = R_{S} + R_{p} - \frac{1}{\omega C_{p}} \\
-\phi = \arctan \frac{1}{\omega R_{p} C_{p}}
\]

(1a)

(1b)

for the upper circuit in Fig. 1b or

\[
Z = R_{S} - \frac{1}{\omega C_{p}} \\
-\phi = \arctan \frac{1}{\omega R_{p} (C_{p} + C_{1})}
\]

(2a)

(2b)

for the lower circuit in Fig. 1b, where \( j \) is the imaginary unit (i.e., \( j^2 = -1 \)) and \( \omega \) is the angular frequency, defined as \( \omega = 2\pi f \), where \( f \) is the frequency. Under these conditions,

\[
R_{p} \ll \frac{1}{\omega C_{p}} \quad \text{and} \quad R_{p} \gg R_{S} + R_{p}
\]

(3)

In the previous papers [9-15], only Eq. (1) was used with a footnote stating that \( C_{p} \) practically includes \( C_{1} \) (see Table 1 in Ref. 12, Tables 1 and 2 in Ref. 13, etc.). Both Eqs. (1) and (2) show that the effect of \( R_{p} \) on \( -\phi \) for intermediate frequencies is negligible. These aspects are completely overlooked, confused, and misunderstood in the comments on the phase-shift method [18-20]. Correspondingly, all of the simulations on the phase-shift method using Eq. (1), which appears in the comments (\( C_{p} \) does not include \( C_{1} \)), are basically invalid and incorrect. All of the analyses of the effect of \( R_{p} \) on \( -\phi \) for intermediate frequencies are meaningless (see Supporting Information in Ref. 18).

The following limitations and conditions of the equivalent circuit elements for \( f_{p} \) are summarized on the basis of the experimental data in the previous papers [9-20]. Neither \( R_{p} \) nor \( C_{p} \) is constant. At \( \theta = 0, R_{S} > R_{p} \), and \( C_{D} > C_{p} \), or vice versa, and so forth. For a wide range of \( \theta \) (i.e., \( 0.2 < \theta < 0.8 \), \( R_{S} >> R_{p} \) or \( R_{D} >> R_{p} \) or \( C_{D} >> C_{p} \)), and so forth. At \( \theta = 1, R_{S} > R_{p} \) or \( R_{D} < R_{p} \) and \( C_{D} >> C_{p} \). The measured \( \phi \) vs. \( f_{p} \) depending on \( E \) and \( \theta \) in contrast to numerical simulations, the limitations and conditions for Eq. (1) or (2) are not considered for the phase-shift method because all of the measured values of \( -\phi \) for intermediate frequencies include (\( R_{S} \), \( R_{p} \)) and (\( C_{p} \)). Correspondingly, the measured \( -\phi \) vs. \( f_{p} \) is valid and correct regardless of the applicability of Eq. (1) or (2). Both the measured values of \( -\phi \) at \( f_{p} \) and the calculated values of \( -\phi \) at \( f_{p} \), using Eq. (1) or (2) are exactly the same (see Supporting Information in Ref. 18). The unique feature and combination of (\( R_{S} \), \( R_{p} \)) and (\( C_{p} \)) vs. \( E \) for \( f_{p} \) are equivalent to those of \( R_{S} \) and \( C_{p} \) vs. \( E \) for \( f_{p} \), i.e., \( -\phi \) and \( \theta \) vs. \( E \) for \( f_{p} \) due to the reciprocal property of \( R_{p} \) and \( C_{p} \), which include \( R_{D} \) and \( C_{D} \). It suggests that only the polar form of the equivalent circuit impedance, i.e., \( -\phi \) described in Eq. (1b) or (2b), is useful and effective for studying the linear relationship between the \( -\phi \) (90° ≤ \( -\phi \) ≤ 0°) vs. \( E \) behavior at \( f_{p} \), and the \( \theta \) (0 ≤ \( \theta \) ≤ 1) vs. \( E \) behavior. The linear relationship between the Gaussian profiles of \( -\phi \) vs. \( E \) and \( \Delta \theta \) for \( f_{p} \) implies that only one Frumkin or Langmuir adsorption isotherm is determined on the basis of the relevant experimental results (see Figs. 2, 7 to 9). The shape and location of the \( (\theta \text{ vs. } E) \) profile for \( f_{p} \) correspond to \( g \) and \( K \) for the Frumkin or Langmuir adsorption isotherm (see Figs. 7b, 8, and 10c). These aspects are the essential nature of the phase-shift method for determining the Frumkin and Langmuir adsorption isotherms.

3. Basic Procedure and Description of the Phase-Shift Method

3-1. The phase-shift curves (\( -\phi \) vs. \( \log f \)) for different potentials

Figure 2 compares the phase-shift curves (\( -\phi \) vs. \( \log f \)) for differ-

Table 1. Measured values of the phase shift (\( -\phi \)) for \( f_{p} = 1.259 \text{ Hz} \), the fractional surface coverage (\( \theta \)) of OPD H and OPD D, and the normalized rates of change of \( -\phi \) and \( \theta \) vs. \( E [\Delta(-\phi)/\Delta E, \Delta \theta/\Delta E] \) at the Pt-Ir alloy/0.1 \text{ M LiOH} (\text{H}_2\text{O} + \text{D}_2\text{O}) solution interface.

| Potential (V) | \(-\phi\) (deg) | \(\theta\) | \(\Delta(-\phi)/\Delta E\) | \(\Delta \theta/\Delta E\) |
|---------------|----------------|-----------|--------------------------|--------------------------|
| -0.659        | 84.7           | ~0        | 0.08304                  | 0.08304                  |
| -0.684        | 84.0           | 0.06287   | 2.20641                  | 2.20641                  |
| -0.709        | 60.8           | 0.28351   | 4.05694                  | 4.05694                  |
| -0.734        | 26.8           | 0.68921   | 2.24199                  | 2.24199                  |
| -0.795        | 7.7            | 0.91340   | 0.07117                  | 0.07117                  |
| -0.809        | 1.3            | 0.99644   | 0.01186                  | 0.01186                  |
| -0.834        | 0.6            | ~1        | 0.02372                  | 0.02372                  |

\(\text{SHE} \text{ (standard hydrogen electrode)} \quad 0 \leq \theta \leq 1 \quad \text{[\}}\text{neighbor phase shift difference}/\text{total phase shift difference}][\text{neighbor potential difference}/\text{total potential difference}]] \quad \text{[\}}\text{neighbor fractional surface coverage difference}/\text{total fractional surface coverage difference}][\text{neighbor potential difference}/\text{total potential difference}]]\}

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This is the reason why a single equation for \( \Delta \theta \Delta E \) at the Pt-Ir alloy/0.1 M LiOH (H\(_2\)O + D\(_2\)O) solution interface [20]. Measured values: \( O \). Vertical solid line: 1.259 Hz; single sine wave; scan frequency range, (10\(^{2}\) to 0.5) Hz; ac amplitude, 5 mV. Dc potentials: (a) 0.061 V, (b) 0.041 V, (c) 0.021 V, (d) 0.001 V, (e) –0.019 V, (f) –0.039 V, (g) –0.059 V, (h) –0.079 V, (i) –0.099 V, (j) –0.119 V, and (k) –0.139 V (all vs. SHE).

At the maximum \( \Delta \theta \), \( E \) and \( f \) is necessary. However, the phase-shift method has been experimentally proposed and verified on the basis of the phase-shift curves (\( \varphi \) vs. \( f \)) at different \( E \) (see Figs. 2 to 6). The electrochemical impedance data, i.e., (\( \varphi \) vs. \( f \)) and (\( \varphi \) vs. \( E \)), were measured and interpreted by using the frequency response analyzer and EIS. In practice, the cyclic, differential pulse, and linear sweep voltammograms are not necessary for the phase-shift method itself [10-12].

3-2. The phase-shift (\( \varphi \) vs. \( E \)) and fractional surface coverage (\( \Delta \theta \) vs. \( E \)) profiles

The procedure and description of the phase-shift method for determining the Frumkin adsorption isotherm of OPD H and OPD D at the Pt-Ir alloy/0.1 M LiOH (H\(_2\)O + D\(_2\)O) solution interface are summarized in Table 1 and Figs. 2~19 are given on the standard hydrogen electrode (SHE) scale. The following qualitative interpretation is valid and effective for studying the linear relationship between \( \Delta(\varphi)/\Delta E \) and \( \Delta \theta \Delta E \) for \( f_0 \) at noble metal and alloy/solution interfaces [8-21].

At the maximum \( \Delta \theta \) shown in curve a of Fig. 2, it appears that the adsorption of OPD H and OPD D and superposition of various effects are minimized; i.e., \( \Delta(\varphi)/\Delta E \) is necessary. However, the phase-shift method has been experimentally proposed and verified on the basis of the phase-shift curves (\( \varphi \) vs. \( f \)) at different \( E \) (see Figs. 2 to 6). The electrochemical impedance data, i.e., (\( \varphi \) vs. \( f \)) and (\( \varphi \) vs. \( E \)), were measured and interpreted by using the frequency response analyzer and EIS. In practice, the cyclic, differential pulse, and linear sweep voltammograms are not necessary for the phase-shift method itself [10-12].

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The values of $-\varphi$ and $\theta$ as a function of $E$ at $f_o = 1.259$ Hz shown in Fig. 7 [20] are illustrated on the basis of the experimental results summarized in Table 1. The values of $-\varphi$ and $\theta$ as a function of $E$ at $f = 0.1$ Hz, 10 Hz, and 100 Hz shown in Fig. 7 are also illustrated through the same procedure summarized in Table 1. However, note that the differences between the $(-\varphi \ vs. \ E)$ profile at $f_o = 1.259$ Hz and the $(-\varphi \ vs. \ E)$ profiles at $f = 0.1$ Hz, 10 Hz, and 100 Hz shown in Fig. 7a do not represent the measurement error but only the frequency response. In practice, the $(\theta \ vs. \ E)$ profiles at $f = 0.1$ Hz, 10 Hz, and 100 Hz shown in Fig. 7b should be exactly the same as the $(\theta \ vs. \ E)$ profile at $f_o = 1.259$ Hz. Because, as stated above, $\theta$ depends on only $E$ and this unique feature most clearly appears at $f_o$. In Table 1, the fitted range of $\theta$ does not influence the determination of the Frumkin adsorption isotherm of OPD H and OPD D. Because, as shown in Fig. 8 [20], only one Frumkin adsorption isotherm $(\theta \ vs. \ E)$ is determined regardless of the fitted range of $\theta$ over the same potential range.

The normalized rates of change of $-\varphi$ and $\theta$ with respect to $E$, i.e., $\Delta(-\varphi)/\Delta E$ and $\Delta\theta/\Delta E$, for four different frequencies at the Pt-Ir alloy/0.1 M LiOH $(H_2O + D_2O)$ solution interface are shown in Fig. 9 [20]. The Gaussian profile shown in Fig. 9b is illustrated on the basis of the Frumkin adsorption isotherm calculated using Eq. (4) for $g = -2.2$ with $K_o = 5.3 \times 10^{-5}$ mol$^{-1}$, i.e., $K = 5.3 \times 10^{-5}$ exp$(2.2/\theta)$ mol$^{-1}$.
and 100 Hz are shown in Figs. 9a, c, and d, respectively. Finally, one can conclude that the (θ vs. E) and Δθ/ΔE profiles at f₀ = 1.259 Hz shown in Figs. 9b and 9d, respectively, are applicable to the determination of the Frumkin adsorption isotherm of OPD H and OPD D at the interface (see Fig. 10).

4. Electrochemical Frumkin, Langmuir, and Temkin Adsorption Isotherms

4-1. The Frumkin and Langmuir adsorption isotherms

The derivation and interpretation of the practical forms of the electrochemical Frumkin, Langmuir, and Temkin adsorption isotherms are described elsewhere [1,2,26]. The Frumkin adsorption isotherm assumes that the surface is inhomogeneous or that the lateral interaction effect is not negligible. It is well known that the Langmuir adsorption isotherm is a special case of the Frumkin adsorption isotherm.

The Langmuir adsorption isotherm can be derived from the Frumkin adsorption isotherm by setting the interaction parameter (g) to be zero, i.e., g = 0. The Frumkin adsorption isotherm (θ vs. E) can be expressed as follows [26]

\[
K = K_0 \exp(-g \theta) \tag{4}
\]

\[
g = \frac{\theta}{1 - \theta} \tag{5}
\]

\[
K = K_0 \exp(-g \theta) \tag{6}
\]

where \(0 \leq \theta \leq 1\) is the fractional surface coverage, \(g\) is the interaction parameter for the Frumkin adsorption isotherm, \(K_0\) is the equilibrium constant at \(g = 0\), \(C^+\) is the concentration of ions (H⁺, D⁺, H²⁺ + D²⁺, etc.) in the bulk solution, \(E\) is the applied potential, \(f_0\) is the optimum intermediate frequency.
potential, $F$ is Faraday’s constant, $R$ is the gas constant, $T$ is the absolute temperature, $r$ is the rate of change of the standard Gibbs energy ($\Delta G_0$) of adsorption with $\theta$ ($0 \leq \theta \leq 1$), and $K$ is the equilibrium constant. Note that when $g = 0$ in Eqs. (4) to (6), the Langmuir adsorption isotherm is obtained. For the Langmuir adsorption isotherm, when $g = 0$, the inhomogeneous and lateral interaction effects are assumed to be negligible.

Figure 10 shows the determination of the Frumkin adsorption isotherm of OPD H and OPD D using Eq. (4) at the Pt-Ir alloy/0.1 M LiOH ($H_2O + D_2O$) solution interface [20]. Curves a, b, c, d, and e show the five numerically calculated Frumkin adsorption isotherms corresponding to $g = -8, -4, -2.2, 0$, and 2.4, respectively, for $K_o = 5.3 \times 10^{-5}$ mol$^{-1}$. The curve c shows that the Frumkin adsorption isotherm, $K = 5.3 \times 10^{-4} \exp(2.2 \theta)$ mol$^{-1}$, is applicable to the adsorption of OPD H and OPD D, and Eq. (5) gives $\Delta H = -5.5$ kJ mol$^{-1}$. The Frumkin adsorption isotherm implies that the lateral interaction between OPD H and OPD D species is not negligible. In other words, the Langmuir adsorption isotherm for $g = 0$, i.e., $K = 5.3 \times 10^{-5}$ mol$^{-1}$, is not applicable to the adsorption of OPD H and OPD D at the interface (see Fig. 10d).

Figures 11, 12, and 13 also show the determination of the Frumkin adsorption isotherms of OPD H using Eq. (4) at the Pt [14], Ir [14], and Pd [12] interfaces, respectively. Similarly, Fig. 14 shows the determination of the Langmuir adsorption isotherm of OPD H using Eq. (4) for $g = 0$ at the Au interface [10]. As stated above, the Langmuir adsorption isotherm implies that the lateral interaction between OPD H species is negligible.

4-2. The Temkin adsorption isotherm

At intermediate values of $\theta$, i.e., $0.2 < \theta < 0.8$, the pre-exponential term, $[\theta(1 - \theta)]$, varies little with $\theta$ in comparison with the variation of the exponential term, $\exp(\theta)$. Under these approximate conditions, the Temkin adsorption isotherm can be simply derived from the Frumkin adsorption isotherm. The Temkin adsorption isotherm ($\theta$ vs. $E$)

\[ \theta = \frac{1}{K} \exp(-E/RT) \]

is applicable to the adsorption of OPD H and OPD D at the interface (see Fig. 10d).

Figures 11, 12, and 13 also show the determination of the Frumkin adsorption isotherms of OPD H using Eq. (4) at the Pt [14], Ir [14], and Pd [12] interfaces, respectively. Similarly, Fig. 14 shows the determination of the Langmuir adsorption isotherm of OPD H using Eq. (4) for $g = 0$ at the Au interface [10]. As stated above, the Langmuir adsorption isotherm implies that the lateral interaction between OPD H species is negligible.
can be expressed as follows [26].

\[ \exp(\theta) = K_o C_o \exp(-EF/RT) \]  

(7)

The physical meaning of \( g \) in the Temkin adsorption isotherm is significantly different from that in the Frumkin adsorption isotherm. Note that \( g \) in Eq. (7) is practically determined by the slope of experimental data for \( 0.2 < \theta < 0.8 \) (see Figs. 15 to 19). The evaluation of the applicability of the Frumkin and Temkin adsorption isotherms over the same potential range is described elsewhere [16, 20].

Figure 15 shows the determination of the Temkin adsorption isotherm corresponding to the Frumkin adsorption isotherm shown in curve c of Fig. 10. The dashed line labeled c in Fig. 15 shows that the numerically calculated Temkin adsorption isotherm of OPD H and OPD D using Eq. (7) is \( K = 5.3 \times 10^{-4} \exp(-2.4\theta) \) mol\(^{-1}\), and Eq. (5) gives \( r = 6.0 \) kJ mol\(^{-1}\).

Figures 16, 17, and 18 also show the determination of the Temkin adsorption isotherms corresponding to the Frumkin adsorption isotherms shown in Figs. 11c, 12c, and 13d, respectively. Similarly, Fig. 19 shows the determination of the Temkin adsorption isotherm corresponding to the Langmuir adsorption isotherm shown in Fig. 14c. The \( g \) and \( K \) for the Frumkin and Temkin adsorption isotherms of OPD H and OPD D at the noble metal and alloy/H\(_2\)O and D\(_2\)O solution interfaces are summarized in Table 2.

### 4.3. The correlation constants between the Frumkin and Temkin adsorption isotherms

For \( 0.2 < \theta < 0.8 \), all the Langmuir adsorption isotherms are parallel to each other (see Fig. 14). Correspondingly, all the slopes of the Langmuir adsorption isotherms, i.e., all \( g \) for the Temkin adsorption isotherms, are the same regardless of the values of \( K \). As summarized in Table 2, we have experimentally found that the values of \( g \) for the Temkin adsorption isotherms are approximately 4.6 greater than those for the Langmuir adsorption isotherms (see Fig. 19). Similarly, the values of \( g \) for the Temkin adsorption isotherms are approximately 4.6 greater than those for the Frumkin adsorption isotherms (see Figs. 15 to 18). Because the Frumkin adsorption isotherm is determined on the basis of the Langmuir adsorption isotherm (see Figs. 10 to 13). In addition, we have experimentally found that \( K_o \) for the Temkin adsorption isotherm is approximately 10 times greater than \( K_o \) for the correlated Frumkin or Langmuir adsorption isotherm (see Figs. 15 to 19 and Table 2). The values of \( g \) and \( K_o \) for the Temkin adsorption isotherm are approximately 4.6 and 10 times greater than those for the correlated Frumkin or Langmuir adsorption isotherm, respectively. These factors (ca. 4.6 and 10) can be taken as correlation constants between the Temkin and Frumkin or Langmuir adsorption isotherms.
As shown in Figs. 10d, 11d, and 12d, the Langmuir adsorption isotherm is not applicable to the adsorption of OPD H and OPD D or OPD H at the interface. At extreme values of $\theta$, i.e., $\theta \approx 0$ and 1, the Langmuir adsorption isotherm is often applicable to the adsorption of intermediates. However, the validity and correctness of the Langmuir adsorption isotherm are unclear and limited even at $\theta \approx 0$ and 1. As stated in the introduction, the values of $g$ and $K_o$ for the Frumkin adsorption isotherm are not experimentally and readily determined using other conventional methods, so the Langmuir adsorption isotherm is often used even though it has the critical limitation and applicability. To solve these problems, the phase-shift method has been originally developed [8]. In addition, the correlation constants between the Temkin and Frumkin or Langmuir adsorption isotherms have been experimentally and consistently found [12-20].

As shown in Figs. 15c, 16c, 17c, 18c, and 19c, the Temkin adsorption isotherm is valid and effective only at $0.2 < \theta < 0.8$. For $0.2 < \theta < 0.8$, note that the short potential range (ca. 28–37 mV) is difficult to observe in the Temkin adsorption isotherm correlating with the Frumkin or Langmuir adsorption isotherm. At other values of $\theta$, i.e., $0 \leq \theta < 0.2$ and $0.8 < \theta \leq 1$, only the Frumkin adsorption isotherm is valid and effective. Finally, one can conclude that the Frumkin adsorption isotherm is more useful, effective, and reliable than the Langmuir and Temkin adsorption isotherms.

5. Standard Gibbs Energy of Adsorption

Under the Temkin adsorption conditions, the relationship between the equilibrium constant ($K$) and the standard Gibbs energy of adsorption ($\Delta G$) is [26].

$$2.3RT \log K = -\Delta G_0^\circ$$

(8)

For the Pt-Ir alloy/0.1 M LiOH (H$_2$O + D$_2$O) solution interface, use of Eqs. (6) and (8) shows that $\Delta G_0^\circ$ of OPD H and OPD D is in the range $(24.4 \geq \Delta G_0^\circ \geq 18.9)$ kJ mol$^{-1}$ for $K = 5.3 \times 10^{-5}$ exp$(2.2\theta)$ mol$^{-1}$ and $0 \leq \theta \leq 1$. This result implies an increase in the absolute value of $\Delta G_0^\circ$, i.e., $|\Delta G_0^\circ|$, of OPD H and OPD D with $\theta$ $(0 \leq \theta \leq 1)$. Note that $\Delta G_0^\circ$ is a negative number, i.e., $\Delta G_0^\circ < 0$ [27]. Table 3 shows $\Delta G_0^\circ$ of OPD H and OPD D at the noble metal and alloy/H$_2$O and D$_2$O solution interfaces.

6. Interaction Parameters for the Frumkin and Temkin Adsorption Isotherms

6-1. The negative value of the interaction parameter for the Frumkin adsorption isotherm

For the Pt, Ir, and Pt-Ir alloy interfaces [15,16,18-20], the negative values of $g$ shown in Table 2 imply the lateral attractive ($g < 0$) interaction between OPD H and OPD D species, which leads to an increase in $|\Delta G_0^\circ|$ of OPD H and OPD D with $\theta$ $(0 \leq \theta < 1)$ (see Table 3). This is a unique feature of OPD H and OPD D species at the interfaces.
### Table 2. Comparison of the interaction parameters (g) and equilibrium constants (K) for the Frumkin and Temkin adsorption isotherms of OPD H and OPD D at the noble metal and alloy/normal (H₂O) and heavy water (D₂O) solution interfaces

| Interface            | Adsorbate | Frumkin g | Frumkin K/mol² | Temkin g | Temkin K/mol² | Ref. |
|----------------------|-----------|-----------|----------------|----------|---------------|------|
| Pt-Ir alloy/0.1 M LiOH | OPD H     | −2.2      | 8.6 × 10⁻⁵ exp(2.2θ) | 2.4      | 8.6 × 10⁻⁵ exp(−2.4θ) | 18   |
| Pt-Ir alloy/0.1 M LiOH (H₂, D₂) | OPD H, D | −2.2      | 5.3 × 10⁻⁵ exp(2.2θ) | 2.4      | 5.3 × 10⁻⁵ exp(−2.4θ) | 20   |
| Pt-Ir alloy/0.1 M LiOH (D₂O) | OPD D     | −2.3      | 2.1 × 10⁻⁵ exp(2.3θ) | 2.3      | 2.1 × 10⁻⁵ exp(−2.3θ) | 18   |
| Pt-Ir alloy/0.5 M H₂SO₄ | OPD H     | −2.5      | 3.3 × 10⁻⁵ exp(2.5θ) | 2.1      | 3.3 × 10⁻⁵ exp(−2.1θ) | 19   |
| Pt/0.1 M KOH         | OPD H     | −2.4      | 1.2 × 10⁻⁵ exp(2.4θ) | 2.2      | 1.2 × 10⁻⁵ exp(−2.2θ) | 16   |
| Pt/0.5 M H₂SO₄       | OPD H     | −2.4      | 3.5 × 10⁻⁵ exp(2.5θ) | 2.1      | 3.5 × 10⁻⁵ exp(−2.1θ) | 14   |
| Ir/0.1 M KOH         | OPD H     | −2.4      | 9.4 × 10⁻⁵ exp(2.4θ) | 2.2      | 9.4 × 10⁻⁵ exp(−2.2θ) | 16   |
| Ir/0.5 M H₂SO₄       | OPD H     | −2.4      | 2.7 × 10⁻⁵ exp(2.4θ) | 2.2      | 2.7 × 10⁻⁵ exp(−2.2θ) | 14   |
| Pd/0.5 M H₂SO₄       | OPD H     | 1.0°      | 3.3 × 10⁻⁶ exp(−1.6θ) | 6.2      | 3.3 × 10⁻⁶ exp(−6.2θ) | 12   |
| Au/0.5 M H₂SO₄       | OPD H     | 0°        | 2.3 × 10⁻⁶          | 4.6      | 2.3 × 10⁻⁶ exp(−6.6θ) | 10   |
| Re/0.1 M KOH         | OPD H     | 0°        | 1.9 × 10⁻⁶          | 4.6      | 1.9 × 10⁻⁶ exp(−4.6θ) | 11   |
| Re/0.5 M H₂SO₄       | OPD H     | 0°        | 4.5 × 10⁻⁷          | 4.6      | 4.5 × 10⁻⁷ exp(−6.6θ) | 11   |

*a*Adapted for this work.  
*b*Langmuir adsorption isotherm. Note that the values of g and K for the Temkin adsorption isotherm are approximately 4.6 and 10 times greater than those for the correlated Frumkin or Langmuir adsorption isotherm, respectively. All the Temkin adsorption isotherms are valid and effective only at 0.2 < θ < 0.8.

### Table 3. Comparison of the standard Gibbs (∆G°) energies of adsorption and the rates (r) of change of ∆G° with θ (0 ≤ θ ≤ 1) for the Frumkin adsorption isotherms of OPD H and OPD D at the noble metal and alloy/normal (H₂O) and heavy water (D₂O) solution interfaces

| Interface            | Adsorbate | ∆G°/kJ/mol² | r/kJ mol⁻¹ | Ref. |
|----------------------|-----------|-------------|------------|------|
| Pt-Ir alloy/0.1 M LiOH | OPD H     | 23.2 ± ∆G° | −5.5       | 18   |
| Pt-Ir alloy/0.1 M LiOH (H₂, D₂) | OPD H, D | 24.4 ± ∆G° | −5.5       | 20   |
| Pt-Ir alloy/0.1 M LiOH (D₂O) | OPD D     | 26.7 ± ∆G° | −5.7       | 18   |
| Pt-Ir alloy/0.5 M H₂SO₄ | OPD H     | 25.6 ± ∆G° | −6.2       | 19   |
| Pt/0.1 M KOH         | OPD H     | 22.4 ± ∆G° | −6.0       | 16   |
| Pt/0.5 M H₂SO₄       | OPD H     | 25.4 ± ∆G° | −6.2°      | 14   |
| Ir/0.1 M KOH         | OPD H     | 23.0 ± ∆G° | −6.0       | 16   |
| Ir/0.5 M H₂SO₄       | OPD H     | 26.1 ± ∆G° | −6.0       | 14   |
| Pd/0.5 M H₂SO₄       | OPD H     | 25.6 ± ∆G° | −6.0       | 14   |
| Au/0.5 M H₂SO₄       | OPD H     | 32.2°      | 0°         | 10   |
| Re/0.1 M KOH         | OPD H     | 32.6°      | 0°         | 11   |
| Re/0.5 M H₂SO₄       | OPD H     | 36.2°      | 0°         | 11   |

*a*Adapted for this work.  
*b*Langmuir adsorption isotherm

The dashed lines of Fig. 10a show that the lateral attractive (g < 0) interaction between OPD H and OPD D species may lead to a two-dimensional phase formation. Taking into account the critical value of g, i.e., g = −4 (see Fig. 10b), for the electrochemical case [27], the values of g, i.e., g > −4 (see Fig. 10c), shown in Table 2 are reasonable. For more negative values, i.e., g < −4 (see Fig. 10a), the hysteresis loop of two-dimensional phase formation will be observed. Note that g = −4.4 corresponds to r = −9.9 kJ mol⁻¹ with θ (0 ≤ θ ≤ 1) (see Eq. (5)). The negative values of g for the Frumkin adsorption isotherms at the Pt, Ir, and Pt-Ir alloy interfaces are qualitatively and quantitatively interpreted elsewhere [15,16,18,20].

### 6-2. The positive value of the interaction parameter for the Frumkin adsorption isotherm

For the Pd interface [12], the positive value of g shown in Table 2 implies the lateral repulsive (g > 0) interaction between OPD H species, which leads to a decrease in |ΔG°| of OPD H with θ (0 ≤ θ ≤ 1) (see Table 3). The lateral repulsive (g > 0) interaction between OPD H species at the Pd interface is distinctly different from the lateral attractive (g < 0) interaction between OPD H and OPD D species at the Pt, Ir, and Pt-Ir alloy interfaces. Note that the Pd belongs to the same Pt group metal.

For the Au and Re interfaces [10,11], the lateral interaction between OPD H species is negligible, i.e., g = 0 or g = 0. As previously described, this implies that the Langmuir adsorption isotherm is applicable to the adsorption of OPD H at the interfaces (see Fig. 14).

### 6-3. The positive value of the interaction parameter for the Temkin adsorption isotherm

Table 2 also shows that all g for the Temkin adsorption isotherms of OPD H and OPD D at the same interfaces are positive values. In other words, all the lateral interactions between OPD H and OPD D species are repulsive. It is not true except the Pd interface. As previously described, the physical meaning of g in the Temkin adsorption isotherm is significantly different from that in the Frumkin adsorption isotherm regardless of their mathematical approximations. This
is the critical limitation of the Temkin adsorption isotherm of OPD H and OPD D at the Pt group metal and alloy interfaces.

7. Summary

The Frumkin, Langmuir, and Temkin adsorption isotherms (θ vs. E) cannot be experimentally and readily determined using conventional methods. At present, the phase-shift method and correlation constants seem to be the most accurate, useful, and effective techniques for determining the Frumkin, Langmuir, and Temkin adsorption isotherms of intermediates (OPD H, OPD D, OH, etc.) for the sequential reactions (HER, DER, OER, etc.) and related electrode kinetic and thermodynamic parameters (θ vs. E, K, g, ΔG°, r) at electrode/normal (H₂O) and heavy water (D₂O) solution interfaces.

For the Pt, Ir, and Pt-Ir alloy interfaces, the lateral attractive (g < 0) interaction between OPD H and OPD D species is determined. In contrast to the Pt, Ir, and Pt-Ir alloy interfaces, the lateral repulsive (g > 0) interaction between OPD H species is determined at the Pd interface. For the Au and Re interfaces, the lateral interaction between OPD H species is negligible (g = 0 or g ≈ 0).

For 0.2 < θ < 0.8, the Temkin adsorption isotherm correlating with the Frumkin or Langmuir adsorption isotherm, and vice versa, is readily determined using the correlation constants. The Temkin and Frumkin or Langmuir adsorption isotherms appear to fit the same data regardless of their adsorption conditions. This implies that the Frumkin adsorption isotherm is the most useful, suitable, and correct for studying the adsorption processes of intermediates for the sequential reactions at the interfaces.

Finally, we expect that reliable simulations with a single equation for (θ vs. E) as functions of E and f for relevant experimental data for the phase-shift method and correlation constants will be obtained and interpreted using other conventional methods. We also expect that this review article should support and encourage the investigators in the fields of interfacial electrochemistry, electrode kinetics, hydrogen technology, EIS, and fuel cells.

Acknowledgments

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