ZERO-CHARGE POINTS IN THE EQUATIONS OF ELECTROCHEMICAL KINETICS

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The rate of an electron-transfer reaction is determined both by the electrode potential φ, measured with respect to a comparison electrode, and by the structure of the electrical double layer; the latter, to a first approximation, depends on the electrode potential with respect to the zero-charge potential $\varphi-\varphi_0$. It is shown that knowledge of only a single value of $\varphi-\varphi_0$ is insufficient for comparing reaction rates at different electrodes. The author discusses the effect of hydrogen and oxygen, adsorbed at the electrode surface, on the reaction rate.

In the equations of electrochemical kinetics (which express the reaction rate in terms of the potential, solution composition and electrode type), potentials can be referred either to a fixed comparison electrode, or to the electrode's own zero-charge potential (Antropov's φ-scale [1] or Grahame's rational potential [2]). In this paper I wish to discuss the advantages and drawbacks of various methods of referring to the potential, when comparing the rates of reactions on different electrodes. This is closely connected with the question: is it necessary to introduce the electronic work function at the metal-vacuum interface into the electrochemical kinetic equations? Although the theoretical considerations which I shall set out contain nothing new in principle, I feel that it is necessary to return to this question, since the answers so far proposed are mutually contradictory.

The first expression for an electrochemical reaction rate in which the potentials were referred to the zero-charge point was suggested for the discharge of hydrogen ions on mercury [3]. However, in this case no discussion was given of the effect on the process kinetics of the nature of the metal. Antropov [1] was the first to suggest kinetic relations in which allowance was made for the zero point of electroreduction. According to Bockris and Potter [4], the rates of processes on different electrodes must be compared at the zero-charge potential.

Hydrogen-Ion Discharge. Let us consider the form in which the electrode potential occurs in the equations of electrochemical kinetics. As an example, let us take the often-discussed case of hydrogen ion discharge, in the simplest case when the process rate is determined by the discharge stage at low surface coverage by adsorbed hydrogen. We shall assume that the H_3O^+ ion is neutralized [5, 6]. We shall take the potential in the body of the solution as zero. Let g_H be the standard free energy of desorption of a hydrogen atom from the electrode surface (so that $g_H > 0$), φ the potential of the electrode with respect to that of the solution, and ψ_1 the solution potential at the point occupied by the electrical center of the reacting particle during the transitional stage of the reaction. (A more exact definition of φ will be given below.) The reaction rate is determined by the difference between the standard free energies of the transitional and initial states of the system. This difference is equal to

$$[(1-\alpha)\psi_1F-(1-\alpha)\varphi F-\alpha g_H]-[-\varphi F]=\alpha(\varphi F-\psi_1F-g_H)+\psi_1F_1 \quad (1)$$

so that, according to our assumptions, the charge per mole in the transitional state is equal to $(1-\alpha)F$, the charge on the electrode is $-(1-\alpha)F$, and a fraction α of a mole of H appears on the electrode*; using our assumptions, in the initial state we must allow for the free energy of one mole of electrons at potentials φ. In this elementary discussion

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*The allowance for the non-Coulomb part of the standard free energy of desorption of the transitional state, αg_H, is a very rough approximation, which however does not affect the succeeding conclusions. In what follows, we shall not take account of the dependence of α on the nature of the metal.

we shall not take account for the fact that the electron energy level (Fermi level) depends on the nature of the metal as well as the electrode potential. This will not cause errors, as long as we consider the behavior of only a single metallic electrode, e.g., mercury, as in [6]. However, if we use (1) to compare the electrode behavior of two different metals and assume that φ is the metal-solution potential difference (the Galvani potential), we shall get incorrect results: with two electrodes of different metals, equal Galvani potentials with respect to the same solution will correspond to different electron energy levels. On the other hand, if φ is the potential in some particular metal, e.g., Pt, connected to the electrode metal and in electronic equilibrium with it (i.e., the metal of the connections), equal values of φ will then correspond to a single electron energy level. But in this case φ will differ from the potential, measured with respect to any fixed comparison electrode, by a constant amount which does not depend on the metal of the electrode under investigation. This constant amount is the sum of the Galvani potentials between the solution and the comparison electrode and between the comparison electrode and the platinum.

This conclusion becomes particularly clear if we compare the rates of hydrogen-ion discharge, $\vec{v}$, and of the reverse reaction of ionization of an adsorbed atom, $\overleftarrow{v}$. By (1) we find:

$$\vec{v} = k_1[\mathrm{H}^+]\exp\left\{-\frac{\alpha F}{RT}\left[\varphi + \frac{1-\alpha}{\alpha}\psi_1\right]\right\}\exp(\alpha g_{\mathrm{H}}/RT), \tag{2}$$

where $[\mathrm{H}^+]$ is the hydrogen ion concentration in the solution.

As we stated above, (1) does not allow for the term determined by the chemical potential of the electron in the metal studied. For the potential to the metal of the connections, this term is constant; this leads to the appearance in k_1 of a constant factor independent of the metal. Provided that we remain within the framework of the theory of absolute reaction rates, the other factor in k_1 is kT/h. So k_1 is independent of the nature of the electrode metal.

The difference between the levels of the transitional and final states of the ionization reaction is thus, instead of (1),

$$[(1-\alpha)\psi_1 F - (1-\alpha)\varphi F - \alpha g_{\mathrm{H}}] - [-g_{\mathrm{H}}] = [(1-\alpha)\psi_1 F - (1-\alpha)\varphi F + (1-\alpha)g_H], \tag{3}$$

whence, for $\overleftarrow{v}$,

$$\overleftarrow{v} = k_2[\mathrm{H}]\exp\left\{-\frac{(1-\alpha)F}{\mathrm{RT}}[-\varphi + \psi_1]\right\}\exp((\alpha-1)g_{\mathrm{H}}/RT), \tag{4}$$

where [H] is the surface concentration of H atoms. The constant k_2, like k_1, does not depend on the electrode metal.

Equating $\vec{v}$ and $\overleftarrow{v}$, we obtain the following expression for the equilibrium value of φ:

$$\varphi = \frac{RT}{F}\ln\frac{[\mathrm{H}^+]}{[\mathrm{H}]} + \frac{g_{\mathrm{H}}}{F} + \frac{RT}{F}\ln\frac{k_1}{k_2}. \tag{5}$$

Comparing (5) with the value, obtained from thermodynamics, for the reversible potential of adsorbed hydrogen at atomic concentration [H] and free desorption energy g_{H},

$$\varphi_r = \frac{RT}{F}\ln\frac{[\mathrm{H}^+]}{[\mathrm{H}]} + \frac{g_{\mathrm{H}}}{F} + \mathrm{const} \tag{6}$$

it follows that φ, like φ_r, must be referred to a fixed comparison electrode, and not to the zero-charge point.

The Equations of Electrochemical Kinetics and the Electronic Work Function. We thus have the conclusion that the expression for the discharge kinetics, (2), contains not the potential difference in the double layer at the metal-solution interface, but the potential referred to the auxiliary comparison electrode: its physical meaning becomes clear if we consider that this expression does not contain the work function of an electron in the metal, W_e. In fact, if we replaced φ in (2), referred to a fixed comparison electrode, by $(\varphi - \varphi_0)$, referred to the zero point, we should then have to take account of the difference in the electron energy levels of different metals, and introduce an additional factor containing the work function. Dahms and Bockris [7], when comparing the oxidation rates of ethylene on different metals, following [4], use a factor containing $\alpha W_e F/RT$ in the index. However, we must remember that

$$\exp\left[-\frac{\alpha F}{RT}(\varphi-\varphi_0)\right]\exp\left(-\frac{\alpha W_e F}{RT}\right)=A\exp\left(-\frac{\alpha F}{RT}\varphi\right), \tag{7}$$

(where A ~ const.), as there is an approximate relation between the work function and the position of the zero-charge point,

$$\varphi_0 - W_e = \text{const.} \tag{8}$$

This relation, like the equivalent one between the zero-charge potential difference and the Volta potential, has been repeatedly discussed in the literature (see for example [8-13]). The existence of compensation between the effect of displacement of the zero-charge point and that of change of the work function was first pointed out by the present author (quoted in [14]); this question was also discussed* by Rüetschi and Delahay [13]. In the course of a discussion [16] with Poltorak, who took a different view, Temkin and Frumkin showed that Q, the difference between the heats of discharge of a hydrogen ion at two different metals (measured at the same potential relative to a comparison electrode) is given by the following expression (neglecting the temperature coefficient of the Volta potential between the metals):

$$Q = Q_{\text{I}} - Q_{\text{II}} = u_{\text{I}} - u_{\text{II}}, \tag{9}$$

where u_{I} and u_{II} are the bond energies between an H atom and metals I and II, respectively; the difference between the electronic work functions for metals I and II does not enter this expression.

As (8) is only approximate, the compensation here discussed might be supposed incomplete. However, this is not so. In fact, if we wish to introduce the work function into the equations of electrochemical kinetics as some quantity characteristic of a given metal, we must use, not the work function relative to a vacuum, but the work function W_e^s relative to the solution†. And this is obviously a function of the electrode potential. $\vec{V}$ can depend only on the work function for an electron in the solution at potential φ, which is $\varphi - \varphi_0 + (W_e^S)_{\varphi_0}$. However, at a definite potential φ, measured relative to a fixed comparison electrode, the electron's work function cannot depend on the nature of the metal. On the other hand, the equilibrium between two electrodes in the same solution, and at the same potential relative to a comparison electrode, would be violated if any electron conductivity, however small, appeared in the solution. Hence

$$W_e^s = (W_e^s)_{\varphi_0} + \varphi - \varphi_0 = \text{const} \tag{10}$$

and W_e^S does not depend on the nature of the metal.

The same conclusion can be arrived at by various other routes. Consider a circular process in which an electron passes from the metal into a vacuum, then from a point near the metal surface to a point near the solution surface, through the solution surface and finally returns to the metal via the metal-solution interface; then we have

$$W_e^s = W_e + V_{\text{Me-}s} - U_e^s, \tag{11}$$

where $V_{\text{Me-s}}$ is the Volta potential between the electrode and solution at a given electrode potential, φ, and U_e^S is the true free energy of hydration of the electron‡.

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* A recent paper [40] by Butler and Makrides also concludes that these effects display mutual compensation.

† Bockris and Wroblowa [17] have recently discussed what kind of work function should be used in the equations of electrochemical kinetics.

‡ Using (11) we can try to estimate W_e^S for mercury. According to Baxendale [41], the total energy gain on hydration of an electron is 1.75 ev. Using this value as a rough approximation in (11) instead of V_e^S, and taking $W_e = 4.52$ and $V_{\text{Me-s}} = -0.26$ at $\varphi = \varphi_0$ (see Randles [42, 43]), we find that at this potential $W_e^S \approx 2.5$ v. From this value, and assuming that the usual laws of metal-vacuum thermionic emission are applicable to the mercury-solution interface, we should expect that for $\varphi - \varphi_0 = -2.2$ v the emission current of electrons into the solution would be of order 10^{-2} a/cm^2. This effect is not in fact observed experimentally; when $\varphi = \varphi_0$, W_e^S must apparently be somewhat greater than 3 v. Of the approximations and assumptions here made, we have not yet been able to determine exactly which are responsible for this discrepancy.

By (11) we can write, for two metals I and II,

$$(W_e^s)_I - (W_e^s)_{II} = (W_e)_I - (W_e)_{II} + V_{Me_I\text{-}Me_{II}} \qquad (12)$$

where $V_{MeI\text{-}MeII}$ is the Volta potential between metals I and II.

Since metals I and II are at the same potential φ relative to a comparison electrode, nothing will be changed by connecting them by means of a metallic conductor. But in this case the r.h.s. of (12) becomes zero, so W_e^s must be independent of the nature of the metal.

Thus φ in (2) must be referred to a fixed comparison electrode. It must be emphasized that this result is derived here without reference to (2) and in fact does not depend on the assumptions made in deriving this equation. If we wish to refer φ to the zero-charge potential, it is convenient to insert in the reaction equation a factor $\exp(-\alpha W_e F/RT)$, as done in [7]*. This correction, however, is in practice made difficult by the unreliability of the data for W_e for most metals. Furthermore, it is approximate, owing to the approximate character of (8). If the reaction-rate measurements are themselves made at the zero-charge potential (this has certain advantages, see below), it is most convenient to compare the results after multiplication by $\exp(\alpha\varphi_0 F/RT)$. In this case, by (2), the nature of the metal influences the resultant value for the rate via g_H, which must be regarded as a measure of the electrochemical activity of the electrode in the discharge of a hydrogen ion with formation of an adsorbed atom. It is incorrect to express the reaction rate by means of relations containing, instead of φ, the potential referred to the zero-charge point, without correction for W_e—as is done, for example, in [18, 19].

These considerations lose their force if, before interacting with the solution, the electron leaving the electrode has to surmount an activation barrier comparable with or greater than W_e^s; this is encountered when we consider a metal covered by a fine film of semiconductor. This case requires special examination [20].

Levich, Dogonadze and Chizmadzhev [21] discuss the way in which the pre-exponential factor k_1 (or k_2) depends on the nature of the metal for the simplest case of a reaction not accompanied by rupture of a chemical bond; they did not make use of the assumptions of the theory of absolute reaction rates. According to these authors, this dependence is apparently not very strong; it never involves the value of W_e.

Electro-Reduction of Anions. Taking the logarithm of the r.h.s. of (2) and generalizing to the case of particles with charge n, we get the following expression for the current density i [22, 23]:

$$\ln i = \alpha(-\varphi F + g)/RT + (\alpha - n)F\psi_1/RT + \ln c + \text{const}, \qquad (13)$$

where c is the concentration of reacting particles and g the non-Coulomb free energy of desorption of the reaction products.

In the absence of concentration polarization, (13) is applicable to an irreversible first-order reaction, provided that the rate-determining stage is electron transfer, specific (non-Coulomb) adsorption of reacting particles is absent, and the surface coverage of the electrode by reaction products is small. As shown above, to a first approximation we can neglect the dependence of the constant term on the nature of the metal. The first term on the r.h.s. of (13) contains the value of φ referred to a fixed comparison electrode; this term, as in the theory of the transition complex, takes account of the way in which the kinetics of the electrochemical process depends on its thermodynamics (as accurately as possible without considering the structure of the double layer). The second term, containing ψ_1, expresses the influence of adsorption factors for this very simple case; this term vanishes at the zero-charge point and its values must be almost independent of the nature of the metal at potentials equidistant from the zero charge point (see below). So, by (13), in comparing the behavior of two electrodes it is necessary to make use of both the usual scale of potentials and the scale referred to the corresponding zero-charge point.

When there is no specific adsorption of the reaction products (g = 0), it follows from (13) that

$$\ln i + n\psi_1 F/RT = -\alpha F/RT(\varphi - \psi_1) + \ln c + \text{const.} \qquad (14)$$

By (14), the polarization curve of $\ln i + n\psi_1 F/RT$ versus $(\varphi - \psi_1)$—the corrected Tafel curve—should not in the first approximation depend on the electrode material, as pointed out by Delahay et al. [24]. However, there are as yet few experimental data by which to test this conclusion [23, 24, 25]. The necessity of satisfying the condition g = 0 limits the applicability of this criterion to the reduction of anions at negative electrode charges.

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[*] Dahms and Bockris were discussing oxidation rather than reduction, so they had the opposite sign for W_e.

In considering the convenience of referring the electrode potential to the zero-charge potential, we have so far assumed that, at potentials equidistant from the zero-charge point, ψ_1 is the same or nearly the same for different electrodes, owing to the similar structures of the electrical double layer. A similar assumption is made in other cases when the zero-charge potential is used in electrochemical kinetics. However, an investigation [26] of the electrocapillary behavior of gallium showed that this assumption is not always correct. For example, the difference between the zero-charge potentials of mercury and gallium is 0.51 v, whereas the potentials corresponding to identical, sufficiently high negative charges on the surfaces of mercury and gallium differ by 0.17 v. This phenomenon was explained by the different ways in which the orientation of the water molecules depends on the potentials of these two electrodes. Whether or not this explanation is true, the possibility of such a phenomenon may make it necessary to introduce additional corrections when using the zero-charge potential in electrochemical kinetics.

Reactions Involving Adsorbed Neutral Molecules. Another case which we must discuss is the kinetics of electron transfer to an adsorbed neutral molecule. Let us assume that ψ_1 can be neglected and that the surface coverage is small. The adsorption of organic molecules, plotted against potential at a given concentration in solution, follows a bell-shaped curve with a maximum close to the zero-charge potential, though not in general coinciding with it [27, 28]. Under the above-mentioned conditions, this curve gives [29, 30]:

$$\ln i = -\alpha\varphi F/RT - [2RT\Gamma_\infty(C-C')]^{-1}[C(\varphi-\varphi_0) - C'(\varphi-\varphi_N)]^2 + \ln c + g_m/RT + \text{const}, \tag{15}$$

where Γ_∞ is the limiting adsorption of the initial substance, C the double layer capacity*, C' the double layer capacity when the surface is covered with adsorbed particles, φ_N the zero-charge potential under the same conditions, and g_m the free energy of desorption of adsorbed particles in the transitional stage of the reaction at the potentials corresponding to maximum adsorption†. It would be more correct to refer not only g_m, but also the other quantities in (15) (Γ_∞, φ_N and C'), to the transitional rather than the initial stage of the reaction. However, for particles of appreciable size the error introduced should be small.

The r.h.s. of (15), as well as the first term in φ, measured relative to a fixed comparison electrode, contains also (like (13)) a second term $(\varphi-\varphi_N)$, i.e., in $(\varphi-\varphi_0)$ and depending on the potential relative to the zero-charge points for empty and occupied surfaces. g_m, which comes into the third term, is a measure of the electrochemical activity of the electrode. In this case also, no definite answer can be given to the question of which potentials must be used to compare the kinetics of processes at different electrodes. At potentials equidistant from φ_0 (in particular, at $\varphi = \varphi_0$), adsorption takes place in comparable conditions. However, the rates of electron transfer, referred to a single adsorption value, must be compared at φ = const.; otherwise corrections must be made for the work function of the electrode or for the position of the zero-charge point, as shown above. It is only if the process rate is determined by a preceding chemical stage that the whole picture is revealed by comparing the rates at the zero-charge potentials.

Effect of Adsorption of Particles Which do not Take Part in the Process. Up till now we have not considered the effect which might be exerted on the reacting particles and the electrochemical process kinetics by the presence in the surface layer of foreign adsorbed particles, e.g., halide anions, organic inhibitor cations, etc. In many cases there is a marked relation between the adsorption of these particles and the sign and value of the surface charge, and hence, in explaining the factors determining the kinetics, special attention must be paid to the position of the zero-charge point. As this type of effect has been discussed in several recent papers [1, 6, 31, 32], we need not dwell on it here.

A rather different picture is found in the case of atomic hydrogen and oxygen. Appreciable quantities of these are adsorbed by many electrodes (e.g., platinum) in certain potential ranges. The activity of adsorbed hydrogen and oxygen (or OH radicals) in equilibrium with the solution at a given adsorption energy evidently depends on the electrode potential with reference to a reversible or other comparison electrode in the same solution. The position of the zero-charge point also has an effect, owing to the polarity of the bond between the adsorbed atoms and the metal.

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*The above relation is derived on the assumption that C = const., which is a crude approximation. The adsorption-potential curve for the general case is analysed in [28].

†If g_0 represents the same quantity at $\varphi = \varphi_0$, then in the same approximation

$$g_m = g_0 + \tfrac{1}{2}(C')^2(\varphi_N-\varphi_0)^2/\Gamma_\infty(C-C'). \tag{16}$$

However, although (for example) the adsorption of hydrogen on platinum in acid solutions depends markedly on the structure of the electrical double layer [32, 33], at a given pH the principal value is φ.

Occupation of the surface by adsorbed hydrogen and oxygen hinders adsorption of organic molecules. Reference [34] analyses the thermodynamics of adsorption of an organic substance on a metal with adsorbed hydrogen. The result can be written in the following form:

$$(\partial g_{org} / \partial \varphi)_{\Gamma_{org}} = (\partial q / \partial \Gamma_{org})_{\varphi} - F(\partial A_{H} / \partial \Gamma_{org})_{\varphi}. \tag{17}$$

Here g_{org} is the standard free energy of desorption of the organic substance, q the charge per unit surface, A_H the amount of adsorbed atomic hydrogen not entering the solution as ions (per cm^2), and Γ_{org} the Gibbs adsorption of the organic substance per cm^2 (assuming that $\Gamma_{H_2O} = 0$). Equation (17) was derived on the assumption that the adsorption of the organic substance is reversible: this is sometimes far from the truth when organic substances are adsorbed on metals of the platinum group, but is a necessary assumption for treating the problem by thermodynamics. The first term on the r.h.s. of (17) expresses an effect due to the electrical double layer. This leads to the relations used in deriving (15). However, a rough calculation shows that, if there is appreciable adsorption of hydrogen, the second term should be much larger than the first. Owing to the presence of this term in (17), the adsorption of the organic substance decreases when the surface coverage by hydrogen increases. The adsorption of oxygen causes a similar effect*. We can therefore expect that, for metals which adsorb hydrogen and oxygen, the adsorption of organic molecules will have a maximum at potentials for which the surface coverage by hydrogen and oxygen is a minimum—or at any rate that the potential of maximum adsorption will be displaced from the zero-charge point towards this range of potentials†.

To sum up, we conclude that the electrochemical characteristics of two electrodes can be compared from the electron transfer rates at identical potentials, or from the rate referred to the zero-charge point. In the first of these cases, we must introduce a correction associated with the different adsorption of the reactants or the different ψ_1-potentials for a given φ-potential. In the second case, the adsorption conditions for the two electrodes are made similar; however, for rational comparison of the electron transfer kinetics, we must correct the observed electroreduction rate by means of the factor $\exp(\alpha \varphi_0 F/RT)$. In the latter case, we must also allow for the possible effect of adsorbed hydrogen or oxygen on the adsorption of the reactants.

I should like to thank V. G. Levich, L. I. Krishtalik and B. B. Damaskin for taking part in discussion of this paper‡.

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*For an electrode which reversibly adsorbs oxygen and an organic substance and acts as an oxygen electrode, (17) is replaced by

$$(\partial g_{org} / \partial \varphi)_{\Gamma_{org}} = (\partial q / \partial \Gamma_{org})_{\varphi} + 2F(\partial A_{O} / \partial \Gamma_{org})_{\varphi}, \tag{18}$$

where A_0 is the number of gm-atoms of oxygen adsorbed per cm^2, and not entering the solution as OH^- ions.

† These considerations may in part help to explain the results of Bockris, Green and Swinkels [35], who studied how the adsorption of naphthalene by several metals depends on potential and solution composition. According to these authors, in acid solutions the adsorption maximum lies between 0.1 and 0.4 v w.r.t. a normal hydrogen electrode, depending on the naphthalene concentration, while $\varphi_0 = 0.11$-0.17 [36]. In alkaline solutions the adsorption maximum is at −0.4 v (w.r.t. normal hydrogen electrode); the authors compare this with the results of Kheifets and Krasikov [37], who state that this potential corresponds to the zero charge point. As a matter of fact, for alkaline solutions not containing anions which are strongly adsorbed on platinum, it is impossible to determine the zero-charge point in the usual sense of the phrase, as the surface charge remains negative between −0.7 and +0.5 v (the electrode adsorbs cations), and the potential seems to be mainly determined by the dipole moment of the bond between the platinum and chemisorbed hydrogen and oxygen atoms [36, 38]. At any rate, this conclusion is unavoidable if we are not to ascribe a high specific adsorbability to the OH^- ion.

‡ When this paper was already in the press, Dr. Parsons kindly allowed me to see his article [39], the results in which although arrived at by a somewhat different route, agree with mine in a number of cases.

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