CHAPTER 1

Volcano Curves in Electrochemistry

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1.1 INTRODUCTION

The effect of bonding of a reactant with the catalyst is qualitatively described by Sabatier [1], who pointed out that some bonding is necessary for the reaction to be catalyzed but that strong bonding with the catalyst would block the surface and slow the reaction. He did not consider the implication that the rate as a function of the strength of the bond between the intermediate and the catalyst would form a curve with a maximum. This conclusion was reached by Balandin [2], who plotted "volcano" curves [3] from a thermochemical point of view. However, these were only a small part of his theory of catalysis, which he called "multiplet theory," a theory mainly concerned with the steric relation between reactant and the surface structure of the catalyst.

The origin of the volcano curve for a catalytic reaction can be demonstrated using a very simplified model. To do this it is necessary to invoke the Brønsted relation between rate constants and equilibrium constants [4]. This was based on a study of the relation between the catalytic constant (k) for homogeneous acid-catalyzed reactions and the dissociation constant (K) of the acid concerned:

$$k = GK^{\alpha} \tag{1.1}$$

where G and α are constants characteristic of the reaction and α is often close to $\frac{1}{2}$. The well-known relations between K and the Gibbs energy of reaction ΔG and between k and the Gibbs energy of activation $\Delta G^{\#}$ leads directly to

$$\Delta G^{\#} = \alpha\, \Delta G + \text{const} \tag{1.2}$$

This is an example of the linear Gibbs energy relationship, one of the best known being that of Hammett [5]. Frumkin [6] pointed out the common significance of

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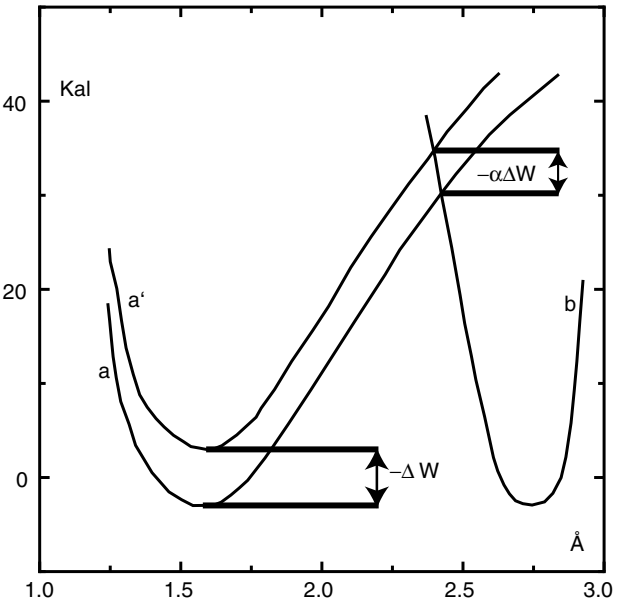

FIGURE 1.1 Relation between adsorption energy of hydrogen atom and activation energy. (Plot adapted from Horiuti and Polanyi [8].)

Brønsted's α and the transfer coefficient introduced by Erdey-Gruz and Volmer [7] to explain the slope of the Tafel plot obtained for electrochemical hydrogen evolution [7]. The meaning of Eq. (1.2) was explained by Horiuti and Polanyi [8] for a wide variety of proton transfer reactions when they represented the reaction path by a scheme of two approximately parabolic curves for the initial and final states, their intersection being the transition state (Fig. 1.1).

The relative slopes of the two curves at this intersection gave the value of α . They pointed out that this model could be applied to the proton transfer from a hydroxonium ion to a metal surface in the electrochemical process of hydrogen evolution. Although they discussed the effect of the metal–hydrogen bond strength on this process, this did not lead them to derive a volcano curve because they did not consider the effect of the coverage of the surface by hydrogen atoms.

Dogonadze, et al. [9] criticized the work of Horiuti and Polanyi because they used a quasi-classical approach. This cannot be valid at room temperature because the energy levels in each state are too widely spaced and a quantal approach is essential.

1.2 VOLCANO CURVES IN HETEROGENEOUS CATALYSIS

That the consideration of the surface coverage leads to a volcano curve may be demonstrated by using the simplest type of catalytic reaction, that known as the Eley–Rideal

mechanism [10]. The reaction between two gases,

$$\mathrm{A(g)} + \mathrm{B(g)} \rightarrow \mathrm{AB(g)} \tag{1.3}$$

is assumed to proceed by a two-step mechanism with only species A adsorbed:

$$\mathrm{A(g)} \rightarrow \mathrm{A(ads)} \tag{1.4}$$

$$\mathrm{B(g)} + \mathrm{A(ads)} \rightarrow \mathrm{AB(g)} \tag{1.5}$$

The catalyst surface is assumed uniform so that the adsorption of A follows the Langmuir isotherm, so that, if reaction (1.4) were in equilibrium, the surface coverage θ would be given by

$$\theta = \frac{\left(p_{\mathrm{A}}/p_{\mathrm{A},1/2}\right)}{1 + p_{\mathrm{A}}/p_{\mathrm{A},1/2}} \tag{1.6}$$

where p_{A} is the pressure of A is the gas phase and $p_{\mathrm{A},1/2}$ is the pressure at equilibrium with the half-covered surface. This may be related to the enthalpy of adsorption of A, ΔH_{ads},

$$p_{\mathrm{A},1/2} = K_{\mathrm{ads}} \exp\left(\frac{\Delta H_{\mathrm{ads}}}{RT}\right) \tag{1.7}$$

where K_{ads} is a constant.

The rate of adsorption of A may be written as

$$\vec{v}_1 = \vec{k}_1 (1 - \theta)\, p_{\mathrm{A}} \tag{1.8}$$

and that of the reverse reaction as

$$\overleftarrow{v}_1 = \overleftarrow{k}_1 \theta \tag{1.9}$$

where $\vec{k}_1$ and $\overleftarrow{k}_1$ are rate constants. If (1.8) and (1.9) are equated, of course the equilibrium isotherm is obtained and it follows that

$$p_{\mathrm{A},1/2} = \frac{\overleftarrow{k}_1}{\vec{k}_1} \tag{1.10}$$

and $p_{\mathrm{A},1/2}$ is the reciprocal of the equilibrium constant of reaction (1.4). Brønsted's relation (1.1) together with the equilibrium constant (1.10) may be used to express the dependence of the rate constants on the enthalpy of adsorption:

$$\vec{k}_1 = \vec{k}_1^{\,0} \exp\left(-\frac{\alpha_1 \Delta H_{\mathrm{ads}}}{RT}\right) \tag{1.11}$$

$$\overleftarrow{k}_1 = \overleftarrow{k}_1^0 \exp\left(\frac{(1-\alpha_1)\Delta H_{\text{ads}}}{RT}\right) \tag{1.12}$$

where $\vec{k}_1^0$ and $\overleftarrow{k}_1^0$ are the rate constants when $\Delta H_{\text{ads}} = 0$. Similarly the rate constants of reaction (1.5) may be related to the enthalpy of that reaction, ΔH_2. However, the sum of this enthalpy and that of reaction (1.3) is the enthalpy of the overall reaction, which is independent of the nature of the catalyst. Thus it is convenient to express the rates of reaction (1.5) in terms of the enthalpy of reaction (1.3) and include the latter in the constant terms. The analogues of Eqs. (1.8), (1.9), (1.11), and (1.12) for reaction (1.5) can then be written:

$$\vec{v}_2 = \vec{k}_2 p_{\text{B}} \theta \tag{1.13}$$

$$\overleftarrow{v}_2 = \overleftarrow{k}_2 p_{\text{AB}} (1-\theta) \tag{1.14}$$

$$\vec{k}_2 = \vec{k}_2^0 \exp\left(\frac{\alpha_2 \Delta H_{\text{ads}}}{RT}\right) \tag{1.15}$$

$$\overleftarrow{k}_2 = \overleftarrow{k}_2^0 \exp\left(-\frac{(1-\alpha_2)\Delta H_{\text{ads}}}{RT}\right) \tag{1.16}$$

Note that $\vec{k}_2^0$ and $\overleftarrow{k}_2^0$ in (1.15) and (1.16) are the rate constants for $\Delta H_{\text{ads}} = 0$.

The rate of the overall reaction can be obtained for three limiting conditions (the intermediate regions occur under small regions of conditions):

(a) Adsorption is fast and remains in equilibrium; reaction (1.5) controls the rate.
(b) Adsorption controls the rate and reaction (1.5) remains in equililibrium.
(c) Both reactions control the rate \and the back reactions may be neglected.

For case (a) equation (1.6) may be substituted in equation (1.13) and then substituting (1.7) and (1.15) in the result gives

$$v = \frac{\left(\vec{k}_2^0 / K_{\text{ads}}\right) p_{\text{A}} p_{\text{B}} \exp\left[-(1-\alpha_2)\,\Delta H_{\text{ads}}/RT\right]}{1 + (p_{\text{A}}/K_{\text{ads}})\,\exp(-\Delta H_{\text{ads}}/RT)} \tag{1.17}$$

From this it can be seen that ln v increases linearly with ΔH_{ads} at large negative values of ΔH_{ads}, goes through a maximum at

$$\Delta H_{\text{ads}} = RT\left(\frac{p_{\text{A}}\alpha_2}{K_{\text{ads}}\,(1-\alpha_2)}\right) \tag{1.18}$$

and then decreases at large positive values of ΔH_{ads}. If ΔH_{ads} is eliminated between (1.7) and (1.18) it can be seen that the maximum rate in fact occurs when $\theta = (1-\alpha_2)$

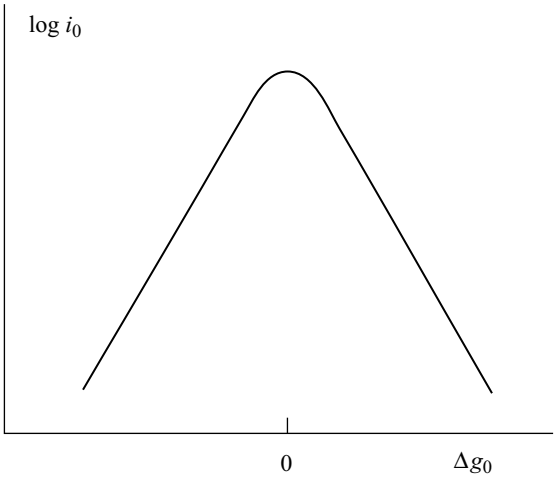

FIGURE 1.2 Form of relation between exchange current at hydrogen electrode and standard free energy of adsorption of hydrogen on electrode surface assuming that adsorbed atoms obey a Langmuir adsorption isotherm.

or at about half coverage. Similar results are obtained for conditions (b) and (c). The above can be seen in Figure 1.2. This shows that volcano curves are obtained whatever the detailed mechanism of the reaction.

It seems as though most workers on catalysis had little interest in volcano curves, perhaps because real mechanisms of catalytic reactions are more complex, involving more than one adsorbed species. Also, until the development of ultra-high-vacuum technology, it was difficult to obtain decisive data on clean surfaces. The above analysis was published in 1975 [11] (and even then in a rather inaccessible place) nearly 20 years after the comparable work on electrochemical reactions.

1.3 ATTEMPTS TO EXPLAIN EFFECTS OF NATURE OF ELECTRODE ON HYDROGEN EVOLUTION

It is generally accepted that hydrogen evolution can be explained in terms of three partial reactions:

1. The discharge reaction $H^+ + e^- \rightarrow H$, where H^+ is a solvated proton, e is an electron in the metal electrode, and H is a hydrogen atom adsorbed on the electrode surface. This was originally assumed to be the rate-determined reaction by Erdey Gruz and Volmer [7].
2. The recombination reaction $H + H \rightarrow H_2$, which was originally proposed as the rate-determining reaction by Tafel [12].

3. The alternative desorption reaction $H^+ + H \rightarrow H_2$ proposed by Heyrovsky [13] and later by Horiuti and Okamoto [14], who assumed that this would occur via the formation of an intermediate H_2^+.

While Bonhoeffer [15] noted the parallelism between the catalytic recombination of gaseous hydrogen and the rate of electrolytic hydrogen evolution, the first systematic attempt to study the effect of the nature of the metal electrode on the kinetics of hydrogen evolution was made by Bockris [16]. But, as with the catalysts at this time, it was difficult to ensure that the metal surface was not contaminated. Nevertheless, he made an attempt to correlate his results with other physical properties on metals [17]. This was apparently based on the theoretical approach to charge transfer due to Gurney [18] and modified by Butler [19] since it introduced the electronic work function as a main influence on the reaction rate. Although Bockris expected three types of behavior based on the above three partial reactions being rate determining, his plots of the logarithm of the exchange current (the rate of the reaction at equilibrium), versus the electronic work function showed two groups. Most of the metals lay on one line while the three least active metals (Tl, Pb, Hg) lay on a line parallel to it. However, it was shown later [20] that without strong interaction with the electrode the rate of a simple redox reaction is independent of the nature of the electrode material. This was confirmed experimentally [21, 22]. Consequently it is unlikely that the work function of the electrode has a direct influence on the kinetics of an electrode reaction. Of course it may relate directly to the formation of the bond between the electrode and an adsorbed species such as H.

A further attempt to correlate the effect of the metal on the rate of hydrogen evolution was made by Rüetschi and Delahay [23]. They calculated the strength of the metal–hydrogen bond from the strengths of the H–H bond and that of the metal atom in the metal M–M using the Pauling equation [24]:

$$D(\text{M–H}) = \tfrac{1}{2}[D(\text{M–M}) + D(\text{H–H})] + 21.06\,(X_{\text{M}} - X_{\text{H}})^2\ \text{kcal mol}^{-1} \qquad (1.19)$$

Where X_i is the electronegativity of atom i. On the basis of the observation by Eley [25] that the polarity of the M–H bond is small, they neglected the electronegativity term. Their plot of the experimental values of the hydrogen overpotential at a current density of $1\ \text{mA cm}^{-2}$ versus the energy of adsorption of H showed a linear relation for a number of metals having a negative slope with a few of the most active metals Pt, Pt, Au as well as Mo and Ta deviating. This slope would be expected if the discharge reaction is rate determining, as in the Horiuti and Polanyi model. Since they estimated the value of D(M–M) in terms of the energy of sublimation of the metal, this amounts to a correlation with this quantity. Conway and Bockris [26] criticized their neglect of the electronegativity term. They repeated the calculation of D(M–H) using values of electronegativity from Pritchard and Skinner [27] and Gordy and Thomas [28].

They found they there was still some evidence for a linear relation, but one with the opposite slope to that found by Rüetschi and Delahay (Fig. 1.3). They this interpreted in terms of a rate-determining ion+atom reaction which involved the desorption of the H atom so that the overpotential is greater for the more strongly bound H. The

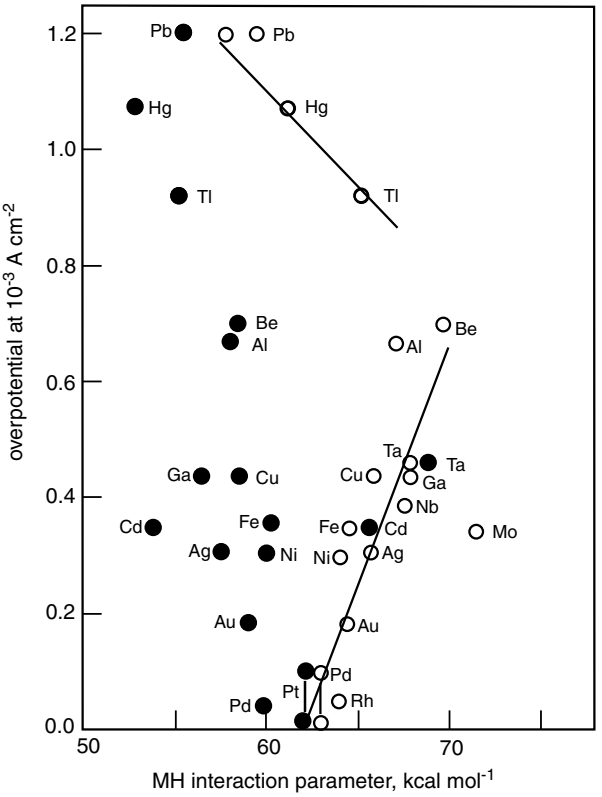

FIGURE 1.3 Plot of hydrogen overpotential at $10^{-3}\,\mathrm{A\,cm^{-2}}$ as function of metal–H interaction energy parameter. (•) Rüetschi and Delahay's values [23]. (○) True values of $D_{\mathrm{M\text{–}H}}$ calculated from Pauling's equation using known electronegativity values. Values η at $10^{-3}\,\mathrm{A\,cm^{-2}}$ are calculated from the experimental Tafel parameters recorded by Conway and Bockris [26].

exceptions to this were Hg, Pb, and Tl, which fell on a line with negative slope, in accord with the expectation for a rate-determining discharge reaction.

An approach which takes account of the kinetics of the three proposed component reactions in hydrogen evolution was made by Gerischer [29] following the work of Parsons and Bockris [30]. He attempted to predict the relative rates of these reactions as a function of the energy of adsorption of hydrogen. This led to the conclusion that under normal conditions (current density of 1 mA cm^{-2}), at metals weakly adsorbing hydrogen, the mechanism was discharge followed by the ion + atom reaction with the former controlling the rate. For very strongly adsorbing metals the mechanism would be the same but the ion + atom reaction would control the rate. There was a small region in between these two where the recombination reaction was rate controlling. He did not consider the back reactions and so could not include a discussion of the exchange current.

1.4 ELECTROCHEMICAL VOLCANO CURVE

Gerischer did include the back reaction in his next paper [31]. Independently and simultaneously he and Parsons [32] showed that the exchange current of the hydrogen reaction plotted versus the adsorption energy would follow a volcano-shaped curve. The special feature of electrochemical reactions is that their rate is dependent on the electrode potential. It is also frequently found that the equilibrium state is accessible where the rate of the forward and reverse reactions is equal. In the special case of the hydrogen reaction the probable existence of a single adsorbed intermediate atomic hydrogen can be assumed. It is first assumed that this follows the Langmuir isotherm:

$$\left(\frac{\theta^*}{1-\theta^*}\right)^2 = p_{\mathrm{H}_2} \exp\left(-\frac{\Delta g^0}{kT}\right) \tag{1.20}$$

where θ is the fraction of the available surface occupied by H and the asterisk denotes that it is the equilibrium value, p is the pressure of molecular hydrogen in the gas phase, and Δg^0 is the standard Gibbs energy for the reaction:

$$\mathrm{H}_2 + 2\mathrm{M} \leftrightarrow 2\mathrm{H} - \mathrm{M} \tag{1.21}$$

the standard states being 1 atm for the gaseous hydrogen and $\theta = \frac{1}{2}$ for the adsorbed atoms. The Gibbs energy of adsorption of hydrogen molecules and their coverage of the surface are assumed negligible. For the discharge reaction the rates of the discharge reaction may be written as

$$\vec{v}_1 = \left(\frac{kT}{h}\right) a_{\mathrm{H}^+} (1-\theta) \exp\left(\Delta \vec{g}_1^0 + \frac{\alpha_1 \phi e_0}{kT}\right) \tag{1.22}$$

and

$$\overleftarrow{v}_1 = \left(\frac{kT}{h}\right) \theta \exp\left(-\Delta \vec{g}_1^0 + \frac{(1-\alpha_1)\phi e_0}{kT}\right) \tag{1.23}$$

where a_{H^+} is the activity of protons in solution (strictly not measurable but will be assumed constant) and α_1 is defined as in eq. (1.1), φ is the inner potential difference between the metal and the solution, and $\Delta \vec{g}_1^0$ and $\Delta \overleftarrow{g}_1^0$ are the standard Gibbs energies of activation for the forward and reverse reactions, respectively, when $\varphi = 0$. These three quantities are not accessible to experiment or to theoretical calculation. Equations (1.22) and (1.23) can be rearranged in terms of accessible quantities following Tëmkin [33].

At equilibrium, $\vec{v}_1 = \overleftarrow{v}_1$, where

$$\exp\left(\frac{\phi^* e_0}{kT}\right) = a_{\mathrm{H}^+} \left(\frac{1-\theta^*}{\theta^*}\right) \exp\left(\frac{\Delta \overleftarrow{g}_1^0 - \Delta \vec{g}_1^0}{kT}\right) \tag{1.24}$$

The potential $\varphi = \eta + \varphi^*$, where η is the overpotential. Then rate equations (1.22) and (1.23) may be written as

$$\vec{i}_1 = i_{0,1}\theta \exp\left(-\alpha_1 e_0 \eta\right) \tag{1.25}$$

$$\overleftarrow{i}_1 = i_{0,1}(1-\theta) \exp\left[(1-\alpha_1)\, e_0 \eta\right] \tag{1.26}$$

where i_0 is the exchange current of the discharge reaction and for $\theta = \theta^*$, where θ^* is the coverage at equilibrium

$$i_{0,1} = e_0 \left(\frac{kT}{h}\right) a_{\mathrm{H}^+}^{1-\alpha} \left(\theta^*\right)^{\alpha} \left(1-\theta^*\right)^{1-\alpha} \exp\left(-\frac{(1-\alpha)\,\Delta\vec{g}_1^0 + \alpha\Delta\overleftarrow{g}_1^0}{kT}\right) \tag{1.27}$$

The quantity in the exponential of (1.27) is experimentally accessible as the Gibbs energy of activation at the equilibrium potential and theoretically as the height of the Gibbs energy barrier when the Gibbs energy levels of the initial and final states are equal [33, 34]. The effect of the strength of adsorption of H on the exchange current is expressed in (1.27) entirely through the value of the equilibrium coverage θ^*. The dependence of the exchange current upon the standard Gibbs energy of adsorption is obtained by eliminating θ^* between (1.27) and (1.20):

$$i_{0,1} = a_{\mathrm{H}^+}^{1-\alpha} \left[p_{\mathrm{H}_2} \exp\left(-\frac{\Delta g^0}{2} kT\right)\right] \left[1 + p_{\mathrm{H}_2} \exp\left(-\frac{\Delta g^0}{2} kT\right)\right]^{-1} G_1 \tag{1.28}$$

where

$$G_1 = e_0 \left(\frac{kT}{h}\right) \exp\left(-\frac{(1-\alpha)\,\Delta\vec{g}_1^0 + \alpha\Delta\overleftarrow{g}_1^0}{kT}\right) \tag{1.29}$$

From (1.28) it follows that when $\Delta g^0/2kT \gg 1$, that is adsorption is weak, the exchange current increases exponentially with a decrease of Δg^0. There is a maximum at $\Delta \mathrm{g}^0 = 0$ and the volcano curve is as shown in Figure 1.2.

The other two partial reactions can be analyzed in the same way. The rate equations for the ion + atom reaction are

$$\vec{v}_2 = \left(\frac{kT}{h}\right) a_{\mathrm{H}^+}\, \theta \exp\left[-\frac{\Delta\vec{g}_2^0 + \beta e_0 \phi}{kT}\right] \tag{1.30}$$

$$\overleftarrow{v}_2 = \left(\frac{kT}{h}\right) p_{\mathrm{H}_2}(1-\theta) \exp\left[-\frac{\Delta\overleftarrow{g}_2^0 - (1-\beta) e_0 \phi}{kT}\right] \tag{1.31}$$

and the resulting volcano curve is given by

$$i_{0,2} = a_{H^+}^{1-\beta}\left[p_{H_2}^{\beta/2}\exp\left(-\frac{\beta\Delta g^0}{2}kT\right)\right]\left[1 + p_{H_2}^{\beta/2}\exp\left(-\frac{\Delta g^0}{2}kT\right)\right]^{-1} G_2 \quad (1.32)$$

where

$$G_2 = e_0\left(\frac{kT}{h}\right)\exp\left(-\frac{(1-\beta)\,\Delta\vec{g}_2^0 + \beta\Delta\overleftarrow{g}_2^0}{kT}\right) \quad (1.33)$$

Clearly (1.32) has the same form as (1.28) and in fact they are identical if $G_1 = G_2$ and $\alpha = \beta$.

For the recombination reaction the rate equations are

$$\vec{v}_3 = \left(\frac{kT}{h}\right)\theta^2\exp\left(-\frac{\Delta\vec{g}_3^0}{kT}\right) \quad (1.34)$$

$$\overleftarrow{v}_3 = \left(\frac{kT}{h}\right)p_{H_2}(1-\theta)^2\exp\left(-\frac{\Delta\overleftarrow{g}_3^0}{kT}\right) \quad (1.35)$$

In this case the Gibbs energies of activation are independent of the electrode potential just as in an ordinary catalytic reaction, but of course they depend on the Gibbs energy of adsorption of H and this can be expressed using Eq. (1.2):

$$\Delta\vec{g}_3 = \Delta\vec{g}_3^0 - \gamma\,\Delta g^0 \quad (1.36)$$

$$\Delta\overleftarrow{g}_3 = \Delta\overleftarrow{g}_3^0 + (1-\gamma)\,\Delta g^0 \quad (1.37)$$

where γ depends on the relative slopes of the energy curves at their intersection in the same way as α and β. The term Δg_3^0 is the Gibbs energy of activation when the Gibbs energies of the initial and final states are equal. These lead to

$$i_{0,3} = p_{H_2}\exp\left(-\frac{(1-\gamma)\Delta g^o}{kT}\right)\left[1 + p_{H_2}^{1/2}\exp\left(-\frac{\Delta g^0}{kT}\right)\right]^{-2} G_3 \quad (1.38)$$

$$G_3 = 2e_0\left(\frac{kT}{h}\right)\exp\left(-\frac{\Delta\vec{g}_3^0}{kT}\right) \quad (1.39)$$

Equation (1.38) has the same form as (1.28) and (1.32), but if $\alpha = \beta = \gamma$, the slopes of the branches of the plots away from the maximum are twice those for the other

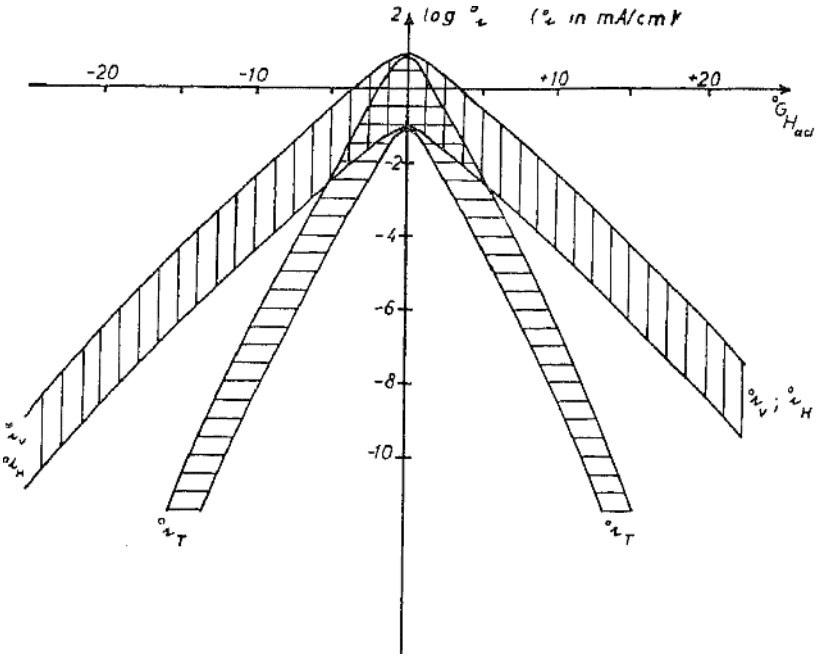

FIGURE 1.4 Standard exchange current dependence on $^{\circ}G_{\mathrm{Had}}$ at equilibrium conditions for three partial reactions. (Data adapted from Parsons and Bockris [30].)

two reactions. Gerischer [30] reached this conclusion by similar arguments, and his result is shown in Figure 1.4, in which he assumed that the maximum was the same for the three partial reactions. Parsons [32] used the well-established experimental observation that the rate of hydrogen evolution was the greatest on Pt, which must then be at the peak of the volcano. Also, the experimental results of Frumkin Dolin and Ershler [35] and those of Azzam and Bockris [36] suggest that the exchange current is the greatest for the discharge reaction and the least for the ion+atom reaction. Parsons also used the Tëmkin model [37] for a heterogeneous surface which leads to an adsorption isotherm and kinetic equations which differ from the Langmuir equations in the region of moderate adsorption. The resulting volcano curves are shown in Figure 1.5. They show a flat maximum in the region of moderate adsorption, but away from that they are identical to the Langmuir-based curves. Given the values of the exchange currents for the three partial reactions, it is straightforward to calculate the current–potential curves, and these are shown in Figure 1.6 for the labeled positions on the volcano curve. It is necessary to take account of the degree of coverage in doing this so that the correct version of the kinetics, that is, the Langmuir or Tëmkin, is used. The regions covered by the latter are indicated on each plot. The relation to experiment was discussed qualitative. Thus the very high overpotential metals Pb, Cd, and Tl and possibly Zn and Sn, which adsorb H weakly, would be expected to have the form shown

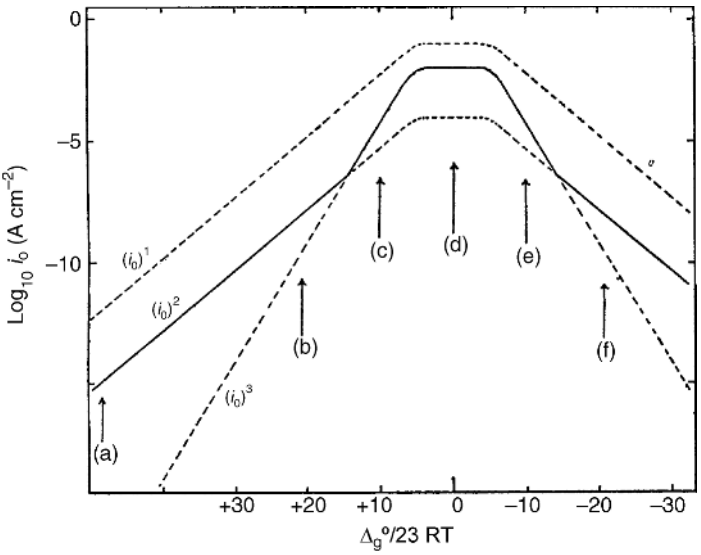

FIGURE 1.5 Proposed relation between exchange current of three partial reactions at hydrogen electrode and standard free energy of adsorption of hydrogen on electrode surface: $(i_0)^1$, exchange current for discharge reaction; $(i_0)^2$, exchange current for ion atom reaction; $(i_0)^3$, exchange current for combination reaction. Full line gives the observable exchange current. (Data adapted from Parsons [32].)

in Figure 1.7(a). In most cases the lower part of this curve might not be accessible because the currents are so small. Metals like NI, Fe, Mo, W, and Ta adsorb H strongly and so would be expected to follow Figure 1.6(f); thus their current–potential characteristic is much the same as that of the weakly adsorbing metals in the observable region. Copper and Ag seem to behave like Figure 1.6(b) and Pt was shown by Azzam and Bockris [36] to behave like Figure 1.6(d) when very high current densities were studied. Trasatti [38] made a detailed assessment of the available data used to plot the volcano curve (Fig. 1.7). Like Krishtalik [39], he came to the conclusion that there was no evidence for the flat top. This might mean that the metals near the peak of the volcano had uniform surfaces. They were all polycrystalline, and no systematic evidence has been gathered for well-defined surfaces. Conway and Tilak [40] in a comprehensive survey of the behavior of hydrogen at electrodes pointed out that on Pt hydrogen coverage was approximately complete at the equilibrium potential. They concluded that some other species of adsorbed hydrogen must be the intermediate on Pt and suggested that it was adsorbed on a surface already covered with the well-known adsorbed hydrogen. In a theoretical review of the hydrogen electrode reaction, Krishtalik [39], included the possibility of activationless and barrierless reactions in addition to the three reactions considered above.

Some further considerations of the simple model were published by Parsons, including the reverse reaction and the adsorption capacity in a generalized version

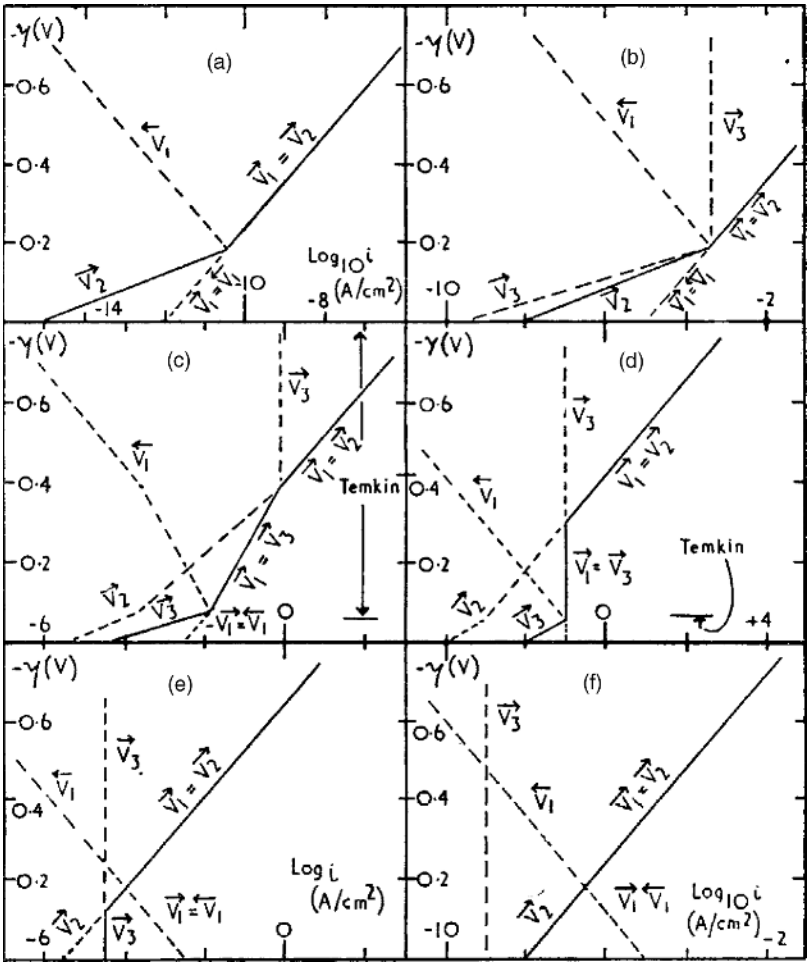

FIGURE 1.6 Tafel lines calculated using of exchange currents from Figure 1.5. Full line gives the observable Tafel line. (Data adapted from Parsons [32].)

[20] and the variation of the coefficients α , β, and γ with potential or with adsorption energy as a result of the parabolic shape of the potential energy curves [41]. In the same paper he set up a model of an electrode with two patches with different strengths of adsorption of hydrogen to estimate whether such electrodes might be better electrocatalysts, but this did not lead to any hope of improved performance. He also tried to use the kinetic approach to predict the yield of products in a branched electrochemical reaction [42]. However, this was a hypothetical scheme and it has not yet found application. Recently Nørskov et al. [43] have used density functional theory to calculate the energy of the chemisorption of H and rediscovered the volcano curve. Their kinetic analysis was criticized by Schmickler and Trasatti [44].

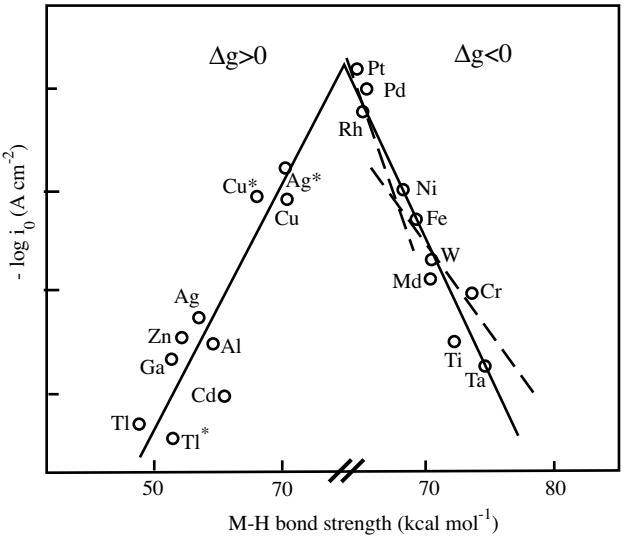

FIGURE 1.7 Exchange currents for electrolytic hydrogen evolution versus strength of metal–hydrogen bond derived from heat of hydride formation. (Data adapted from Trasatti [38].)

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