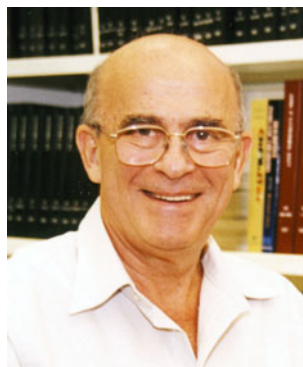


Problems in interfacial electrochemistry that have been swept under the carpet

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Abstract A critical view of interfacial electrochemistry in the past 50 years is discussed, with emphasis on tacit assumptions, which are sometimes hard to justify. The important role of the Tafel equation in studies of the mechanism of electrode reactions and in the development of electrode kinetics in the past century is recognized. However, it is shown that the validity of the ways it was implemented can be questioned, particularly in view of the uncertainty in the value of the symmetry factor commonly assumed. For example, the value of β pertinent to a species in the outer-Helmholtz plane cannot be the same as that applicable to a species already adsorbed on the surface. Three factors are involved in considering charge transfer to an adsorbed species: (a) The electrostatic field at the adsorption site is highly distorted; thus, the overpotential imposed may not apply at the point

where the reaction takes place; (b) the effective charge on the adsorbed species may not equal the nominal charge assigned to it; and (c) the metal surface may already be modified by a monolayer of adsorbed species of the same kind, which is, however, inactive with respect to the reaction taking place. Similarly, in studies of the kinetics of metal deposition and dissolution, where charge is transferred across the interface by the ions, one cannot legitimately assume a value of β , although it can be measured experimentally. It is very risky to predict the future of interfacial electrochemistry, but one might extrapolate present trends. Thus, the importance of the fundamental aspects of the field may have declined in the past two or three decades, and this trend will probably continue. On the other hand, the importance of *understanding interfacial electrochemistry* as a basis for related fields such as nano-science, biology, micro- and nano-implanted biosensors, interaction of tissue with metal implants, materials science, as well as technologies such as corrosion and alloy plating is likely to increase.

Keywords Tacit assumptions · The symmetry factor · Charge transfer · Adsorbed species · Discreteness of charge

Introduction

This is a very special volume of the *Journal of Solid-State Electrochemistry* and probably of any other journal. Correspondingly, my contribution to this journal is also different from any other paper I have published so far. It is obviously not a regular research article nor is it a review. It is a highly personal view of the way I followed the development of *Electrode Kinetics*, or more generally *Interfacial Electrochemistry*, in the past 50 years, since I was first introduced to it.

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I suppose that interfacial electrochemistry is not the only field of science in which tacit assumptions are made, some that can readily be justified and some that are dubious or totally wrong. Being an electrochemist, I shall stay in my home base where I can, hopefully, distinguish between right and wrong. Here I shall discuss some of the tacit assumptions that I consider dubious, or outright incorrect. I have been aware of some of the problems discussed below for quite a while. At one point I suggested to some leading electrochemists to establish an annual symposium on “Unsolved Problems in Interfacial Electrochemistry,” but I could not find anybody who would pick up the glove. This special issue of the *Journal of Solid-State Electrochemistry* may be a good opportunity to air my thoughts about some of the problematic issues in interfacial electrochemistry, even though I cannot offer a solution to most of them.

I shall avoid making this a polemic paper, as much as possible. A tacit assumption is by definition tacit, namely quiet, un-noticed, or knowingly ignored. I shall point out problems, without making reference to specific papers. If my view is accepted, then there were many of us making the mistakes (including myself, of course) and I should not single out one or a few authors who were wrong. My purpose is not to show someone wrong, rather I would like to shine the light on some yet unsolved problems, hoping that there will be some bright young scientists out there who would be encouraged to solve them.

The first law of electrode kinetics

I arrived in Ottawa, Canada in August of 1960, to start my studies toward a Ph.D. in electrochemistry, under the supervision of (the late) Prof. Brian Conway. The first thing I learned was the Tafel equation

$$\eta = a - b \log j \quad (1)$$

which we called then *the first law of electrode kinetics*. Brian had a strong background in physical chemistry, and he was hoping, I think, to find the second and third laws of electrode kinetics, mimicking the three laws of thermodynamics. But that did not happen, and the Tafel equation remained just that. The more elegant name did not stick.

Another unsuccessful attempt to rename the field was made in the mid-1960s by Bockris. He suggested using the term *Electrodics* for what we call these days *Interfacial Electrochemistry* and *Ionics* for what we call *Solution Electrochemistry*. In retrospect, it was not a bad idea, but by that time he had already generated so much antagonism, that his suggestion was by and large ignored.

It should be noted that the main interest of Tafel, who first suggested the relationship shown in Eq. 1, was not electrochemistry. He was doing organic synthesis and used

electrochemistry as a tool. Most oxidation and reduction processes in organic chemistry do not follow the linear Tafel relationship. But Tafel studied also hydrogen evolution on mercury and on lead in acid solutions, where his equation does apply. It was his deep insight that must have led him to propose that the linear relationship between the overpotential, η , and the logarithm of the current density, j , was the meaningful correlation, and all other observations represented deviation from the rule, even though they may have been the majority.¹

Next I learned how to calculate the Tafel slope for any assumed mechanism. This was done assuming that the symmetry factor, β , is one half. In some carefully written papers, it was noted that β is not exactly one half, just close to it, but in the analysis of the mechanism of a reaction involving the transfer of several electrons, it was assumed to be 0.5.

For a single-step, one-electron charge-transfer reaction, the symmetry factor is related to the Tafel slope in the literature as

$$b = \frac{2.3RT}{\beta F} \quad (2)$$

On the other hand, the quantity one measures is the transfer coefficient, α , which is properly defined by the empirical equation

$$\left(\frac{\partial \eta}{\partial \log j} \right)_{\mu, T, P} = \frac{2.3RT}{\alpha F} \quad (3)$$

As we can see in Eq. 3, the transfer coefficient is the inverse Tafel slope in dimensionless form. Admittedly the numerical values of α and β may be equal for certain mechanisms, but it cannot be overemphasized that α is an experimentally observed parameter, while β is a fundamental property of the reaction, which can, at least in principle, be evaluated from theory or assumed based on some tentative model.

In addition to assuming a value of about 0.5 for β , it was tacitly assumed in those days that the symmetry factor was a constant, independent of the overpotential and of temperature. These assumptions are hard to justify theoretically, but they are observed experimentally in certain cases, as we shall see below.

Occasionally, mechanistic conclusions were based on unsatisfactory experimental measurements of α , or by stretching the validity of linearity of the Tafel plot. For example, sometime in the mid-1960s I was highly disappointed when one of the noted electrochemists in the world at the time published a paper regarding the mechanism of hydrogen evolution and reported a Tafel

¹ Politicians often like to use this logic when they lose an election, claiming that the minority may be right. They may indeed be right, but I have yet to see a politician who won the election adhering to this wise observation.

slope of $b=97$ mV, claiming that this was close enough to 118 mV to prove that the first electron-transfer step was rate determining, according to the simple equation



A discussion of the value of the symmetry factor and its possible dependence on overpotential is given below.

The “discreteness of charge” effect

Interfacial electrochemistry is usually discussed as a one-dimensional problem. Processes like charge transfer, monolayer adsorption, and double-layer capacitance all occur on a scale of less than 1 nm, so that the radius of curvature of the electrode, even if it is a fine wire or a tiny drop, is very large compared to it, justifying this approximation.²

Let us consider, for the purpose of demonstration, the adsorption and oxidation of Br^- on a Pt electrode. We shall assume that the fractional coverage by Br^- is very small (for example, $\theta \leq 0.01$). Even if one assumes that the local capacitance at an occupied adsorption site is significantly different from that at free sites, which is a reasonable assumption, this would have little effect on the observed double-layer capacitance. The capacitance of the different sites is measured in parallel, so that the total capacitance can be written as

$$C_{dl} = C_{(1-\theta)}(1 - \theta) + C_{\theta}\theta \quad (5)$$

where $C_{(1-\theta)}$ and C_{θ} represent the double-layer capacitance of free and occupied sites, respectively. Thus, having a different capacitance over 1% of the surface would not have a significant effect on the total capacitance observed.

On the other hand, when considering an electrochemical reaction, namely a process involving charge transfer, the situation could be quite different. Since the large Br^- ion is known to be specifically adsorbed on the surface of Pt, the first step in the bromine evolution reaction would be



The implicit assumption in formulating the kinetics of electrode reactions and testing them experimentally is that the current density is uniform and the potential varies only in the direction perpendicular to the surface. This is another way to state that the equipotential lines are parallel to the surface. This may be valid over most of the surface, but it is certainly not valid right on top of an adsorbed Br_{ads}^- ion. In fact one would expect a curvature of the equipotential lines, with a maximum deviation right on top of the adsorbed

anion, as shown schematically in Fig. 1. The reaction shown in Eq. 6 occurs only where there is an adsorbed Br_{ads}^- ion. Hence, unlike the case of the double-layer capacitance discussed above, the empty sites do not play a role because the probability of electron transfer taking place declines exponentially with distance. The point is that *electron transfer occurs where the deviation of the potential from its average measured value is a maximum!* Even for the very small value of $\theta \leq 0.01$ assumed here, this could lead to a major error because the overpotential applied to drive the reaction could be quite different from that measured in the external circuit.

A somewhat similar situation, on the macroscopic scale, relates to the positioning of the tip of the Luggin capillary close to the working electrode. The common wisdom is to place it “as close as possible” to the surface, to minimize the uncompensated solution resistance, but there is a problem. The capillary screens the electrode and distorts the uniformity of the current distribution and of the equipotential lines over a region that is estimated to be about three times the outer diameter of the capillary [1]. As in the case discussed above, the information could be grossly distorted because *measurement is made in the region where the deviation of the current density from its average value is a maximum!*³

Which part of the applied overpotential matters?

Let us view the discreteness of charge from another angle. Consider again the first step in the bromine evolution reaction, shown in Eq. 6. The outer-Helmholtz plane (OHP) is determined by the sum of the diameter of a water molecule at the surface of the electrode, plus the radius of the hydrated cations, which amount to about 0.6 nm. The inner Helmholtz plane (IHP) is characterized by the radius of the specifically adsorbed ions. In the case of the Br^- ion, this is about 0.2 nm. Thus, while the overpotential is applied between the metal and the OHP, the part of it that is driving the charge-transfer process is only 0.2/0.6, since the electron is transferred only across one third of the interface. Assuming (arbitrarily) that the activated state is halfway between the initial and the final states, the symmetry factor would hence be $\beta=1/6$. Whatever we assume for the position of the activated state, the value of the symmetry factor in this particular case would have to be in the range of $0 \leq \beta \leq 0.3$, not in the range of $0 \leq \beta \leq 1$, as it is commonly stated.

The concept of charge transfer through only part of the double layer has been discussed in the literature by

² This does not apply to diffusion or solution resistance, for which the characteristic length may be a hundred micrometers or more.

³ The best advice for the experimentalist is to remove the tip of the capillary from the electrode surface far enough to eliminate the screening effect, since modern potentiostats enable electronic compensation for most of the residual solution resistance.

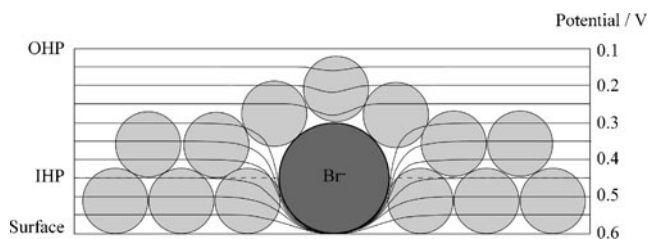


Fig. 1 Schematic representation of the curvature of the equipotential lines near a specifically adsorbed ion (smaller circles represent water molecules)

Frumkin et al., Fawcett, Anson and Rodgers, Weaver and Anson, Kashti et al., and Kashti and Kirowa-Eisner [2–7], for cases where charge is transferred to a species adsorbed on the surface. This species is located inside the double layer, at a plane x , where the potential is ϕ_x , and only a fraction of the potential applied, given by ϕ_x/ϕ_M , is involved in enhancing the rate of charge transfer. This gives rise to a lower value of the symmetry factor, i.e., a higher Tafel slope. It was found, for example, that the reduction of 2-chloro and 4-chloropyridine occurs by the same mechanism, but the Tafel slope is different in the two cases. This was observed only under conditions where the chloropyridine was adsorbed perpendicular to the surface, and the chlorine atom was at a different distance from the metal surface (i.e., the value of ϕ_x/ϕ_M was different). When the pH was set such that the molecule was adsorbed in parallel to the surface, the chlorine atom was located at the same distance from the surface and the Tafel slope observed was the same [7]. Thus, it cannot be argued that this issue has been “swept under the carpet,” although it has been ignored in most studies of the mechanism of formation of molecular chlorine and bromine.

A similar situation is encountered in discussion of the mechanism of deposition of divalent metal. Consider, for example, the electrodeposition of nickel. The steps in the reaction are commonly written as



Followed by



Two tacit assumptions are involved here: (a) It is assumed that electrons are *always* transferred one at a time and (b) that the monovalent nickel ion is highly unstable in solution and it is stabilized by forming a chemical bond with the surface. The validity of the former assumption has been questioned in a recent publication of the present author [8], while the second is valid. If it is assumed that the first step (Eq. 7) is rate determining, one should obtain a Tafel slope of about 0.12 V, assuming that $\alpha = \beta \approx 0.5$, which is indeed observed in certain cases. But what if the second step (Eq. 8) is rate determining. Then, according to most

publications, the first step would be at quasi-equilibrium, written as

$$\frac{\theta}{1-\theta} = K_1 c_b \exp\left(-\frac{F}{RT}\right) \eta \quad (9)$$

followed by

$$j_2 = Fk_2\theta \exp\left[-\frac{\beta F}{RT}\right] \eta \quad (10)$$

where K_1 and k_2 are the equilibrium constant for the first step and the rate constant for the second step, respectively. If it is further assumed that the fractional coverage is low, so that $(1-\theta) \approx 1$, the equation for the overall rate can be written as

$$j = 2FK_1k_2c_b \exp\left[-\frac{(1+\beta)F}{RT}\right] \eta \quad (11)$$

But what is the value of the symmetry factor for the second step? First, it should be obvious that the symmetry factors for the first and second steps cannot be identical because the $\text{Ni}_{\text{soln}}^{2+}$ ion is located at the OHP, a distance of about 0.6 nm from the metal surface, while the Ni_{ads}^+ ion, which is the initial state for the second step, is located very close to the surface, probably even closer than the Br_{ads}^- ion discussed above. For example, assuming that the Ni_{ads}^+ ion is at a distance of 0.15 nm from the metal surface (which is a reasonable estimate for a chemical bond) and further assuming that the activated complex is halfway between the initial and the final states, we obtain a value of $0.075/0.6 = 0.125$; hence, the values of the transfer coefficient and the slope of the Tafel line are

$$\alpha = (1 + \beta) = 1.125 \text{ and } b = 52.4 \text{ mV} \quad (12)$$

as compared to a value of $b = 39$ mV, usually given in the literature.

What is the charge on a specifically adsorbed ion?

A further uncertainty applies to the charge of a specifically adsorbed ion. Can a Br_{ads}^- ion be considered to have a full electronic charge, or has it interacted with the metal surface, reducing its effective charge? Similarly, what exactly is the state of the Ni_{ads}^+ ion that is formed as an intermediate in Eq. 7 above?

When the adsorption of the Br^- ion on mercury is studied in the potential region where the interface behaves like an ideally polarizable interface, the highest value of the fractional coverage observed is $\theta \approx 0.15$. This limitation is attributed to the electrostatic repulsion between ions.⁴ But when molecular

⁴ Note that this explanation is based on the tacit assumption that the Br^- ion adsorbed maintains its charge. Even if this assumption is valid for the case of Hg, it may not be valid for other metals.

Br_2 is generated on a Pt surface, an adsorbed bromine atom is formed as an intermediate. But is this a neutral atom, an ion, or something in between?

The three issues discussed above: (a) the deviation of the potential from its average value at the very point where charge transfer takes place, (b) the dependence of the numerical value of the symmetry factor on the position of the species reacting in a given step, and (c) the effective charge on a specifically adsorbed ion during charge transfer all qualify as “problems being swept under the carpet.” It can be concluded that in many cases, particularly when the reactant is already adsorbed on the surface, or when the rate-determining step involves an adsorbed intermediate, there is no justification for the assumption that $\beta \approx 0.5$.

I would like to note here that the mechanism implied by Eqs. 7 and 8 is, in my view, incorrect in the case of metal deposition and dissolution, because charge is carried across the double layer by the positive ions, not by the electrons, as shown in several recent publications [9–15]. However, this is a controversial issue that is discussed only briefly below.

Electrode reactions rarely occur on the bare metal surface

Interfacial electrochemistry revolves around the structure of the metal–solution interface and the mechanism of charge transfer taking place across it. We discuss the metal–solution potential difference, the capacitance associated with it, the catalytic activity of the metal, and so on. Theories have been proposed, for example, concerning the so-called d-band character of the metal and its effect on its catalytic activity with respect to oxygen evolution and reduction, the relationship between the potential of zero charge and the work function, and so on. But looking at it more carefully, we realize that often electrode reactions do not occur on the bare metal surface. We do not know exactly the reason for this observation, but it is experimentally observed in a number of different cases, some of which are discussed below.

Oxygen evolution

It is safe to state that oxygen evolution has never been observed on a bare metal. One can study this reaction on different metals, of course, but by the time the potential is positive enough to allow oxygen evolution, the metal is already covered with a layer of oxide. This applies to all metals, including the noble metals. Sometimes it is a monolayer, sometimes multi-layers. In some cases, it is a highly conducting oxide; in others, it is a semi-conductor, but oxygen is never evolved on the bare surface of the metal. Borrowing from the field of metal deposition, we

call it “underpotential deposition of oxygen,” but this is not exactly correct. In metal deposition, the first monolayer formed consists of discharged metal atoms, the same as that observed during deposition of thick layers. In contrast, what we call underpotential deposition of oxygen is actually the formation of an oxide or an oxyhydroxide layer, while the product at higher positive overpotentials is, of course, molecular oxygen. But why is it that in all cases it seems thermodynamically easier to form a surface oxide than to form molecular oxygen? Admittedly, the O_2 molecule is very stable, but that could explain why it is so difficult to find an effective catalyst for its reduction, but it should enhance the formation of molecular oxygen, not retard it.

Hydrogen evolution

For the case of hydrogen evolution, the situation is different. Metals can be classified in two groups: those that are poor catalysts for hydrogen evolution (notably Hg, Pb, and some other so-called soft metal)⁵ and those that are highly catalytic, such as Pt, Pd, Ir, Rh, and Re. On Hg and Pb, no hydrogen adsorption has been observed, even at the highest overpotential applied. On Pt and Pd, a complete layer of adsorbed hydrogen is formed, well before the reversible potential for hydrogen evolution is reached. The exchange current density for hydrogen evolution on Pt is about 10 orders of magnitude higher than that on Pb, for example. So, although hydrogen evolution *can be observed on bare metal surfaces*, it is very sluggish. Formation of a monolayer of adsorbed hydrogen is apparently necessary to create a catalytic surface for this reaction. Moreover, in a certain range of low negative overpotential, the kinetics of hydrogen evolution on Pt correspond to a mechanism where first charge transfer is rate determining, and the coverage by adsorbed hydrogen atoms is low. But how could the coverage be low at a negative overpotential, although we know that at the reversible potential for hydrogen evolution there is already a full monolayer of adsorbed hydrogen?

Formation of molecular iodine

In the 1960s, Osteryoung and Anson conducted studies in thin-layer cells (10–50 μm). The small volume of the cells allowed total electrolysis and made it possible to measure the amount of reactant adsorbed on the surface. In their experiments with oxidation of Γ^- , they observed adsorption of the Γ^- ion on the surface, which was expected. However, they also observed that molecular I_2 was formed *from* Γ^-

⁵ In the old literature, they were called “high-overpotential metals”. A better choice would be “low-exchange-current-density metals,” although this sounds rather cumbersome.

ions in the bulk of the solution, not those already adsorbed on the surface. This looked so odd to me at the time that I tried hard to find an error in their argument, but finally I had to throw the towel in—they were right. They might have been the first to prepare (perhaps inadvertently) surface-modified electrodes [16, 17].

The physical reason for these observations has not been discussed in detail in the literature, to the best of my knowledge. It would seem that in all three cases the first monolayer has become a surface compound. It is no longer a layer of I_{ads}^- or H_{ads} or O_{ads} but rather a two-dimensional phase consisting of Pt and the adsorbate. The surface has been modified.

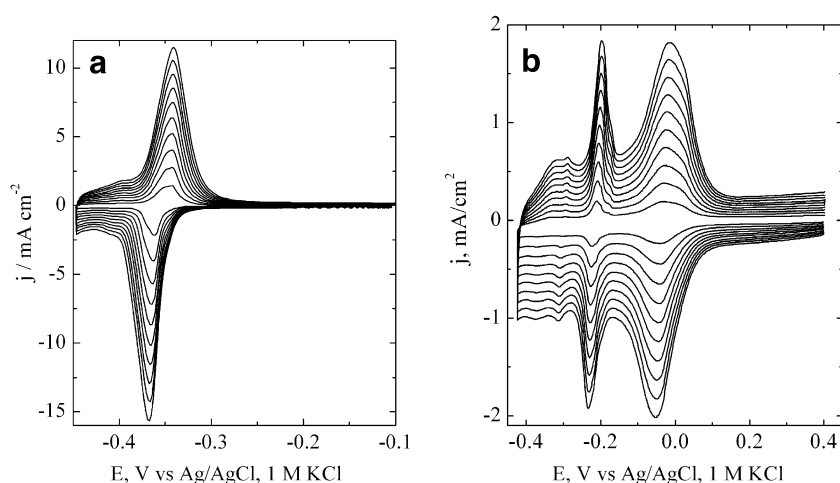
Underpotential deposition of metals

This is a prime example for formation of a monolayer, before bulk deposition starts. It is not a universal phenomenon, but it does happen in many cases of metal deposition. For example, one can form a monolayer of Pb on an Au surface at potentials that are several hundred millivolts positive with respect to the reversible potential for deposition of Pb in the same solution. Underpotential deposition of metals has been studied in great detail, *but some questions have not been asked*.

For example, the cyclic voltammograms of formation of a UPD layer of Pb on silver and on gold are quite different, as shown in Fig. 2. With polycrystalline silver as the substrate, one obtains a very sharp single peak, as seen in Fig. 2a [18]. The Frumkin adsorption isotherm can be fitted to this shape with a fairly strong lateral energy of attraction between adjacent Pb atoms in the UPD layer.

$$\frac{\theta}{1-\theta} \exp\left(\frac{r\theta}{RT}\right) = Kc_b \exp\left(-\frac{EF}{RT}\right) \quad (13)$$

Fig. 2 Underpotential deposition of Pb on polycrystalline **a** silver and **b** gold. $\text{Pb}(\text{NO}_3)_2$ 12 mM, NaCl 10 mM, HNO_3 100 mM. Curves were obtained at sweep rates ranging from 0.10 to 1.0 V/s



where r is the rate of change of the apparent standard Gibbs energy of adsorption with coverage. This parameter is often written in dimensionless form as

$$f \equiv r/RT \quad (14)$$

The width of the cathodic curves at half height is $\Delta E_{1/2} = 29$ mV, corresponding to an attractive lateral interaction energy, characterized by a value of $f = -1.2$, as discussed elsewhere [19]. When gold is used instead of silver, two distinct peaks can be observed. The first is wide, yielding a value of $\Delta E_{1/2} = 100$ mV that fits the same isotherm, with a repulsive lateral interaction parameter of $f = +4.0$. The second peak on gold, which is sharper, shows a value of $\Delta E_{1/2} = 60$ mV, corresponds to a smaller repulsion parameter of $f = +1.0$.

Now, Ag and Au have the same fcc crystal structure and the unit cell dimensions differ only by 0.17%, so why should the lateral energy of interaction between Pb atoms in the UPD layer on the two metals be so different. Moreover, assuming that the two peaks observed on gold correspond to different crystal faces, why should one crystal face give rise to a different lateral interaction energy than the other, for the very same metal? One explanation proposed was that the two metals expose different crystal faces to the solution. But that is a rather weak argument because it leaves us wondering why would different crystal faces be exposed to the solution for the two polycrystalline metals. Moreover, it might be possible to explain the fact that the energy of lateral interaction would be influenced by the density of atoms on different crystal faces, but it is hard to see how it could change sign, from attractive to repulsive interaction.

Single-crystal electrochemistry

Until sometime in the second half of the twentieth century, measurements in electrochemistry were difficult. The

classical work of Grahame on double-layer capacitance on mercury was done with a rather primitive instrumentation, compared to that which is available today (but highly sophisticated for its time). It was hard and tedious work, but the results were accurate and are still being used as a standard against which new measurements could be calibrated.

In those days, measurement of the current to within 0.1% was a challenge and determination of changes of the potential over a range of 1–2 V required switching of scales on an analog voltmeter, which reduced the accuracy. Most of these problems were gradually eliminated with the introduction of digital electronics. At present the limitation on accuracy and on resolution of the measurements is often determined by the chemical stability of the system, not by the quality of the measuring instruments. For example, one could readily measure a potential of 1 V between the working and the reference electrode with an accuracy of $\pm 1 \mu\text{V}$, but the potential of the reference electrode itself changes typically by $\pm 1 \text{ mV}/^\circ\text{C}$ at least. Thus, in order to make use of the high accuracy and resolution of the multimeter, the temperature would have to be controlled to within $\pm 0.001 \text{ }^\circ\text{C}$.

One of the important advances in interfacial electrochemistry that came along with the new digital era was single-crystal electrochemistry. It started with single crystals of Au and Pt and spread to many other metal. Reliable methods for preparing single crystals exposing different crystal faces to the solution were introduced in research laboratories and a little later could be purchased commercially [20–23].

For ideally oriented crystals, one should be able to obtain atomically flat surfaces. In practice, the quality of the orientation determines the size of the terraces, separated by atomic size steps. This can be measured with scanning tunneling microscopy (STM), and terraces on the scale of micrometers (which is very large on the atomic scale) can be prepared in practice. But the excitement about what could be done (and observed by STM) did not generate a similar interest in the interpretation of the data obtained. One day I asked a friend working in this field, why was the behavior on different crystal faces so different? He shrugged his shoulders and said: “well, probably because the density of the atoms is different for each crystal face.” He was right but seemed to be quite uninterested in a deeper understanding of these observations. On another occasion I visited a laboratory where a colleague showed me measurements of the potential of zero charge on about 20 different crystal faces of the same metal. He was very proud of his data, and rightly so. But when I asked him what was the purpose of these measurements or, as I like to put it when a bright and enthusiastic student suggests an experiment, “*what was the question?*” He looked at me

rather puzzled. I just collect the data, he said, you can go ahead and interpret them, if you wish. So, following several years of hard work, we know the value of the potential of zero charge on 20 different crystal faces of a given metal. What can we learn from that concerning the thermodynamics of the metal/solution interface, or the kinetics of charge transfer across it?

It should be noted that this problem is not unique to electrochemistry. The development of instrumentation in the past half century has been meteoric. Things that we would not dream of performing 50 years ago have become routine. Many of us are fascinated with the opportunities of developing new technologies, making new types of measurements and new types of electrodes. A generation hence, if the rate of development of new technologies will slow down asymptotically, there may be time to shift the efforts back to a deeper understanding of the data generated.

Can the Tafel Slope serve as a diagnostic criterion?

Six years ago, we celebrated a century for the publication of the Tafel equation. This equation was undoubtedly a major step in the development of electrode kinetics and was used by most electrochemists as a major source of experimental information, providing data for evaluation of the mechanism of electrode reactions. But the latter was usually done by assuming a value of $\beta \approx 0.5$. Indeed it was commonly noted that, if we remove this restriction and consider the symmetry factor as an adjustable parameter (still in the range of $0 \leq \beta \leq 1$), we would be in “no-man’s land,” in the sense that just about any mechanism could be forced to fit the experimental data. In the complex case of oxidation of a specifically adsorbed ion discussed above, one should at least have a way of estimating the value of β , based on a reasonable model. For example, in the situation discussed in “The “discreteness of charge” effect,” the symmetry factor should be much less than 0.5, and it should decrease with decreasing size of the adsorbed ion, in the order of Γ^- , Br^- , and Cl^- . This, to the best of my knowledge, has neither been discussed nor tested experimentally. The uncertainty regarding the true value of the symmetry factor makes the mechanism based on the assumption that $\beta = 0.5$ at least dubious, if not totally unreliable.

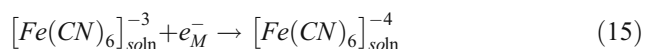
Charge transfer and mass transport

It should be recognized that charge transfer can be of (at least) three different kinds: (a) outer-sphere charge transfer, in which the only species crossing the interface are electrons; (b) metal deposition, in which mass crosses the

interface, carrying the charge with it; and (c) cases where charge crosses only a fraction of the interface

Outer-sphere electron transfer

A representative case for this is the ferri/ferrocyanide system, which has been studied in the literature in great detail.



On the face of it, the only thing that happens in this reaction is an electron transfer. No bonds are broken and no new bonds are formed, but the outer solvation shell of the ion is modified by the change in its charge. The subscript “soln” indicates that the molecule is on the solution side of the interface, at the OHP, which represents the distance of closest approach of a hydrated ion to the surface.

The theory of electron transfer published by Marcus in 1956 [24] and refined in later publications by him [25, 26] and by the group of Dogonadze, Dogonadze and Chismadzhev, and Levich [27–29] made it possible to calculate the symmetry factor. However, it is important to note that the numerical value derived from this theory is not exactly 0.5. Moreover, the theory predicts that it would be a function of the overpotential applied, following the equation

$$\beta = \frac{1}{2} + \frac{\Delta G^0}{2\lambda} - \frac{F|\eta|}{4\lambda} \quad (16)$$

where λ is the solvent reorganization energy and ΔG^0 is the change of the standard Gibbs energy of the overall reaction.

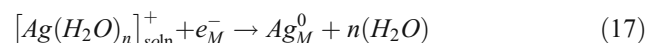
The choice of the value of $\beta \approx 0.5$ was made many years before the development of the theory of Marcus, by Butler, Erdey-Gruz, and Volmer, but Eq. 16, derived from the Marcus theory, may have encouraged many of us to conclude that there is a theoretical basis to assume that choosing this value of the symmetry factor was at least a good approximation, even though the Marcus theory made no claim to be applicable to reactions such as metal deposition or hydrogen evolution.

Metal deposition and dissolution

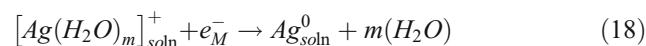
It has been stated by Graham in 1955 and repeated by other noted electrochemists [30–33] that in the process of metal deposition and dissolution, charge is carried across the interface by the metal ion, not by the electrons. Nevertheless, in most mechanistic studies of metal deposition, electron transfer was assumed. In some cases, detailed calculations were made for the movement of a metal ion from the OHP to the metal surface, and then it was assumed

that an electron was transferred. Moreover, the symmetry factor for this electron transfer was taken to be about 0.5, which has no justification, considering that the electron passes (in the framework of this model), from a species already adsorbed on the surface, namely only through a fraction of the distance between the OHP and the surface of the metal, as discussed above. Thus, it is influenced only by a fraction of the overpotential applied. The assumption that the symmetry factor is the same for electron transfer (in outer-sphere charge-transfer reactions) and for metal deposition (where charge is carried by an ion) is not acceptable because the two types of processes represent entirely different physical phenomena. Although in most cases this must have been an implicit assumption, in one particular case it was explicit. In a chapter in one of the well-known series, I found the following (highly disturbing) statement: “although we know that in metal deposition charge is carried across the interface by ions, we shall treat it as if it were electron transfer.” The author did nothing different from what everybody else in the field was doing, except that he was explicit about it.

In a series of publications by the present author [9–15], it was shown that charge transfer in metal deposition and dissolution could not possibly involve electron transfer across the interface. There are a number of arguments to support this statement, which I shall not repeat there, but the physical model is based on the notion of *time-resolved kinetics*. Using deposition of silver as an example, we can write



This implies that electron transfer and movement of the neutral atom formed at the OHP could be considered to be a single step. However, the time scale of electron transfer and atom transfer differ by about 6 orders of magnitude; therefore, electron transfer should occur first, according to the hypothetical reaction



leading to the formation of a highly unstable neutral atom in solution. It was shown that the reversible potential for the process shown in Eq. 18 would be about -2.5 V vs. the reversible potential for silver deposition in the same solution, which corresponds to Eq. 17. Thus, electron transfer is not a possible route for metal deposition.

An alternative mechanism was proposed for treating reactions in which mass is carrying the charge across the interface [11, 13, 14]. It was proposed that the ions move from the OHP toward the metal surface under the influence of the high electrostatic field generated by the overpotential applied. During this process, the ion loses its hydration shell and its effective charge, while it is gradually stabilized

by interaction with the metal surface. If the model proposed in the above publications is accepted, an interesting consequence follows. There are no adsorbed intermediates, even when the ion is divalent or trivalent. The effective charge could decrease gradually from 3+ to 0, but there is no meaning to the point where it happens to have a value of exactly unity. Under these circumstances, one can relate the symmetry factor to the transfer coefficient by the simple equation

$$\alpha = n \times \beta \quad (19)$$

where n is the number of unit charges needed to reduce the ion to the neutral atom. Thus, the value of β is not assumed. It can be obtained directly from measurement of the Tafel slope. The corresponding transfer coefficients can no longer be used as diagnostic criteria for determination of the mechanism. On the other hand, the value of β obtained could be used to estimate the position of the activated complex along the reaction coordinate.

Having been encouraged by the editor to include some anecdotal material or personal impressions and having published already several papers trying to introduce these concepts regarding the mechanism of metal deposition [9–15], I can venture to say that the road was rather bumpy. Several reviewers who tried to prevent publication of my papers on this subject started with a statement such as “I agree with the views presented here but...” The “but” was never a scientific argument. In one case, it was argued that there should be a quantum mechanical calculation included; in another, it was claimed that the journal was not the suitable place to publish this work (although this was one of the mainstream journals in electrochemistry) and so on. This is regrettable but should not be surprising: A new approach to a problem is often rejected at first. I shall be delighted to see someone improving the model I suggested, extending it, making detailed calculations, or offering a different model. But there is one point that cannot be questioned. *The mechanism of metal deposition cannot be derived assuming that charge is carried across the interface by electrons.* Doing that would be sweeping the problem under the carpet.

The unexpectedly high rate of metal deposition

When we compare the rate of typical outer-sphere electron-transfer reactions with that of metal deposition, we would tentatively expect the former to be much higher than the latter. This expectation is derived from the fact that in the former there is no chemical reaction (in the sense of breaking or making chemical bonds) taking place. Equation 15 shows two rather large anions that cause the water molecules in their vicinity to be rearranged somewhat differently than in the bulk. Changing the charge on the ion

can change the extent and nature of this rearrangement, but nothing beyond that. In contrast, metal deposition involves the removal of all the hydration shell of the ion, as shown in Eq. 17 for the case of silver. Now, the energy of hydration of ions can be expressed approximately by

$$U_{\text{hydr}} \approx 5 \times n^2 \text{ eV} \quad (20)$$

For $n=2$, this yields a value of $U_{\text{hydr}} \approx 20$ eV, which corresponds to an average of 5 eV, for the bonding energy of each water molecule, assuming that there are four of them in the hydration shell. Thus, the bonds holding water molecules as ligands are quite strong, similar to chemical bonds.⁶ In comparison, the solvent reorganization energy is usually less than 2 eV. The above expectation is not borne out by experiment, as shown in Table 1. Indeed, experiments performed on mercury (to eliminate the possible effects of surface structure) show that the two types of processes have similar rate constants. The data shown in Table 1 have been performed a long time ago, but the challenge of explaining the reason for what seems to be an unusually high rate constant for metal deposition has not been met. In our previous publications [11, 13, 14], we addressed this problem and suggested a qualitative explanation, but no quantitative answer has yet been given.

Charge transfer from species already adsorbed on the surface

The case of charge transfer to a species adsorbed on the surface has already been discussed above (cf. “The “discreteness of charge” effect” and “Which part of the applied overpotential matters?”), but there is a special case in this category that should be discussed. Consider the deposition of a metal or an alloy from a solution containing a strong complexing agent, such as citrate. The first step in the reaction (performed at pH 8, where the only species derived from citric acid is $\text{Cit}_{\text{soln}}^{-3}$) could be written in the form



or, in the presence of a large excess of the ligand, it could be written as



Both nickel/citrate complexes are large negative ions that may be expected to be adsorbed on the surface. If charge is transferred to this adsorbed complex directly, the arguments

⁶ Removing the first water molecule would require more energy than the average because it represents transition from a stable form of a species to an unstable one, while removing the following water molecules represents changing from one unstable species to another.

Table 1 Comparison of rate constants, showing pairs of outer-sphere charge transfer and for metal deposition on mercury electrodes [34]

The reaction	The heterogeneous rate constant (cm/s)
Pb ²⁺ /Pb	2.0
[Cr(CN) ₆] ^{3-/4-}	0.91
Tl ⁺ /Tl	1.8
[Fe(CN) ₆] ^{3-/4-}	9.0 × 10 ⁻²
Cd ²⁺ /Cd	1.0
Fe ³⁺ /Fe ²⁺	5.3 × 10 ⁻³
Cs ⁺ /Cs	0.20
Ce ⁴⁺ /Ce ³⁺	3.7 × 10 ⁻⁴
Zn ²⁺ /Zn	7.01 × 10 ⁻²
V ³⁺ /V ²⁺	3.21 × 10 ⁻³
Ni ²⁺ /Ni	1.6 × 10 ⁻⁷
Cr ³⁺ /Cr ²⁺	1.01 × 10 ⁻⁵

Where different values are reported for different supporting electrolytes, the highest value is used here

above for oxidation of the Br⁻ ion apply. If, on the other hand, the equilibria shown in Eqs. 21 and 22 are fast and there is a small concentration of hydrated nickel ions at the OHP, charge transfer could occur by this species, following the mechanism for metal deposition in the absence of a complexing agent⁷ The two possibilities would give rise to highly different values of the symmetry factor and the resulting Tafel slopes.

In a series of publications concerning the deposition of nickel/tungsten alloys in our laboratory [35–38], we reached the conclusion that the precursor for deposition of the NiW alloy is a complex containing both metals and citrate, having the form



But we failed to address the role of Ni in making the deposition of W possible. Indeed it is well-known that similar complex of W and citrate do exist, such as



but they cannot act as a precursor for deposition of pure W. In retrospect, it may be speculated that adding the Ni²⁺ ion to the complex increases its size and reduces its charge, allowing the adsorption of the ion shown in Eq. 23 on the surface, even at the negative potentials where NiW alloys are deposited, while the highly negative ion shown in Eq. 24 cannot be adsorbed. Electron transfer to the species

⁷ This is a somewhat problematic statement because the hydrated ion could be considered as a complex, with water molecules as the ligands. The distinction can be justified by considering such “aqua-complexes” as the standard state because of their omnipresence in aqueous solutions.

adsorbed on the surface could then lead to deposition of both metals simultaneously. Unfortunately, measurement of the Tafel slope in such a system would be meaningless because there could be half a dozen reactions taking place in parallel, each having its own reversible potential, rate constant, and Tafel slope. Thus, at any potential set or measured, these parallel reactions would be at different overpotentials. Even if a linear Tafel line would be observed in such a complex system, there would be no way to use the slope of this line to evaluate the mechanism.

Conclusion

The Tafel equation

The centennial of the Tafel equation was celebrated in 2005. There is no doubt that this equation had a major impact on the development of interfacial electrochemistry and the understanding of the mechanism of electrode reactions.⁸ Yet, there are many cases where this equation has been misused and the mechanisms derived employing it were often based on tacit assumptions that could not be supported. As shown above, there is no solid theory for assigning a value of 0.50 to the symmetry factor, and its dependence on potential, which would lead to deviation of the Tafel plot from linearity, cannot be excluded a priori. Even the simple equation,

$$0 \leq \beta \leq 1 \quad (25)$$

which is given in textbooks as an unquestionable truth, independent of the mechanism of the reaction taking place, has its limits. It does not apply to cases where the rate-determining charge-transfer step involves a species that is already adsorbed on the surface. For the case of bromine evolution, the proper expression is

$$0 \leq \beta \leq 0.3 \quad (26)$$

and in more general form, it may be written as [6,7]

$$0 \leq \beta \leq (x_{\text{IHP}}/x_{\text{OHP}}) \quad (27)$$

where $(x_{\text{IHP}}/x_{\text{OHP}})$ is the ratio of the distances from the surface of the metal to the IHP and the OHP.

It was also shown above that for metal deposition and dissolution the value of β cannot be assumed, although it could be determined experimentally. This applies in fact to all cases in which both mass and charge are transferred across the interface, such as corrosion and reactions taking place in some types of batteries. This, as we noted above, is

⁸ Imagine what the number of citations of Prof. Tafel would be, if every paper in the past century mentioning his equation would cite the proper reference!

the result of the time-resolved kinetics, namely the widely different time scales for electron and ion transfer. Thus, while we celebrate the centennial of the Tafel equation, we might consider playing its requiem as well, or at least demoting it from its central importance in interfacial electrochemistry.

Are there truly linear Tafel lines ever observed? The word “truly” is used here to distinguish between a reliable Tafel line, measured over two decades of current density or more, with at least ten experimental points per decade, as opposed to lines based on a small number of experimental point over a short range of current densities. The answer is definitely positive. Careful determination of the current/potential relationship on a hanging–dropping mercury electrode allowed us to determine the Tafel slope based on at least four decades of current density, with about 100–150 experimental point, taken at intervals of 3 mV. In the six-electron reduction of nitromethane and its homologs with up to four carbon atoms [6], as well as the two-electron reduction of chloro-, dichloro-, and dibromopyridine [7], the Tafel lines differed in slope, but they were all strictly linear, with a correlation coefficient of $R \geq 0.9998$. In other studies, the hydrogen evolution reaction [39], the two-electron reduction of hydroxylamine [40], and the six-electron reduction of the bromate ions [41, 42] were studied over a wide range of temperatures (5–95 °C). The Tafel slopes were also strictly linear. Moreover, the transfer coefficient showed no dependence on temperature. The same applied to the six-electron reduction of the iodate ions, but in this particular case the transfer coefficient was found to depend quite strongly on temperature [43]. We could not find a satisfactory explanation for the different behavior of BrO_3^- and the IO_3^- ions. It should be recalled that this does not prove that the symmetry factor is temperature dependent because the measured quantity is, as always, the transfer coefficient. Interestingly, the Tafel slopes of the above reactions were quite different, as might be expected, in view of the difference in the molecules being reduced, and only for the hydrogen evolution reaction was the transfer coefficient close enough to 0.50, in order to assume that it represented the value of the symmetry factor. Yet, they were all independent of potential. But does this prove that the symmetry factor is also independent of potential, bearing in mind that we can only measure the transfer coefficient? For a purist the answer is *no*, but in practice it is *yes*. Thus, even for a single case, it is highly unlikely that β depends on potential, but there is another factor (e.g., change of the degree of coverage by an intermediate) that would compensate for this potential dependence exactly, over four decades of current density, to produce values of α that are entirely independent of potential. The probability of such a coincidence happening for half a dozen totally different processes must be essentially zero.

One tends to be happy when a linear Tafel line is obtained experimentally for a given reaction. This seems to fit our expectations. But in view of the difficulties involved in determining the value of the symmetry factor, which were discussed above, should we not wonder what is common to all these reactions that make the symmetry factor independent of potential? This is of particular interest in view of the different values of α that we find in the above reactions, which may or may not be determined by different values of β .

Past, present, and future

Electrochemists can be rightly proud of the contribution of their field in the past and present. It is a highly multidisciplinary field dealing both with the fundamental science of interfaces: adsorption, charge transfer and electrocatalysis, and with a wide range of engineering processes. These include the vast field of metal winning and purification (production of Al, Mg, Cl_2 , Li, etc.), electroplating, corrosion, electrosynthesis, and more. Batteries became available already in the middle of the nineteenth century, and for one century, two types of batteries dominated the market: the lead acid battery still used in large quantities in cars and the Leclanché primary cell (which has been replaced by the so-called alkaline battery, which is a small variation of it). These have been replaced by Li primary and secondary batteries in the second half of the twentieth century. Batteries are perhaps the most commonly used product that can be associated with the electrochemical industry.

Abner Brenner worked at the National Bureau of Standards (renamed National Institute of Standards and Technology), inventing different processes for electroplating and electroless plating. He was the first to introduce a method for depositing amorphous Ni/P coatings by electroless plating. He was more of an inventor than a scientist, and he certainly had no inferiority feelings in this respect. Taking to him, it seemed that the theory behind his inventions was of lesser importance for him, but he was extremely successful in developing new methods and technologies. On one occasion he told me that all new inventions in electrochemistry (of batteries, plating baths for deposition of metals and alloys, finding suitable additives, and so on) were made by inventors like him. The scientists in universities and research institutes usually moved in later, explaining how and why these technologies work, but they never invented new technologies based on theories they developed. This rather harsh observation was embarrassing, particularly because it is by and large true, even if the word “never” is an exaggeration.

What about the future? The twentieth century is replete with scientific predictions made by highly respected

scientists and engineers, which failed miserably. Can one predict a scientific breakthrough? Certainly not. If we already know about it, it is no longer a breakthrough. My view in this matter is expressed in a little poster in my office that says:

WE CAN PREDICT ONLY THAT WHICH WE
ALREADY KNOW

What this means in practice is that we can only extrapolate, not predict.

Thus, it could be stated, to a good approximation, that the first half of the twentieth century was the period in which quantum theory and relativity were invented and developed. The second half saw the huge impact of the new physical understanding to everyday life. Similarly it could be said that the second half of the twentieth century was the period of the development of molecular biology, and in the first half of the twenty-first century we shall see the implementation of the corresponding technologies to everyday life. This is surely an extrapolation, not a prediction, because we have already seen this process taking place before the turn of the twenty-first century.⁹

Interfacial electrochemistry does not exactly fit into this model. In fact, many important electrochemical technologies (such as batteries and electroplating) were developed already in the nineteenth century or the first half of the twentieth century, mostly by trial and error, before the theory behind them had been developed. But extrapolating present trends to the first half of the twenty-first century is relatively easy. The interest in studying the fundamental aspects of interfacial electrochemistry is declining rapidly. My own graduate students who continued their career in academia consider themselves to be electrochemists, but the next generation is in materials science, nano-technology, corrosion, batteries, sensors, bio-electrochemistry, and some electrochemical aspects of medicine. This may be considered to be unfortunate for electrochemistry, but it does not have to be. All the above fields of research require a solid understanding of the thermodynamic and kinetic properties of the metal–solution interface. The development of a better Li-ion battery involves solid-state chemistry, but one could not really develop any battery without a good knowledge of the electrochemistry involved.

In the future, the role of interfacial electrochemistry in many fields of science and technology may be similar to some extent to that of mathematics: One does not have to

be a mathematician to be a first class chemist or biologist, but it is necessary to know and be able to apply some aspects of mathematics. Similarly, progress in corrosion of all types, hydrogen embrittlement, and batteries can be regarded as a challenge in materials science, but none of them can succeed without a proper understanding of interfacial electrochemistry.

In a discussion of the future of interfacial electrochemistry, it is necessary to discuss batteries and fuel cells on the one hand, compared to bio-electrochemistry on the other hand. The first century after the invention of batteries left us in about 1960 with the alkaline version of the Leclanché cell with a potential of about 1.35 V and the lead acid rechargeable battery delivering just above 2 V. With the introduction of Li-thionyl chloride primary cells and the rechargeable Li-ion batteries, the voltage doubled and the energy density increased by a factor of four or more. But we cannot expect a similar improvement in the next 50 years because at a potential of 4 V for a Li-ion battery, we are already at about 65% of the theoretical limit of voltage of any battery, which is determined by the electromotive series for all the elements. So it can be safely predicted that there will never be a battery with a voltage that is twice that of the present Li-ion battery.

Among fuel cells, the so-called direct methanol fuel cell is presently the most highly funded (and consequently the most intensively studied) fuel cell system. Operating at 0.7 V, it is already at more than half the theoretical maximum voltage, so that doubling the voltage is impossible. In this area, there are several issues that are swept under the carpet, but a discussion of those is outside the scope of the current paper. In contrast to the above, the field of electrochemical devices in biochemistry and medicine is wide open to the imagination, as are the fields of biochemistry, genetic, and medical engineering.

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⁹ Take, for example, the discovery of the double-helix structure of DNA in 1954, which led to the routine use of sequencing in forensic laboratories, to identify a criminal by a very small sample of DNA he may have left behind.

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