ORIGINAL PAPER

Tafel slopes from first principles

Stephen Fletcher

Abstract Tafel slopes for multistep electrochemical reactions are derived from first principles. The derivation takes place in two stages. First, Dirac's perturbation theory is used to solve the Schrödinger equation. Second, current–voltage curves are obtained by integrating the single-state results over the full density of states in electrolyte solutions. Thermal equilibrium is assumed throughout. Somewhat surprisingly, it is found that the symmetry factor that appears in the Butler–Volmer equation is different from the symmetry factor that appears in electron transfer theory, and a conversion formula is given. Finally, the Tafel slopes are compiled in a convenient look-up table.

Keywords Schrödinger equation · Golden rule · Butler–Volmer equation · Tafel slopes · Electron transfer

Introduction

To help celebrate the 80th birthday of my long-time friend and colleague Keith B. Oldham, I thought it might be fun to present him with a table of Tafel slopes derived from first principles (i.e. from Schrödinger's equation). A total proof of this kind has been technically feasible for a number of years but—so far as I know—it has never been attempted before. This seems an auspicious moment to undertake this task.

This article is dedicated to Professor Keith B. Oldham on the occasion of his 80th birthday.

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The wavefunction of an electron

The amount of theoretical ground one has to cover before being able to solve problems of real practical value is rather large...

P.A.M. Dirac, in "The Principles of Quantum Mechanics", Clarendon Press, Oxford, 1930.

Electrochemists want to understand how electrons interact with matter. But, before they can even begin to construct a model, they must first specify the positions of the electrons. This is not as easy as it sounds, however, because the positions of electrons are not determined by the laws of newtonian mechanics. They are determined by the probabilistic laws of quantum mechanics. In particular, the location of any given electron is governed by its wavefunction Ψ. This is a complex-valued function that describes the probability amplitude of finding the electron at any point in space or time. Now, it is a well-known postulate of quantum mechanics that the maximum amount of information about an electron is contained in its wavefunction. If we accept this postulate as true (and we currently have no alternative), then we are forced to conclude that *the wavefunction is the best available parameter for characterizing the behaviour of an electron in space–time.*

It is natural to enquire how well wavefunctions do characterize electron behaviour. In general, the answer is "very well indeed". For example, wavefunctions permit the calculation of the most probable values of all the known properties of electrons or systems of electrons to very high accuracy. One problem remains, however. Due to the probabilistic character of wavefunctions, they fail to

describe the *individual* behaviour of any system at very short times. In such cases, the best they can do is describe the *average* behaviour of a large number of systems having the same preparation. Despite this limitation, the analysis of wavefunctions nevertheless provides measures of the *probabilities of occurrence of various states* and the *rates of change of those probabilities*. Here, following Dirac, we are happy to interpret the latter as *reaction rate constants*.

The uncertainty principle

This principle was first enunciated by Werner Heisenberg in 1927 [1]. The principle asserts that one cannot simultaneously measure the values of a pair of conjugate quantum state properties to better than a certain limit of accuracy. There is a minimum for the product of the uncertainties. Key features of pairs of conjugate quantum state properties are that they are uncorrelated, and, when multiplied together, have dimensions of *energy × time*. Examples are (1) momentum and location, and (2) energy and lifetime. Thus

$$\Delta p \, \Delta x \geq \hbar/2 \tag{1}$$

$$\Delta U \, \Delta t \geq \hbar/2 \tag{2}$$

Here, p is momentum of a particle (in one dimension), x is location of a particle (in one dimension), U is energy of a quantum state, t is lifetime of a quantum state, and h is the reduced Planck constant,

$$\hbar = \frac{h}{2\pi} = 0.6582 \ (\text{eV} \times \text{fs}) \tag{3}$$

The formal and general proof of the above inequalities was first given by Howard Percy Robertson in 1929 [2]. He also showed that the uncertainty principle was a deduction from quantum mechanics, not an independent hypothesis.

As a result of the "blurring" effect of the uncertainty principle, quantum mechanics is unable to predict the precise behaviour of a single molecule at short times. But, it can still predict the average behaviour of a large number of molecules at short times, and it can also predict the time-averaged behaviour of a single molecule over long times. For example, the energy of an electron measured over a finite time interval Δt has an uncertainty

$$\Delta U \geq \frac{\hbar}{2 \, \Delta t} \tag{4}$$

and therefore, to decrease the energy uncertainty in a single electron transfer step to practical insignificance (<1 meV, say, which is equivalent to about 1.602×10^{-22} J/electron), it is necessary to observe the electron for $t > 330$ fs.

The quantum mechanics of electron transfer

As shown by Erwin Schrödinger [3], the wavefunction Ψ of a (non-relativistic) electron may be derived by solving the time-dependent equation

$$(i\hbar) \frac{\partial \Psi}{\partial t} = H\Psi \tag{5}$$

Here, H is a linear operator known as the *Hamiltonian*, and $\hbar$ is the *reduced Planck constant* ($=h/2\pi$). The Hamiltonian is a differential operator of total energy. It combines the kinetic energy and the electric potential energy of the electron into one composite term:

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi - eV\Psi \tag{6}$$

where m is the electron mass, $-e$ is the electron charge, and V is the electric potential of the electric field. Note that the electric potential at a particular point in space (x, y, z), created by a system of charges, is simply equal to the change in potential energy that would occur if a test charge of +1 were introduced at that point. So $-eV$ is the potential energy in the electric field. The *Laplacian* ∇^2, which also appears in the Schrödinger equation, is the square of the vector operator ∇ ("del"), defined in Cartesian co-ordinates by

$$\nabla\varphi(x, y, z) = \frac{\partial \varphi}{\partial x}\widehat{x} + \frac{\partial \varphi}{\partial y}\widehat{y} + \frac{\partial \varphi}{\partial z}\widehat{z} \tag{7}$$

Every solution of Schrödinger's equation represents a possible state of the system. There is, however, always some uncertainty associated with the manifestation of each state. Due to the uncertainty, the square of the modulus of the wavefunction $|\Psi|^2$ may be interpreted in two ways: firstly and most abstractly, as the probability that an electron might be found at a given point and, secondly and more concretely, as the electric charge density at a given point (averaged over a large number of identically prepared systems for a short time or averaged over one system for a long time).

Transition probabilities

Almost all kinetic experiments in physics and chemistry lead to statements about the relative frequencies of events, expressed either as deterministic rates or as statistical transition probabilities. In the limit of large systems, these formulations are, of course, equivalent. By definition, a transition probability is just the probability that one quantum state will convert into another quantum state in a single step.

The theory of transition probabilities was developed independently by Dirac with great success. It can be said that the whole of atomic and nuclear physics

works with this system of concepts, particularly in the very elegant form given to them by Dirac.

Max Born, "The Statistical Interpretation of Quantum Mechanics", Nobel Lecture, 11th December 1954.

Time-dependent perturbation theory

It is an unfortunate fact of quantum mechanics that exact mathematical solutions of the time-dependent Schrödinger equation are possible only at the very lowest levels of system complexity. Even at modest levels of complexity, mathematical solutions in terms of the commonplace functions of applied physics are impossible. The recognition of this fact caused great consternation in the early days of quantum mechanics. To overcome the difficulty, Paul Dirac developed an extension of quantum mechanics called "perturbation theory", which yields good approximate solutions to many practical problems [4]. The only limitation on Dirac's method is that the coupling (orbital overlap) between states should be weak.

The key step in perturbation theory is to split the total Hamiltonian into two parts, one of which is *simple* and the other of which is *small*. The simple part consists of the Hamiltonian of the unperturbed fraction of the system, which can be solved exactly, while the small part consists of the Hamiltonian of the perturbed fraction of the system, which, though complex, can often be solved as a power series. If the latter converges, solutions of various problems can be obtained to any desired accuracy simply by evaluating more and more terms of the power series. Although the solutions produced by Dirac's method are not exact, they can nevertheless be extremely accurate.

In the case of electron transfer, we may imagine a transition between two well-defined electronic states (an occupied state $|D\rangle$ inside an electron donor D, and an unoccupied state $|A\rangle$ inside an electron acceptor A), whose mutual interaction is weak. Dirac showed that, provided the interaction between the states is weak, the transition probability P_{DA} for an electron to transfer from the donor state to the acceptor state increases linearly with time. Let us see how Dirac arrived at this conclusion.

Electron transfer from one single state to another single state

If classical physics prevailed, the transfer of an electron from one single state to another single state would be governed by the conservation of energy and would occur only when both states had exactly the same energy. But in the quantum world, the uncertainty principle (in its time-

energy form) briefly intervenes and allows electron transfer between states whose energies are mismatched by a small amount $\Delta U = \hbar/2\Delta t$ (although energy conservation still applies *on average*). As a result of this complication, the transition probability of electrons between two states exhibits a complex behaviour. Roughly speaking, the probability for electron transfer between two precise energies increases as t^2, while the width of the band of allowed energies decreases as t^{-1}. The net result is an overall transition probability that is proportional to t.

To make these ideas precise, consider a perturbation which is "switched on" at time $t=0$ and which remains constant thereafter. In electrochemistry, this corresponds to the arrival of the system at the transition state. The time-dependent Schrödinger equation may now be written

$$(i\hbar)\,\frac{\partial\Psi}{\partial t} = (H_0 + H_1)\,\Psi \tag{8}$$

where $\Psi(x,t)$ is the electron wavefunction, H_0 is the unperturbed Hamiltonian operator, and H_1 is the perturbed Hamiltonian operator:

$$H_1(t) = 0 \quad \text{for} \quad t<0 \tag{9}$$

$$H_1(t) = H_1 \quad \text{for} \quad t \geq 0 \tag{10}$$

This is a step function with H_1 being a constant independent of time at $t \geq 0$. Solving Eq. 8, one finds that the probability of electron transfer between two precise energies U_D and U_A is

$$P_{DA}(U,t) \approx \frac{2|M_{DA}|^2}{|U_A - U_D|^2}\left[1 - \cos\left(\frac{[U_A - U_D]t}{\hbar}\right)\right] \tag{11}$$

where the modulus symbol denotes the (always positive) magnitude of any complex number. This result is valid provided the "matrix element" M_{DA} is small. The matrix element M_{DA} is defined as

$$M_{DA} = \int \Psi_D V \Psi_A \, dv \tag{12}$$

where Ψ_D and Ψ_A are the wavefunctions of the donor and acceptor states, V is their interaction energy, and the integral is taken over the volume v of all space. M_{DA} is, therefore, a function of energy E through the overlap of the wavefunctions Ψ_D and Ψ_A and accordingly has units of energy.

In an alternative representation, we exploit the identity

$$1 - \cos x = 2\sin^2(x/2) \tag{13}$$

so that

$$P_{DA}(U,t) \approx \frac{4|M_{DA}|^2}{|U_A - U_D|^2}\sin^2\left(\frac{[U_A - U_D]t}{2\hbar}\right) \tag{14}$$

If we now recall the *cardinal sine function*

$$\mathrm{sinc}(x) = \frac{\sin x}{x} \qquad (15)$$

and define

$$x = \frac{[U_A - U_D]t}{2h} \qquad (16)$$

then we can substitute these formulas into the equation for the transition probability to yield

$$P_{DA}(U,t) \approx \frac{|M_{DA}|^2 t^2}{h^2} \mathrm{sinc}^2(x) \qquad (17)$$

This result is wonderfully compact, but unfortunately, it is not very useful to electrochemists because it fails to describe electron transfer into *multitudes* of acceptor states at electrode surfaces, supplied by the 10^8–10^{14} reactant molecules per square centimetre that are typically found there. These states have energies distributed over several hundred meV, and all of them interact simultaneously with all the electrons in the electrode. They also fluctuate randomly in electrostatic potential due to interactions with the thermally agitated solvent and supporting electrolyte (dissolved salt ions). Accordingly, Eq. 17 must be modified to deal with this more complex case.

Electron transfer into a multitude of acceptor states

To deal with this more complex case, it is necessary to define a probability density of acceptor state energies $\varphi_A(U)$. Accordingly, we define $\varphi_A(U)$ as the number of states per unit of energy and note that it has units of joule^{-1}. If we further assume that there is such a high density of states that they can be treated as a continuum, then the transition probability between the single donor state $|D\rangle$ and the multitude of acceptor states $|A\rangle$ becomes

$$P_{DA}(t) \approx \int_{-\infty}^{\infty} \frac{|M_{DA}|^2 t^2}{h^2} \mathrm{sinc}^2\left(\frac{[U - U_D]t}{2\hbar}\right) \varphi_A(U)\, dU \qquad (18)$$

Although this equation appears impossible to solve, Dirac, in a *tour de force* [5], showed that an asymptotic result could be obtained by exploiting the properties of a "delta function" such that

$$\int_{-\infty}^{+\infty} \delta(x - x_0) F(x)\, dx = F(x_0) \qquad (19)$$

and

$$\delta(ax) = \frac{1}{|a|}\delta(x) \qquad (20)$$

By noting the identity

$$\lim_{t \to \infty} \mathrm{sinc}^2\left(\frac{[U - U_D]t}{2\hbar}\right) = \frac{2\pi\hbar}{t}\delta(U - U_D) \qquad (21)$$

and then extracting the limit $t \to \infty$, Dirac found that (!)

$$\lim_{t \to \infty} P_{DA}(t) \approx \frac{2\pi t}{\hbar}|M_{DA}|^2 \varphi_A(U_D) \qquad (22)$$

where U_D, the single energy of the donor state, is a constant. As we gaze in amazement at Eq. 22, we remark only that $\varphi_A(U_D)$ is *not* the full density of states function $\varphi_A(U)$ which it is sometimes mistakenly stated to be in the literature. It is, in fact, the *particular value* of the density of states function at the energy U_D.

Upon superficial observation, it may appear that the above formula for $P_{DA}(t)$ is applicable only in the limit of infinite time. But actually, it is valid after a very brief interval of time

$$\Delta t > \frac{\hbar}{2\Delta U} \qquad (23)$$

This time is sometimes called the *Heisenberg time*. At later times, Dirac's theory of the transition probability can be applied with great accuracy. Finally, in the ultimate simplification of electron transfer theory, it is possible to derive the *rate constant for electron transfer* k_{et} by differentiating the transition probability. This leads to Dirac's final result

$$k_{et} = \frac{2\pi}{\hbar}|M_{DA}|^2 \varphi_A(U_D) \qquad (24)$$

A remarkable feature of this equation is the absence of any time variable. It was Enrico Fermi who first referred to this equation as a "Golden Rule" (in 1949—in a university lecture!), and the name has stuck [6]. He esteemed the equation so highly because it had by then been applied with great success to many non-electrochemical problems (particularly the intensity of spectroscopic lines) in which the coupling between states (overlap between orbitals) was small. Because the equation is often referred to as "Fermi's Golden Rule", the ignorant often attribute the equation to Fermi. This is a very bad mistake.

Despite its successful application to many diverse problems, it is nevertheless important to remember that the Golden Rule applies only to cases where electrons transfer from a single donor state into a multitude of acceptor states. If electrons originate from a multitude of donor states—as they do during redox reactions in electrolyte solutions—then the transition probabilities from all the donor states must be added together, yielding

$$k_{et} = \int_{-\infty}^{+\infty} \frac{2\pi}{\hbar}|M_{DA}|^2 \varphi_A(U_D)\, \varphi_D(U_D) dU_D \qquad (25)$$

There is, alas, nothing golden about this formula. To evaluate it, one must first develop models of each of the probability densities and then evaluate the integral by brute force.

The density of states functions $\varphi_A(U_A)$ and $\varphi_D(U_D)$ are dominated by fluctuations of electrostatic potential inside electrolyte solutions even at thermodynamic equilibrium. According to Fletcher [7], a major source of these fluctuations is the random thermal motion (Brownian motion) of electrolyte ions. The associated bombardment of reactant species causes their electrostatic potentials to vary billions of times every second. This, in turn, makes the tunnelling of electrons possible because it ensures that any given acceptor state will, sooner or later, have the same energy as a nearby donor state.

Electrostatic fluctuations at equilibrium

The study of fluctuations inside equilibrium systems was brought to a high state of development by Ludwig Boltzmann in the nineteenth century [8]. Indeed, his methods are so general that they may be applied to any small system in thermal equilibrium with a large reservoir of heat. In our case, they permit us to calculate the probability that a randomly selected electrostatic fluctuation has a work of formation ΔG.

A system is in thermal equilibrium if the requirements of detailed balance are satisfied, namely, that every process taking place in the system is exactly balanced by its reverse process, so there is no net change over time. This implies that the rate of formation of fluctuations matches their rate of dissipation. In other words, the fluctuations must have a distribution that is stationary. As a matter of fact, the formation of fluctuations at thermodynamic equilibrium is what statisticians call *strict-sense stationary*. It means that the statistical properties of the fluctuations are independent of the time at which they are measured. As a result, at thermodynamic equilibrium, we know in advance that the probability density function of fluctuations $\varphi_A(U)$ must be independent of time.

Boltzmann discovered a remarkable property of fluctuations that occur inside systems at thermal equilibrium: they always contain the "Boltzmann factor",

$$\exp\left(\frac{-\Delta W}{k_B T}\right) \tag{26}$$

where ΔW is an appropriate thermodynamic potential, k_B is the Boltzmann constant, and T is the thermodynamic (absolute) temperature. At constant temperature and pressure, ΔW is the Gibbs energy of formation of the fluctuation ΔG. Given this knowledge, it follows that the probability density function $\varphi_A(V)$ of electric potentials (V) must have the stationary form

$$\varphi_A(V) = A \exp\left(\frac{-\Delta G}{k_B T}\right) \tag{27}$$

where A is a time-independent constant. In the case of charge fluctuations that trigger electron transfer, we have

$$\Delta G = \frac{1}{2} C(\Delta V)^2 = \frac{1}{2}\frac{(\Delta V)^2}{\Lambda} \tag{28}$$

where C is the capacitance between the reactant species (including its ionic atmosphere) and infinity, and Λ is the elastance (reciprocal capacitance) between the reactant species and infinity. Identifying $\Lambda e^2/2$ as the reorganization energy λ, we immediately obtain

$$\varphi_A(V) = A \exp\left(\frac{-(eV - eV_A)^2}{4\lambda\, k_B T}\right) \tag{29}$$

which means we now have to solve only for A. Perhaps the most elegant method of solving for A is based on the observation that $\varphi_A(V)$ must be a *properly normalized* probability density function, meaning that its integral must equal one:

$$\int_{-\infty}^{+\infty} A \exp\left(\frac{-(eV - eV_A)^2}{4\lambda\, k_B T}\right) dV = 1 \tag{30}$$

This suggests the following four-step approach. First, we recall from tables of integrals that

$$\frac{1}{\sqrt{\pi}} \int_{-\infty}^{+\infty} \exp(-x^2)\mathrm{d}x = 1 \tag{31}$$

Second, we make the substitution

$$x = \frac{eV - eV_A}{\sqrt{4\lambda\, k_B T}} \tag{32}$$

so that

$$\frac{1}{\sqrt{\pi}} \int_{-\infty}^{+\infty} \sqrt{\frac{e^2}{4\lambda\, k_B T}}\exp\left(\frac{-(eV - eV_A)^2}{4\lambda\, k_B T}\right)\ \mathrm{d}V = 1 \tag{33}$$

Third, we compare the constant in the equation with the constant in the integral containing A, yielding

$$A = \sqrt{\frac{e^2}{4\pi\lambda\, k_B T}} \tag{34}$$

Fourth, we substitute for A in the original expression to obtain

$$\varphi_A(V) = \frac{e}{\sqrt{4\pi\lambda \, k_B T}} \, \exp\left(\frac{-(eV - eV_A)^2}{4\lambda \, k_B T}\right) \quad (35)$$

This, at last, gives us the probability density of electrostatic potentials. We are now just one step from our goal, which is the probability density of the energies of the unoccupied electron states (acceptor states). We merely need to introduce the additional fact that, if an electron is transferred into an acceptor state whose electric potential is V, then the electron's energy must be $-eV$ because the charge on the electron is $-e$. Thus,

$$\varphi_A(-eV) = \frac{1}{\sqrt{4\pi\lambda \, k_B T}} \, \exp\left(\frac{-(eV - eV_A)^2}{4\lambda \, k_B T}\right) \quad (36)$$

or, writing $U = -eV$,

$$\varphi_A(U) = \frac{1}{\sqrt{4\pi\lambda \, k_B T}} \, \exp\left(\frac{-(U - U_A)^2}{4\lambda \, k_B T}\right) \quad (37)$$

where U is the electron energy. This equation gives the stationary, normalized, probability density of acceptor states for a reactant species in an electrolyte solution. It is a Gaussian density. We can also get the un-normalized result simply by multiplying $\varphi_A(U)$ by the surface concentration of acceptor species. Finally, we note that the corresponding formula for $\varphi_D(U)$ is also Gaussian

$$\varphi_D(U) = \frac{1}{\sqrt{4\pi\lambda \, k_B T}} \, \exp\left(\frac{-(U - U_D)^2}{4\lambda k_B T}\right) \quad (38)$$

where we have assumed that $\lambda_A = \lambda_D = \lambda$.

Homogeneous electron transfer

As mentioned above, Dirac's perturbation theory may be applied to any system that is undergoing a transition from one electronic state to another, in which the energies of the states are briefly equalized by fluctuations in the environment. If we assume that the relative probability of observing a fluctuation from energy i to energy j at temperature T is given by the Boltzmann factor exp $(-\Delta G_{ij}/k_B T)$, then

$$k_{et} = \frac{2\pi}{h} \, H_{DA}^2 \, \frac{1}{\sqrt{4\pi\lambda k_B T}} \, \exp\left(\frac{-\Delta G^*}{k_B T}\right) \quad (39)$$

where k_{et} is the rate constant for electron transfer, H_{DA} is the electronic coupling matrix element between the electron donor and acceptor species, k_B is the Boltzmann constant, λ is sum of the reorganization energies of the donor and acceptor species, and ΔG^* is the "Gibbs energy of activation" for the reaction. Incidentally, the fact that the reorganization energies of the donor and acceptor species are additive is a consequence of the statistical independence of $\varphi_A(U_A)$ and $\varphi_D(U_D)$. This insight follows directly from the old adage that "for independent Gaussian random variables, the variances add". The same insight also collapses Eq. 25 back to the Golden Rule, except that the density of states functions must be replaced by a *joint* density of states function that describes the coincidence of the donor and acceptor energies.

Referring to Fig. 1, it is clear that ΔG^* is the total Gibbs energy that must be transferred from the surroundings to the reactants in order to bring them to their mutual transition states. This is simply

$$\Delta G^* = \frac{(\lambda + \Delta G^0)^2}{4\lambda} \quad (40)$$

which implies that

$$k_{et} = \frac{2\pi}{h} \, H_{DA}^2 \, \frac{1}{\sqrt{4\pi\lambda k_B T}} \, \exp\left(\frac{-(\lambda + \Delta G^0)^2}{4\lambda k_B T}\right) \quad (41)$$

We can also define a *symmetry factor* β such that

$$\Delta G^* = \beta^2 \lambda \quad (42)$$

and

$$\beta = \frac{d\Delta G^*}{d\Delta G^0} = \frac{1}{2}\left(1 + \frac{\Delta G^0}{\lambda}\right) \quad (43)$$

Evidently, $\beta = 1/2$ *approximately* if ΔG_0 is sufficiently small (i.e. the electron transfer reaction is neither strongly exergonic nor strongly endergonic), and $\beta = 1/2$ *exactly*
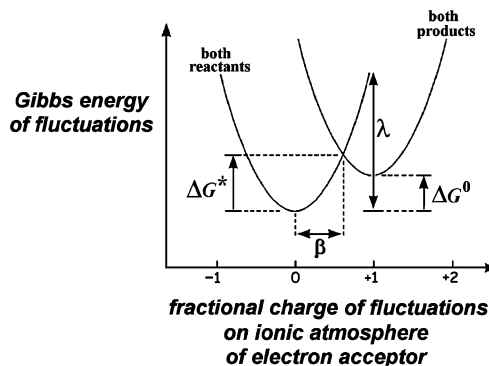

Fig. 1 Gibbs energy diagram for homogeneous electron transfer between two species in solution. At the moment of electron transfer, energy is conserved, so the reactants and the products have the same Gibbs energy at that point. The symmetry factor β corresponds to the fractional charge of the fluctuation on the ionic atmosphere of the acceptor at the moment of electron transfer. After Fletcher [7]

for a self-exchange reaction ($\Delta G^0 = 0$). Finally, from the theory of tunnelling through an electrostatic barrier, we may write

$$H_{DA} = H_{DA}^0 \exp(-\gamma x) \tag{44}$$

where γ is a constant proportional to the square root of the barrier height, and x is the distance of closest approach of the donor and acceptor.

Heterogeneous electron transfer

In the case of electron transfer across a phase boundary (e.g. electron transfer from an electrode into a solution), the law of conservation of energy dictates that the energy of the transferring electron must be added into that of the acceptor species, such that the sum equals the energy of the product species. At constant temperature and pressure the energy of the transferring electron is just its Gibbs energy.

Let us denote by superscript $\overline{bar}$ the Gibbs energies of species in solution after the energy of the transferring electron has been added to them (see Fig. 2). We have

$$\overline{G}_{reactant} = G_{reactant} + qE \tag{45}$$

$$= G_{reactant} - eE \tag{46}$$

where e is the unit charge, and E is the electrode potential of the injected electron. For the conversion of reactant to product, the overall change in Gibbs energy is

$$\Delta \overline{G}^0 = \overline{G}_{product} - \overline{G}_{reactant} \tag{47}$$

$$= G_{product} - (G_{reactant} - eE) \tag{48}$$

$$= (G_{product} - G_{reactant}) + eE \tag{49}$$

$$= \Delta G^0 + eE \tag{50}$$

In the "normal" region of electron transfer, for a metal electrode, it is generally assumed that the electron tunnels
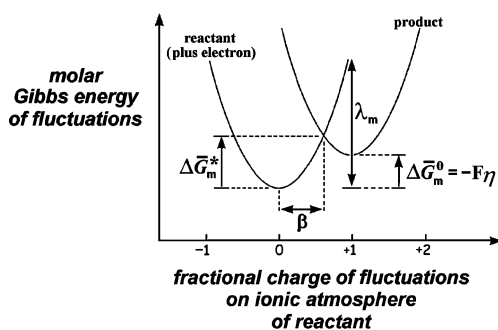

Fig. 2 Gibbs energy diagram for heterogeneous electron transfer from an electrode to an acceptor species in solution. The superscript *bar* indicates that the Gibbs energy of the injected electron has been added to that of the reactant. After Fletcher [7]

from an energy level near the Fermi energy, implying $eE \approx eE_F$. Thus, for a heterogeneous electron transfer process to an acceptor species in solution, we can use the Golden Rule directly

$$k_{et} = \frac{2\pi}{\hbar} H_{DA}^2 \frac{1}{\sqrt{4\pi\lambda k_B T}} \exp\left(\frac{-(\lambda + \Delta G^0 + eE_F)^2}{4\lambda k_B T}\right) \tag{51}$$

where λ is the reorganization energy of the acceptor species in solution, and eE_F is the Fermi energy of the electrons inside the metal electrode. Or, converting to molar quantities

$$k_{et} = \frac{2\pi}{\hbar} H_{DA}^2 \frac{N_A}{\sqrt{4\pi\lambda_m RT}} \exp\left(\frac{-(\lambda_m + \Delta G_m^0 + FE_F)^2}{4\lambda_m RT}\right) \tag{52}$$

where k_{et} is the rate constant for electron transfer, $\hbar$ is the reduced Planck constant, H_{DA} is the electronic coupling matrix element between a single electron donor and a single electron acceptor, N_A is the Avogadro constant, λ_m is the reorganization energy per mole, ΔG_m^0 is the difference in molar Gibbs energy between the acceptor and the product, and $(-FE_F)$ is the molar Gibbs energy of the electron that tunnels from the Fermi level of the metal electrode into the acceptor.

Equation 52 behaves exactly as we would expect. The more negative the Fermi potential E_F inside the metal electrode (i.e. the more negative the electrode potential), the greater the rate constant for electron transfer from the electrode into the acceptor species in solution.

Some simplification is achieved by introducing the notation

$$-\eta \equiv \frac{\Delta G_m^0}{F} + E_F \tag{53}$$

where η is called the "overpotential". Although the negative sign in this equation is not recommended by the International Union of Pure and Applied Chemistry, it is nevertheless sanctioned by long usage, and we shall use it here. With this definition, increasing overpotential η corresponds to increasing rate of reaction. In other words, with this definition, the overpotential is a measure of the "driving force for the reaction". The same inference may be drawn from the equation

$$\eta \equiv -\frac{\Delta \overline{G}_m^0}{F} \tag{54}$$

An immediate corollary is that the condition $\eta = 0$ corresponds to zero driving force (thermodynamic equilib-

rium) between the reactant, the product and the electrode $(\Delta \overline{G}_m^0 = 0)$.

By defining a molar Gibbs energy of activation,

$$\Delta \overline{G}_m^* = \frac{\left(\lambda_m + \Delta G_m^0 + FE_F\right)^2}{4\lambda_m} \tag{55}$$

$$= \frac{\left(\lambda_m - F\eta\right)^2}{4\lambda_m} \tag{56}$$

we can conveniently put Eq. 52 into the standard Arrhenius form

$$k_{et} = \frac{2\pi}{h} H_{DA}^2 \frac{N_A}{\sqrt{4\pi\lambda_m RT}} \exp\left(\frac{-\Delta \overline{G}_m^*}{RT}\right) \tag{57}$$

We can further simplify the analysis by defining the partial derivative $\partial \Delta \overline{G}_m^* / \partial (-F\eta)$ at constant ΔG_m^0 as the *symmetry factor* β, so that

$$\Delta \overline{G}_m^* = \beta^2 \lambda_m \tag{58}$$

where

$$\beta = \frac{\partial \Delta \overline{G}_m^*}{\partial (-F\eta)} = \frac{1}{2}\left(1 - \frac{F\eta}{\lambda_m}\right) \tag{59}$$

This latter equation highlights the remarkable fact that electron transfer reactions require less thermal activation energy $\left(\Delta \overline{G}_m^*\right)$ as the overpotential (η) is increased. Furthermore, the parameter β quantifies the relationship between these parameters.

Expanding Eq. 56 yields

$$\Delta \overline{G}_m^* = \frac{\lambda_m^2 - 2\lambda_m F\eta + F^2\eta^2}{4\lambda_m} \tag{60}$$

which rearranges into the form

$$\Delta \overline{G}_m^* = \frac{\lambda_m}{4} - \left(\frac{2\beta + 1}{4}\right) F\eta \tag{61}$$

Now substituting back into Eq. 57 yields

$$k_{et} = \frac{2\pi}{h} H_{DA}^2 \frac{N_A}{\sqrt{4\pi\lambda_m RT}} \exp\left(\frac{-\lambda_m}{4RT}\right)$$

$$\times \exp\left(\frac{(2\beta + 1)F\eta}{4RT}\right) \tag{62}$$

$$= k_0 \exp\left(\frac{(2\beta + 1)F\eta}{4RT}\right) \tag{63}$$

At thermal equilibrium, an analogous equation applies to the back reaction, except that β is replaced by $(1-\beta)$. Thus, for the overall current–voltage curve, we obtain

$$I = I_0 \left\{ \exp\left(\frac{(2\beta + 1)F\eta}{4RT}\right) - \exp\left(\frac{-(3 - 2\beta)F\eta}{4RT}\right) \right\} \tag{64}$$

where

$$\beta = \frac{1}{2}\left(1 - \frac{F\eta}{\lambda_m}\right) \tag{65}$$

Equation 64 is the current–voltage curve for a reversible, one-electron transfer reaction at thermal equilibrium. It differs from the "textbook" Butler–Volmer equation [9, 10], namely

$$I = I_0 \left\{ \exp\left(\frac{\beta_f F\eta}{RT}\right) - \exp\left(\frac{-\beta_b F\eta}{RT}\right) \right\} \tag{66}$$

because the latter was derived on the (incorrect) assumption of linear Gibbs energy curves. The Butler–Volmer equation is therefore in error. However, its outward form can be "rescued" by defining the following *modified symmetry factors*

$$\beta_f = \frac{2\beta + 1}{4} \tag{67}$$

and

$$\beta_b = \frac{3 - 2\beta}{4} \tag{68}$$

so that

$$\beta_f = \frac{1}{2}\left(1 - \frac{F\eta}{2\lambda_m}\right) \tag{69}$$

and

$$\beta_b = \frac{1}{2}\left(1 + \frac{F\eta}{2\lambda_m}\right) \tag{70}$$

Using these revised definitions, we can continue to use the traditional form of the Butler–Volmer equation— provided we do not forget that we have re-interpreted β_f and β_b in this new way!

Tafel slopes for multi-step reactions

As shown above, the current–voltage curve for a reversible, one-electron transfer reaction at thermal equilibrium may be written in the form

$$I = FACk_0 \left\{ \exp\left(\frac{\beta_f F\eta}{RT}\right) - \exp\left(\frac{-\beta_b F\eta}{RT}\right) \right\} \tag{71}$$
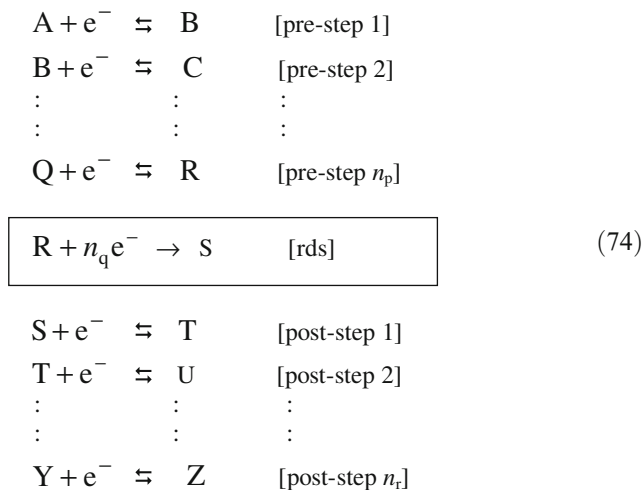
which corresponds to the reaction

$$A + e^- \leftrightarrows B \tag{72}$$

In what follows, we seek to derive the current–voltage curves corresponding to the reaction

$$A + ne^- \leftrightarrows Z \tag{73}$$

In order to keep the equations manageable, we consider the forward and backward parts of the rate-determining step independently. This makes the rate-determining step appear irreversible in both directions. For the most part, we also restrict attention to reaction schemes containing uni-molecular steps (so there are no dimerization steps or higher-order steps). The general approach is due to Roger Parsons [11].

We begin by writing down all the electron transfer reactions steps separately:

$$
\begin{array}{lll}
A + e^- & \leftrightarrows B & \text{[pre-step 1]} \\
B + e^- & \leftrightarrows C & \text{[pre-step 2]} \\
\vdots & \vdots & \vdots \\
Q + e^- & \leftrightarrows R & \text{[pre-step } n_p] \\
\hline
R + n_q e^- & \rightarrow S & \text{[rds]} \\
\hline
S + e^- & \leftrightarrows T & \text{[post-step 1]} \\
T + e^- & \leftrightarrows U & \text{[post-step 2]} \\
\vdots & \vdots & \vdots \\
Y + e^- & \leftrightarrows Z & \text{[post-step } n_r]
\end{array}
\tag{74}
$$

Next, we adopt some simplifying notation. First, we define n_p to be the number of electrons transferred *prior* to the rate-determining step. Then we define n_r to be the number of electrons transferred *after* the rate-determining step. In between, we define n_q to be the number of electrons transferred during one elementary act of the rate-determining step (this is a ploy to ensure that n_q can take only the values zero or one, depending on whether the rate-determining step is a chemical reaction or an electron transfer. This will be convenient later).

Restricting attention to the above system of uni-molecular steps, the total number of electrons transferred is

$$
n = n_p + n_q + n_r
\tag{75}
$$

We now make the following further assumptions. (1) The exchange current of the rate-determining step is at least 100 times less than that of any other step, (2) the rate-determining step of the forward reaction is also the rate-determining step of the backward reaction, (3) no steps are concerted, (4) there is no electrode blockage by adsorbed species, and (5) the reaction is in a steady state. Given these assumptions, the rate of the overall reaction is

$$
\begin{aligned}
I_{total} &= I_0 \left[\exp\left([n_p + n_q \beta_f] \tfrac{F}{RT} \eta \right) - \exp\left(-[n_r + n_q \beta_b] \tfrac{F}{RT} \eta \right) \right] \\
&= I_0 \left[\exp\left(\alpha_f F\eta/RT \right) - \exp\left(-\alpha_b F\eta/RT \right) \right]
\end{aligned}
\tag{76}
$$

In the above expression, α_f should properly be called *the transfer coefficient of the overall forward reaction*, and correspondingly, α_b should properly be called *the transfer coefficient of the overall backward reaction*. But in the literature, they are often simply called *transfer coefficients*.

It may be observed that n_r does not appear inside the first exponential in Eq. 76. This is because electrons that are transferred *after* the rate-determining step serve only to multiply the *height* of the current/overpotential relation and do not have any effect on the *shape* of the current/overpotential relation. For the same reason, n_p does not appear inside the second exponential in Eq. 76.

Although Eq. 76 has the same outward form as the Butler–Volmer equation (Eq. 66), actually the transfer coefficients α_f and α_b are very different from the modified symmetry factors β_f and β_b and should never be confused with them. Basically, α_f and α_b are composite terms describing the overall kinetics of multi-step many-electron reactions, whereas β_f and β_b are fundamental terms describing the rate-determining step of a single electron transfer reaction. Under the assumptions listed above, they are related by the equations

$$
\alpha_f = n_p + n_q \beta_f
\tag{77}
$$

and

$$
\alpha_b = n_r + n_q \beta_b
\tag{78}
$$

A century of electrochemical research is condensed into these equations. And the key result is this: if the rate-determining step is a purely chemical step (i.e. *does not* involve electron transfer), then $n_q=0$, and the modified symmetry factors β_f and β_b disappear from the equations for α_f and α_b. Conversely, if the rate-determining step is an electrochemical step (i.e. *does* involve electron transfer), then $n_q=1$, and the modified symmetry factors β_f and β_b enter the equations for α_f and α_b. Also, in passing, we remark that α_f and α_b differ from β_f and β_b in another important respect. The sum of β_f and β_b is

$$
\beta_f + \beta_b = 1
\tag{79}
$$

whereas the sum of α_f and α_b is

$$
\alpha_f + \alpha_b = n
\tag{80}
$$

That is, the sum of the transfer coefficients of the forward and backward reactions is not necessarily unity. This stands in marked contrast to the classic case of a single-step one-electron transfer reaction, for which the sum is always unity. Furthermore, in systems where the rate-determining steps of the forward and backward reactions are not the same—a common occurrence—the sums of α_f and α_b have no particular diagnostic value.

Regarding experimental measurements, the analysis of Tafel slopes [12] is generally performed by evaluating the expression

$$\alpha_f \text{ or } \alpha_b = \frac{2.303RT}{F} \left(\frac{\partial \log|I|}{\partial \eta} \right) \qquad |I| > I_0 \qquad (81)$$

Such an analysis should be treated with great caution, however, since both precision and accuracy require the collection of data over more than two orders of magnitude of current, with no ohmic distortion, no diffusion control and no contributions from background currents. The kinetics should also be in a steady state. Accordingly, no experimental "Tafel slope" should be believed that has been derived from less than two orders of magnitude of current.

The theoretical analysis of multi-step reactions is also difficult. On one hand, the number of possible mechanisms increases rapidly with the number of electrons transferred, which makes the algebra complex. On the other hand, the assumption that the exchange current of the rate-determining step is 100 times less than that of all other steps is not necessarily true, and hence, there is always a danger of over-simplification. To steer a course between the Scylla of complexity and the Charybdis of over-simplification, we here restrict our attention to quasi-equilibrated reduction reactions for which the number of mechanistic options is small. To simplify our analysis further, we write β_f in the form

$$\beta_f = \frac{1}{2} \left(1 - \frac{F\eta}{2\lambda_m} \right) = \tfrac{1}{2}(1 - \Delta) \qquad (82)$$

We also write 2.303 $RT/F \approx 60$ mV at 25 °C (actually, the precise value is 59.2 mV).

In what follows, the rate-determining step is indicated by the abbreviation "rds". Steps that are not rate-determining are labelled "fast" (though of course in the steady state all steps proceed at the same rate). As a shorthand method of uniquely identifying component steps of reaction schemes, we also adopt the following notation: E indicates an electrochemical step, C indicates a chemical step, D indicates a dimerization step, and a circumflex accent (^) indicates a rate-determining step.

Example 1 $\left(\widehat{E} \right)$

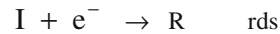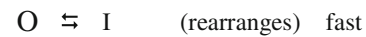$$O + e^- \quad \rightarrow \quad R \quad \text{rds}$$
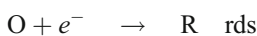
In this case, $n_p=0$, $n_q=1$, $n_r=0$
so that $\alpha_f = n_p + n_q\beta_f \approx \tfrac{1}{2}(1 - \Delta)$, and

$$\frac{\partial \eta}{\partial \log|I|} = \frac{2.303RT}{\alpha_f F} \approx \frac{120}{(1 - \Delta)} \text{ mVdecade}^{-1} \qquad (83)$$

This is the classical result for a single-step one-electron transfer process. Note that fast chemical equilibria before or after the rate-determining step have no effect on the Tafel slope, as the next two examples confirm.
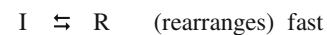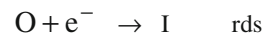
Example 2 $\left(C\widehat{E} \right)$

$$O \quad \leftrightarrows \quad I \qquad \text{(rearranges)} \quad \text{fast}$$

$$I + e^- \quad \rightarrow \quad R \qquad \text{rds}$$

In this case, $n_p=0$, $n_q=1$, $n_r=0$
so that $\alpha_f = n_p + n_q\beta_f \approx \tfrac{1}{2}(1 - \Delta)$, and

$$\frac{\partial \eta}{\partial \log|I|} = \frac{2.303RT}{\alpha_f F} \approx \frac{120}{(1 - \Delta)} \text{ mVdecade}^{-1} \qquad (84)$$
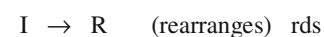
Example 3 $\left(\widehat{E}C \right)$

$$O + e^- \quad \rightarrow \quad I \qquad \text{rds}$$

$$I \quad \leftrightarrows \quad R \qquad \text{(rearranges)} \quad \text{fast}$$

In this case, $n_p=0$, $n_q=1$, $n_r=0$
so that $\alpha_f = n_p + n_q\beta_f \approx \tfrac{1}{2}(1 - \Delta)$, and

$$\frac{\partial \eta}{\partial \log|I|} = \frac{2.303RT}{\alpha_f F} \approx \frac{120}{(1 - \Delta)} \text{ mVdecade}^{-1} \qquad (85)$$
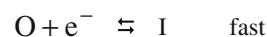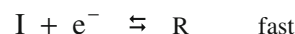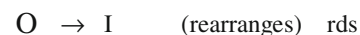
Example 4 $\left(E\widehat{C} \right)$

$$O + e^- \quad \leftrightarrows \quad I \qquad \text{fast}$$

$$I \quad \rightarrow \quad R \qquad \text{(rearranges)} \quad \text{rds}$$

In this case, $n_p=1$, $n_q=0$, $n_r=0$
so that $\alpha_f = n_p + n_q\beta_f = 1$, and

$$\frac{\partial \eta}{\partial \log|I|} = \frac{2.303RT}{\alpha_f F} \approx 60 \text{mVdecade}^{-1} \text{independent of } \beta_f. \qquad (86)$$

Example 5 $\left(\widehat{C}E \right)$

$$O \quad \rightarrow \quad I \qquad \text{(rearranges)} \quad \text{rds}$$

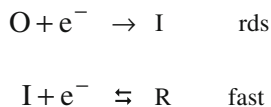$$I + e^- \quad \leftrightarrows \quad R \qquad \text{fast}$$

In this case, $n_p=0$, $n_q=0$, $n_r=1$
so that $\alpha_f = n_p + n_q\beta_f = 0$, and

$$\frac{\partial \eta}{\partial \log|I|} = \frac{2.303RT}{\alpha_f F} \approx \infty \, \text{mV decade}^{-1} \text{independent of } \beta_f. \quad (87)$$

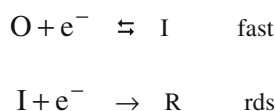Note: the current is independent of potential and is known as a *kinetic current*.

Example 6 $\left(\widehat{EE}\right)$

$$O + e^- \;\rightarrow\; I \qquad \text{rds}$$

$$I + e^- \;\leftrightarrows\; R \qquad \text{fast}$$

In this case, $n_p=0$, $n_q=1$, $n_r=1$
so that $\alpha_f = n_p + n_q \beta_f \approx \frac{1}{2}(1 - \Delta)$, and

$$\frac{\partial \eta}{\partial \log|I|} = \frac{2.303RT}{\alpha_f F} \approx \frac{120}{(1 - \Delta)} \, \text{mV decade}^{-1} \quad (88)$$
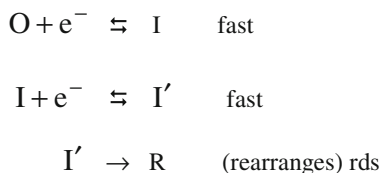
Example 7 $\left(E\widehat{E}\right)$

$$O + e^- \;\leftrightarrows\; I \qquad \text{fast}$$

$$I + e^- \;\rightarrow\; R \qquad \text{rds}$$

In this case, $n_p=1$, $n_q=1$, $n_r=0$
so that $\alpha_f = n_p + n_q \beta_f \approx 1 + \frac{1}{2}(1 - \Delta)$, and

$$\frac{\partial \eta}{\partial \log|I|} = \frac{2.303RT}{\alpha_f F} \approx \frac{40}{\left(1 - \frac{\Delta}{3}\right)} \, \text{mV decade}^{-1} \quad (89)$$
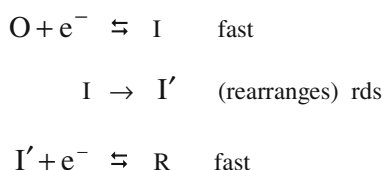
Example 8 $\left(EE\widehat{C}\right)$

$$O + e^- \;\leftrightarrows\; I \qquad \text{fast}$$

$$I + e^- \;\leftrightarrows\; I' \qquad \text{fast}$$

$$I' \;\rightarrow\; R \qquad \text{(rearranges) rds}$$

In this case, $n_p=2$, $n_q=0$, $n_r=0$
so that $\alpha_f = n_p + n_q \beta_f = 2$, and

$$\frac{\partial \eta}{\partial \log|I|} = \frac{2.303RT}{\alpha_f F} = 30 \, \text{mV decade}^{-1} \text{independent of } \beta_f. \quad (90)$$

Example 9 $\left(E\widehat{C}E\right)$

$$O + e^- \;\leftrightarrows\; I \qquad \text{fast}$$

$$I \;\rightarrow\; I' \qquad \text{(rearranges) rds}$$

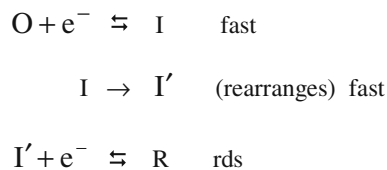$$I' + e^- \;\leftrightarrows\; R \qquad \text{fast}$$

In this case, $n_p=1$, $n_q=0$, $n_r=1$
so that $\alpha_f = n_p + n_q \beta_f = 1$, and

$$\frac{\partial \eta}{\partial \log|I|} = \frac{2.303RT}{\alpha_f F} = 60 \, \text{mV decade}^{-1} \text{independent of } \beta_f. \quad (91)$$

Note: 60 mV decade^{-1} Tafel slopes are very common for the reduction reactions of organic molecules containing double bonds because as soon as the first electron is "on board", there are many opportunities for structural rearrangement compared with inorganic molecules. This rearrangement is usually rate determining.
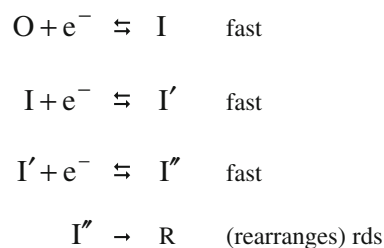
Example 10 $\left(EC\widehat{E}\right)$

$$O + e^- \;\leftrightarrows\; I \qquad \text{fast}$$

$$I \;\rightarrow\; I' \qquad \text{(rearranges) fast}$$

$$I' + e^- \;\leftrightarrows\; R \qquad \text{rds}$$

In this case, $n_p=1$, $n_q=1$, $n_r=0$
so that $\alpha_f = n_p + n_q \beta_f \approx 1 + \frac{1}{2}(1 - \Delta)$, and

$$\frac{\partial \eta}{\partial \log|I|} = \frac{2.303RT}{\alpha_f F} \approx \frac{40}{\left(1 - \frac{\Delta}{3}\right)} \, \text{mV decade}^{-1} \quad (92)$$
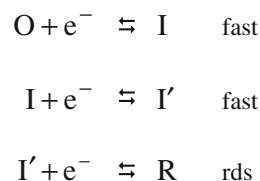
Example 11 $\left(EEE\widehat{C}\right)$

$$O + e^- \;\leftrightarrows\; I \qquad \text{fast}$$

$$I + e^- \;\leftrightarrows\; I' \qquad \text{fast}$$

$$I' + e^- \;\leftrightarrows\; I'' \qquad \text{fast}$$

$$I'' \;\rightarrow\; R \qquad \text{(rearranges) rds}$$

In this case, $n_p=3$, $n_q=0$, $n_r=0$
so that $\alpha_f = n_p + n_q \beta_f = 3$, and

$$\frac{\partial \eta}{\partial \log|I|} = \frac{2.303RT}{\alpha_f F}$$

$$= 20 \, \text{mV decade}^{-1} \text{independent of } \beta_f. \quad (93)$$

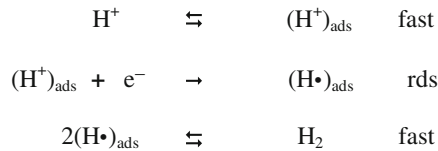**Example 12** $\left(EE\widehat{E}\right)$

$$O + e^- \;\leftrightarrows\; I \qquad \text{fast}$$

$$I + e^- \;\leftrightarrows\; I' \qquad \text{fast}$$

$$I' + e^- \;\leftrightarrows\; R \qquad \text{rds}$$

In this case, $n_p=2$, $n_q=1$, $n_r=0$
so that $\alpha_f = n_p + n_q \beta_f \approx 2 + \frac{1}{2}(1 - \Delta)$, and

$$\frac{\partial \eta}{\partial \log|I|} = \frac{2.303RT}{\alpha_f F} \approx \frac{24}{\left(1 - \frac{\Delta}{5}\right)} \text{ mV decade}^{-1} \qquad (94)$$

Example 13 $\left(C\widehat{E}D\right)$

H^+	$\leftrightarrows$	$(H^+)_{ads}$	fast
$(H^+)_{ads} + e^-$	$\rightarrow$	$(H\bullet)_{ads}$	rds
$2(H\bullet)_{ads}$	$\leftrightarrows$	H_2	fast

In this case, n_p=0, n_q=1, n_r=0, but the presence of the follow-up dimerization step means that the total number of electrons per molecule of product $n = 2(n_p + n_q) + n_r = 2$. However, the dimerization step has no effect on the rate of the reaction, so that $\alpha_f = n_p + n_q \beta_f \approx \frac{1}{2}(1 - \Delta)$, and

$$\frac{\partial \eta}{\partial \log|I|} = \frac{2.303RT}{\alpha_f F} \approx \frac{120}{(1 - \Delta)} \text{ mV decade}^{-1} \qquad (95)$$
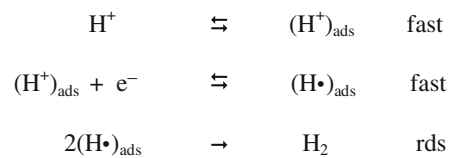
Notes:

(1) This is a candidate model for hydrogen evolution on mercury.
(2) The formation of $(H\bullet)_{ads}$ is slow, and the destruction of $(H\bullet)_{ads}$ is fast. Hence, the electrode surface has a *low coverage* of adsorbed hydrogen radicals.
(3) For simplicity, we have written the hydrogen ion H^+ instead of the hydronium ion H_3O^+.
(4) In the last stage of the reaction, we have assumed that $(H\bullet)_{ads}$ is mobile on the electrode surface, so the mutual encounter rate of $(H\bullet)_{ads}$ species is fast.
(5) At low rates of reaction, the H_2 produced is present in solution as $H_2(aq)$. At high rates of reaction, the H_2 nucleates as bubbles and evolves as a gas.
(6) This mechanism is not one of the textbook mechanisms. The closest textbook mechanism is the "Volmer mechanism", which assumes a *concerted* electron transfer and proton transfer:

$$H^+ + e^- \rightarrow (H\cdot)_{ads} \qquad (96)$$

Recall that two reactions are said to be *concerted* if the overall rate of reaction through their merged transition state is faster than the rate through their separate transition states. Because the Volmer mechanism posits simultaneous electron and nuclear motions, it violates the Frank–Condon principle. However, this is not to say that it does not occur in reality, because H^+ has a low rest mass compared with all other chemical species.

Example 14 $\left(C\widehat{ED}\right)$

H^+	$\leftrightarrows$	$(H^+)_{ads}$	fast
$(H^+)_{ads} + e^-$	$\leftrightarrows$	$(H\bullet)_{ads}$	fast
$2(H\bullet)_{ads}$	$\rightarrow$	H_2	rds

In this case, n_p=1, n_q=0, n_r=0, but the presence of the rate-determining dimerization step means that the total number of electrons per molecule of product $n = 2(n_p) + n_q + n_r = 2$. The overall rate of reaction now depends on the square of the concentration of $(H\bullet)_{ads}$, so that $\alpha_f = 2(n_p) + n_q \beta_f = 2$ and

$$\frac{\partial \eta}{\partial \log|I|} = \frac{2.303RT}{\alpha_f F}$$

$$= 30 \text{ mV decade}^{-1} \text{ independent of } \beta_f. \qquad (97)$$

Notes:

(1) This is a candidate model for hydrogen evolution on palladium hydride.
(2) This mechanism is known in the literature as "The Tafel Mechanism".
(3) A *low coverage* of the electrode is assumed again. However, on this occasion, such an assumption possibly conflicts with the fact that the formation of $(H\bullet)_{ads}$ may be fast and the destruction of $(H\bullet)_{ads}$ may be slow. If that occurs, a more complex reaction scheme has to be considered to take into account the coverage by intermediates.
(4) The hydrogen evolution reaction exemplifies the *metal electrode material effect*. This effect occurs when an electrode surface stabilizes an intermediate that is unstable in solution and thus enhances the overall rate (i.e. decreases the overpotential). In the present case, the palladium surface strongly stabilizes H•, and so its hydrogen overpotential is very low. By contrast, the mercury surface only weakly stabilizes H•, and so its hydrogen overpotential is very high. [The instability of H•(aq) is evident from the standard potential of its formation from H^+, about −2.09 V vs SHE, so free H• (aq) never appears at "normal" potentials between 0 and −2.0 V vs SHE.]
(5) An alternative formulation of the metal electrode material effect is the following: *If the same overall reaction occurs faster at one electrode material than another, then the faster reaction necessarily involves an adsorbed intermediate.* This is, in fact, a very clever way of "observing" short-lived intermediates without using fancy apparatus! However, to be certain that a reaction genuinely involves an adsorbed

intermediate, the overpotential of the faster case should be at least kT/e (25.7 mV) less than that of the slower case to ensure that the difference is not due to minor differences in the density of states at the Fermi energy of the electrodes.

(6) At low rates of reaction, the H_2 produced is present in solution as $H_2(aq)$.

Summary

Table 1 Tafel slopes for multistep electrochemical reactions

Reaction scheme	Tafel slope b (mV decade^{-1})
$\widehat{C}E$	∞
$\widehat{C}ED$	∞
$\widehat{E}$	$120/(1-\Delta)$
$\widehat{E}E$	$120/(1-\Delta)$
$\widehat{E}EE$	$120/(1-\Delta)$
$\widehat{E}C$	$120/(1-\Delta)$
$\widehat{E}CE$	$120/(1-\Delta)$
$C\widehat{E}$	$120/(1-\Delta)$
$C\widehat{E}D$	$120/(1-\Delta)$
$E\widehat{C}$	60 exactly
$E\widehat{C}E$	60 exactly
$E\widehat{E}$	$40/(1-\Delta/3)$
$E\widehat{E}E$	$40/(1-\Delta/3)$
$EC\widehat{E}$	$40/(1-\Delta/3)$
$EE\widehat{C}$	30 exactly
$CE\widehat{D}$	30 exactly
$EE\widehat{E}$	$24/(1-\Delta/5)$
$EEE\widehat{C}$	20 exactly

E indicates an electrochemical step, C indicates a chemical step, D indicates a dimerization step, and a circumflex accent (^) indicates a rate-determining step. The word "exactly" is intended to signify "a result independent of β"

Conclusions

Tafel slopes for multistep electrochemical reactions have been derived from first principles (Table 1). Whilst no claim is made that individual results are original (indeed most of them are known), their derivation en masse has allowed us to identify the assumptions that they all have in common. Thus, the four standard assumptions of electrochemical theory that emerge are: (1) there is weak orbital overlap between reactant species and electrodes, (2) the ambient solution never departs from thermodynamic equilibrium, (3) the fluctuations that trigger electron transfer are drawn from a Gaussian distribution, and (4) there is quasi-equilibrium of all reaction steps other than the rate-determining step.

Finally, we reiterate that the Butler–Volmer equation fails at high overpotentials. The rigorous replacement is Eq. 64, although traditionalists may prefer to retain the old formula by applying the corrections given by Eqs. 67 and 68.

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