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ORIGINAL PAPER

Milestones of the development of kinetics of electrode reactions

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Abstract The birth and the development of the kinetics of electrode processes–mostly focusing on the case of the hindered charge transfer step and the early period–are reviewed. It is shown how this important branch of electrochemistry was established and how and why the ideas of chemical kinetics have been introduced in electrochemistry. The history of electrode kinetics represents a good example for the progress of science in general, since it can be followed how the experimental observations conduce to the development of theory and how the theory influences further research. It is also demonstrated that the acceptance of new ideas is a thorny path. An attempt is made to acknowledge the merit of the scientists whose experimental or theoretical contributions brought paradigmatic changes in the thinking about the nature of electrode processes. In this context, the appropriate naming of equations is also discussed by using the example of the Erdey-Grúz–Volmer vs. Butler–Volmer equation. A discussion concerning the present trends is also included, which perhaps may predict the near future. A longer prognosis is avoided since the history of science teaches us that the real breakthroughs could not be predicted.

Keywords Electrode kinetics · History of science · Erdey-Grúz–Volmer equation · Electrochemistry

Introduction

In classical terms, reaction kinetics (from ancient Greek, κίνησις, “kinesis,” movement or to move) refers simply to the measurements of rates of chemical reactions. The overall reactions usually take place via series of elementary reactions. Therefore, the understanding of the molecular mechanism for a reaction–which is called reaction dynamics (δυναμικός–dynamikos, “powerful,” from δύναμις–dynamis, “power”)–is of primary importance. There is a strong link between the rate of reactions and dynamics of the reactions. Major developments in experimental techniques have allowed the taking of significant steps forward in the understanding of the detailed mechanism of both the elementary and complex reactions. The rate of the reactions can be influenced by a variation of the conditions, e.g., with an increase or decrease in temperature, concentration, or pressure. Electrode processes involve all the changes and processes occurring at the electrode or in its vicinity, while current flows through the cell. The

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electrode reaction is an interfacial reaction that necessarily involves a charge transfer step. The electrode reaction involves all the processes (chemical reaction, structural reorganization, and adsorption accompanying the charge transfer step). Electrode processes consist of the electrode reaction and the mass transport processes. Electrochemical reactions involve charged species (either the reactant or the product or both are charged) whose energy depends on the potential of the phase (more exactly on the location of the species and the potential distribution) containing these species. The essential step of electrode reactions is the transfer of charged species (ions or electrons) across the interface of two adjacent phases. The rate of this process is related to the potential difference between these phases. This potential difference can conveniently be varied by varying the electrode potential; therefore, at least within certain limits, we can regulate the reaction rate. We intend to focus on the case when the charge transfer step is the rate-determining one, since otherwise, our essay would be extremely long.

The road leading to the present understanding has been a long one, and the history of chemistry teaches us that we are still far from the end of this road, which possibly will never be reached. It is very useful to walk along this road, learning how the science advances, and to pay tribute to our scientific fathers (and mothers) whose work have contributed to the development of the science that has been transformed into technological advancements, which eventually made our life more comfortable and better. However, it is almost impossible to recapitulate all the contributions of importance and to mention all the outstanding players who have participated in this game, even concerning a relatively small field like electrochemistry or its even narrower branch, electrode kinetics. Such a compilation is inevitable incomplete, and somewhat subjective. Nevertheless, the author hopes that it will be useful and enjoyable.

Prehistory and early attempts

The announcement of Alessandro Volta on March 20, 1800 regarding an “artificial electrical organ” that can produce “perpetual” electrical motion has initiated an intense research [1, 2]. The importance of Volta's invention can scarcely be overestimated. For the first time, steady currents of electricity could be produced readily. In the 19th century, the experiments with electricity attracted the majority of researchers and even the public. New materials were produced (e.g., by H. Davy in the first decades of the 19th century); Michael Faraday formulated the quantitative law of electrolysis; J.W. Hittorf, F.W.G. Kohlrausch, and S. Arrhenius developed the measurement's methods and theory of electrolytic conductivity; H.L.F. Helmholtz contributed to the understanding of the nature of electricity, galvanic cells, and electrochemical double layer. Practically everybody had his own battery (e.g., J.F. Daniell, G. Leclanché, R.W. Bunsen, and W.R. Grove). The instrumentation has continuously been improved (e.g., by J.C. Poggendorf). The development of thermodynamics by J. W. Gibbs, W.H. Nernst, and G.J. Lippman led to the elaboration of the theory of galvanic cells. Albeit the osmotic model used by Nernst was essentially wrong [3], the equation derived was appropriate, and it remained the basic formula for calculation of the equilibrium electrode potentials. These and other, herein not listed, achievements of the 19th century are well known and included in several books devoted to physical chemistry. The description of the life and activity of these scientists can be found in different sources; the author recommends references [1, 2] as reliable ones.

The field, which is of importance regarding our topic, is the development of chemical kinetics; see e.g., in [4]. While electrochemistry and thermodynamics were the most popular areas in the 19th century, other branches of chemistry, e.g., organic chemistry which was closely associated with industry through the preparation of artificial dyes and pharmaceuticals, also enormously progressed. The time spirit preferred the eternal laws; time was not in the foreground of the thinking and research, however, especially the industrial production of chemicals forced to deal with this question. In electrochemistry, the rate of the processes appeared mostly in connection with transport phenomena.

Nevertheless, in the second half of the 19th century, several experiments were carried out and new perceptions have arisen. The first quantitative kinetic study was performed by Wilhelmy in 1850, who derived a differential equation and showed that it was consistent with his experimental results [5]. In 1864, Guldberg and Wage treated the equilibrium as dynamic, viz, being the result of a forward and backward reaction proceeding at equal rates. This way, they defined what we now call thermodynamic equilibrium constant and also reaction rates. They introduced the proportionality between the reaction rate and the concentrations of the reactants [6, 7]. In 1884, J.H. van't Hoff introduced an equation for the temperature (T) dependence of the equilibrium constant (K):

$$\frac{\mathrm{d}\ln K}{\mathrm{d}T} = \frac{q}{RT^2} \tag{1}$$

where R is the gas constant and q is the heat absorbed by the system if the reaction occurs at constant pressure.

He also considered the equilibrium kinetically, i.e., assuming an equal rate of the forward and backward reactions [8]:

$$\frac{\mathrm{d}\ln k_1}{\mathrm{d}T} - \frac{\mathrm{d}\ln k_{-1}}{\mathrm{d}T} = \frac{\Delta U^o}{RT^2} \tag{2}$$

$$\frac{\mathrm{d}\ln k_1}{\mathrm{d}T} = \frac{E_1}{RT^2} \qquad (3)$$

$$\frac{\mathrm{d}\ln k_{-1}}{\mathrm{d}T} = \frac{E_{-1}}{RT^2} \qquad (4)$$

$$\ln k = \text{constant} - \frac{E}{RT} \quad \text{or} \quad k = Ae^{-E/RT} \qquad (5)$$

where k_1 and k_{-1} are the rate constants (coefficients) of the forward and backward reactions, $\Delta U^{\mathrm{o}} = E_1 - E_{-1}$, i.e., the standard change of the internal energy is the difference of the two energies related to the opposite processes.

The well-known Arrhenius equation, in fact, was based on this idea. In 1889, S. Arrhenius provided interpretation for the temperature dependence of the reaction rate (rate coefficient). Arrhenius argued that, for reactants to transform into products, they must first acquire a minimum amount of energy, called the activation energy, E_a [9].

For years, the dependence of the rate of reaction remained an empirical subject; however, in the beginning of the 20th century, new ideas appeared, which could explain the experimental results better. Everything was ready to introduce the kinetic views in electrochemistry. At the very beginning of the new century, an outstanding researcher, in present terms we may call him organic electrochemist, found that the overpotential (overvoltage), i.e., the difference between the applied and the equilibrium potentials, linearly depends on the logarithm of the current density applied [10–12]. The name of the researcher was Julius Tafel (Fig. 1).

The first milestone

Tafel worked as an organic chemist with H.E. Fischer and L. Knorr and with the physical chemist Wilhelm Ostwald. While studying electrochemistry of organic compounds and cathodic hydrogen evolution [11], he established the equation now bearing his name.

Fig. 1 Julius Tafel (June 2, 1862; Choindez, Switzerland–September 2, 1918; Munich, Germany)

In his paper entitled "Über die Polarisation bei kathodischer Wasserstoffentwicklung" [11], Tafel derived this equation as follows. First, he considered the following kinetic relationship:

$$-\frac{\mathrm{d}c_\mathrm{H}}{\mathrm{d}t} = kc_\mathrm{H}^\mathrm{n} \qquad (6)$$

where k is the rate constant and c_H is the surface concentration of hydrogen atoms. Then, he established the connection between the reaction rate and the current density (I) in the form:

$$kI = kc_\mathrm{H}^\mathrm{n} \quad \text{and} \quad c_\mathrm{H} = K\sqrt[\mathrm{n}]{I} \qquad (7)$$

where K is a constant.

On the basis of Nernst's equation, he gave the relationship between the potential of the hydrogen electrode and the concentrations:

$$E = RT\ln\frac{c_\mathrm{H}}{C_{\mathrm{H}^\bullet}} \qquad (8)$$

where R is the gas constant and T is the temperature.

Replacing ln by log and assuming the concentration of the hydrogen ions ($C_{\mathrm{H}^\bullet}$) remains constant, he arrived at

$$\varepsilon = \frac{0.0002T}{n}\log I + a \qquad (9)$$

where ε is the cathode potential and a is a constant.

By using Hg or Pb cathodes, the experimental results satisfied the following equation:

$$\varepsilon = a + 0.107\log I \qquad (10)$$

Considering that $n=2$, the following equation was obtained:

$$\varepsilon = a + \frac{0.0570}{n}\log I \qquad (11)$$

where n is not less than 1.

Eventually, Tafel generalized the equation:

$$\varepsilon = a + b\log I \qquad (12)$$

where a and b are constants.

Tafel was a very careful researcher, e.g., he suggested the method of pre-electrolysis in order to purify the solution from traces of unwanted metal ions and also to have a clean electrode surface. Tafel cited the paper of W. A. Caspari, who introduced the concept and the symbol of the overpotential (overtension, "Überspannung,"η) [13], as well as F. Haber and R. Russ [14–18], who had reported logarithmic relationships between the current and the potential. Haber and Russ had obtained nice polarization curves for different compounds at different electrodes. Haber also considered the catalytic action of different metals. We show illustrative examples on Figs. 2 and 3. Haber had derived the logarithmic potential–current relationship, even applying kinetic considerations; however, he believed that an equilibrium situation exists at every potential, as opposed to Tafel's idea, who noted that, for irreversible electrode reactions, thermodynamics cannot be applied. It is worth to have a look at Haber's derivation. Haber used the Nernst equation based on the osmotic theory

$$\varepsilon nF = RT \ln \frac{P}{p} \tag{13}$$

where ε is the potential difference between a metal and an electrolyte (Haber called it electromotive force). P is the electrolytic pressure of dissolution; p is the osmotic pressure of the metal ions; n is the charge carried by the ion. It can be expressed in concentrations

$$\varepsilon nF = RT \ln \frac{C_\mathrm{R}}{c_\mathrm{R}} \tag{14}$$

where C_R and c_R are the concentrations of metal or hydrogen at the electrode surface and the ion in solution, respectively.

Haber, by using Nernst's idea, considered very high solution tensions, even more than a million atmospheres, i.e., the change of the potential generates a very high pressure and/or concentration [14]. (This wrong concept has appeared again and again, even in the 20th century. For instance, M. Fleishmann and S. Pons [15] explained the so-called "cold fusion" by assuming 10^{26} atm at an overpotential of 0.8 V.)

Assuming a reaction

$$\mathrm{a} + \mathrm{b} = \mathrm{c} + \mathrm{d} \tag{15}$$

e.g.,

$$\mathrm{C_6H_5NO_2 + H_2 = C_6H_5NO + H_2O} \tag{16}$$

Haber considered the following kinetic equations and equilibrium

$$-\frac{\mathrm{d}C\mathrm{a}}{\mathrm{d}t} = kC\mathrm{a} \cdot C\mathrm{b} \tag{17}$$

where Ca is the concentration in the cathode solution and Cb at the surface of the electrode.Consequently, it can be written

$$-\frac{\mathrm{d}C\mathrm{a}}{\mathrm{d}t} = kC\mathrm{a}C\mathrm{b} - k'C\mathrm{c}C\mathrm{d} \tag{18}$$

where k and k' are rate constants, and the reaction rate is proportional to the current (I).

$$-\frac{\mathrm{d}C\mathrm{a}}{\mathrm{d}t} = I \cdot k'' \tag{19}$$

It follows

$$k''I = kC\mathrm{a} \cdot C\mathrm{b} \tag{20}$$

$$-\frac{k''I}{kC\mathrm{a}} = C\mathrm{b} \tag{21}$$

and, eventually, logarithmic relationships can be obtained:

$$\varepsilon = \frac{RT}{2F} \ln C\mathrm{b} - \mathrm{const} \tag{22}$$

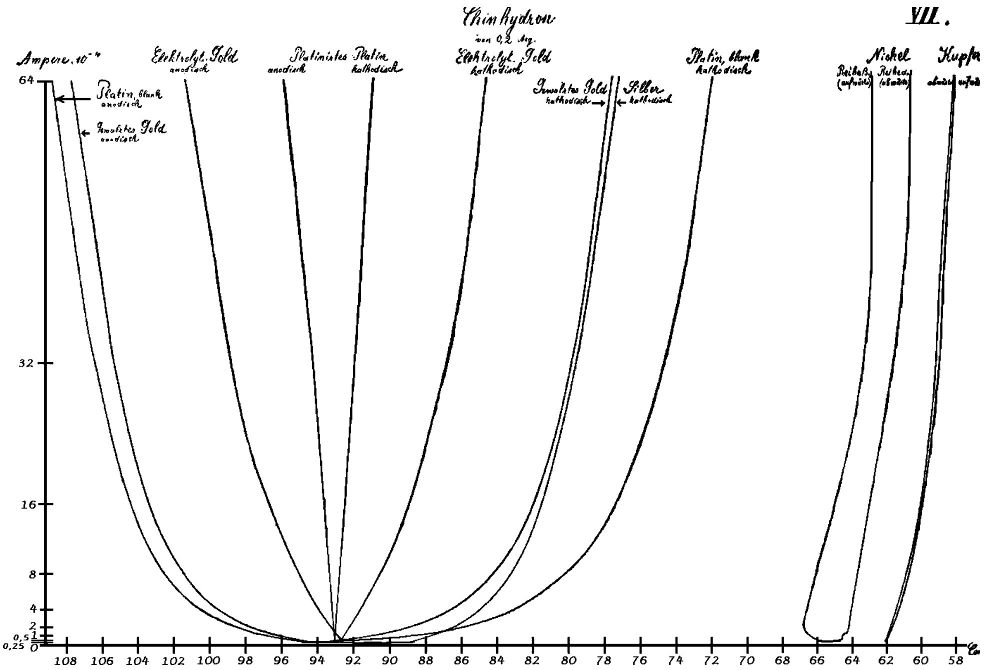

Fig. 2 Anodic and cathodic current–potential curves obtained for the oxidation and reduction of quinhydrone at different electrodes (platinized Pt, Au, Ag, Ni, Cu). From the paper of Russ [17]

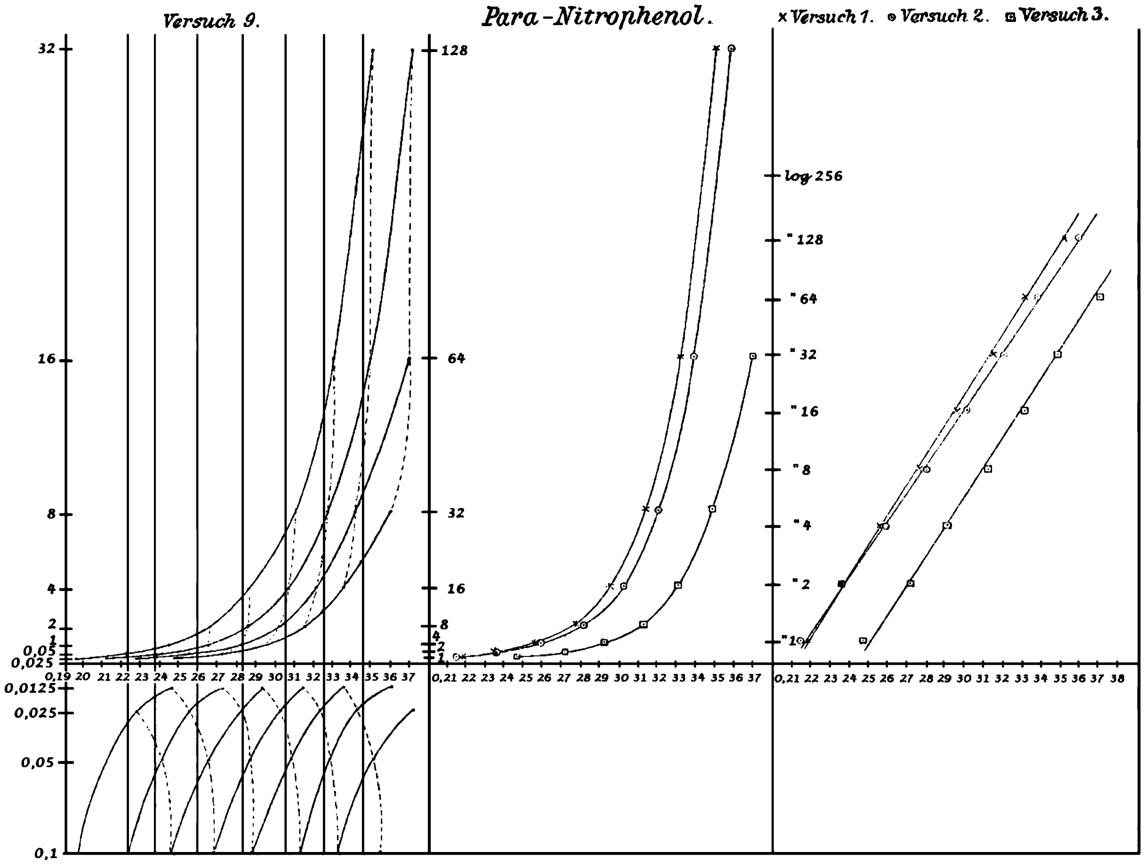

Fig. 3 Current–potential curves and their logarithmic representations for the reduction of p-nitro-phenol at different concentrations. The figure is taken from the paper of Haber and Russ [18]

$$\varepsilon = \frac{RT}{2F} \ln \frac{k''I}{kC\mathrm{a}} - \mathrm{const} \tag{23}$$

A similar derivation for the hydrogen electrode was also presented in [18].

It should be mentioned that until the invention of the potentiostat by Hickling in 1942, mostly the galvanostatic technique has been applied, albeit F. Haber established the importance of the potential in respect of the product distribution [19].

The explanation of the physical meaning of the relationship postulated by Tafel posed a challenge for the electrochemists. Despite the fact that the exponential relationships from the chemical kinetics were already available and the distribution of potential and concentration of the ions, consequently, the energy of the species near the electrode surface could be calculated, since the theory of the electric double layer was elaborated by Gouy and Chapman in the years 1910–1913, the progress was rather slow. It is more or less understandable since the knowledge on the mechanism of the heterogeneous reactions was still rather limited, and the charge transfer was also an unknown territory. Until the discovery of the existence of the electron, the electrochemists could consider only the transfer of ions. From 1897, the electron transfer opened up new vistas in respect of charge transfer.

Steps forward

One of the earliest papers [20] where an exponential relationship appeared was written by J. Heyrovský in 1923. The title of the paper in question was “Electrolysis with a Dropping Mercury Cathode Part I. Deposition of Alkali and Alkaline Earth Metals.”

It is useful to cite the essential statements of this paper: “In increasing the polarizing E.M.F. we increase the minute amalgam concentration in the drop surface and diffusion into the inside must result. The amount which diffuses will be proportional to the concentration of the amalgam in the surface, which is given by the formula

$$\pi = -\frac{RT}{nF} \log K_{\mathrm{Me}} \cdot C_{\mathrm{Me}} \tag{24}$$

where C_{Me} denotes the amalgam concentration and π the potential of the polarized drop. Thus the current

$$i = k \cdot C_{\mathrm{Me}} = K \cdot e^{-\frac{\pi nF}{RT}} \tag{25}$$

i.e., the curve should be an exponential." It is essentially the same derivation that had been made already by Tafel [11].

In the next year, J.A.V. Butler (Fig. 4) [21, 22] and R.-A. Audubert [23] published papers, which are of importance in our story.

Butler published three papers on the heterogeneous equilibria. The title of Butler's second paper, which is mostly but not entirely adequately cited, was "Studies in heterogeneous equilibria. Part II – The kinetic interpretation of the Nernst theory of electromotive force."

Albeit it was certainly a kinetic interpretation, it followed the footsteps of van't Hoff's and Nernst's ideas and contained no connections with the interpretation of Tafel's equation or any experimental facts. The words "current density" or "overpotential" were not even mentioned in these papers. We can see Butler's train of thought by reading the essential paragraphs from his paper:

> "The electromotive process is concerned with the metal ions in the surface layer and those in the solution. Equilibrium is attained when equal numbers of ions are dissolved and deposited at the surface in any interval of time. If the concentration of metal ions in the solution is less than corresponds to equilibrium, that is if the rate of deposition is less than the rate of solution, metal ions will leave the surface of the metal and pass into solution, thereby leaving the surface of the metal with an excess of negative electrons."
>
> "The effect of this negative charge is to retard the passage of positive ions away from the surface and to assist their deposition from solution. The rate of deposition will be increased and the rate of solution decreased; consequently the charge will accumulate until the two processes occur at equal rates."
>
> "The conditions will of course be reversed if the concentration of metal ions in the solution is greater than corresponds to equilibrium."
>
> "Disposition of forces will be modified by the existence of a potential difference at the surface.

Fig. 4 John Alfred Valentine Butler (February 14, 1899; Winchcombe, Gloucestershire, England–July 16, 1977; London) (Courtesy of The Royal Society and The Institute of Cancer Research; photo, Moreman KG, around 1965)

Total potential difference between the surface of the metal and the interior of the solution be E, the work done by a positive ion in passing from the surface into the interior of the solution is nEF per gram ion.

The total work done in reaching the balance point is therefore $W_1' - nE'F$, and the number of ions reaching it in unit time is given by

$$\theta_1 = N_1 \sqrt{T} A' e^{-\frac{W_1' - nE'F}{RT}} \tag{26}$$

where N_1=number of metal ions per square cm, in surface layer of metal.

Similarly from the interior of the liquid an ion does work

$$W_2' - nE''F \tag{27}$$

The number of ions reaching the balance point from the solution per second

$$\theta_2 = N_s A \sqrt{T} \mathrm{e}^{-\frac{W_2' - nE''F}{RT}} \tag{28}$$

For equilibrium $\theta_1 = \theta_2$.

Therefore we have

$$E = \frac{U}{nF} + \frac{RT}{nF} \log_e \frac{AN_0}{1000A'N_1} + \frac{RT}{nF} \log_e C \tag{29}$$

The normal potential E_0 is given by the terms

$$E_0 = \frac{U}{nF} + \frac{RT}{nF} \log_e \frac{AN_0}{1000A'N_1} \tag{30}$$

And this quantity may be regarded as equivalent to $-\frac{RT}{nF}\log P$ in the Nernst formula.

We have thus arrived at a deduction of the Nernst equation by the use of a kinetic mechanism which is physically acceptable in place of the formal thermodynamical process of Nernst. The values of the heat effects at single electrodes are scarcely known but it has been stated that the heat absorbed at the hydrogen electrode is almost zero."

"Summary. The Nernst theory of the electrolytic P.D. of metals is developed on kinetic grounds and a kinetic deduction of the Nernst equation is given."

Butler dealt with the kinetic explanation of equilibrium (in fact, he treated a situation when a piece of metal is immersed in a solution containing the ions of this metal [21] or an inert electrode in contact with a solution containing a redox couple [22], and not with electrode kinetics, when current flows at different overpotentials. Nevertheless, Eqs. 26 and 28 may represent the current–potential relationship, but Butler did not exploit it for this purpose.

Audubert [23] introduced the hypothesis of an ion energy distribution which, among other things, leads to the classical equation for the potential (the Nernst law). Audubert's ideas played a role in the further developments.

In the following years, important experiments [24–27] have been carried out regarding the rate-determining steps. The relationship between the overpotential and the current should be logarithmic if the discharge is fast, and the Nernst law applies. In the case of the discharge of hydrogen ions, we have

$$\eta = \text{constant} - \frac{RT}{F}\log[\mathrm{H}]_s \qquad (31)$$

In this equation, η is the measured overpotential, and $[\mathrm{H}]_\mathrm{s}$ is the concentration of hydrogen atoms at the surface of the electrode. If, on the other hand, hardly any hydrogen ions are discharged, i.e., at very low overpotentials, but there is merely an increase in the charge on the capacitors forming the double layer, the polarization tension will be a linear function of the quantity of current. Therefore, if $[c^+]$ and $[c^-]$ are the surface densities of the charges on the surfaces of the double layer,

$$\eta = \text{constant} - kF\Delta([c^+] - [c^-]) \qquad (32)$$

The experiments [24–27] appeared to favor the second hypothesis, as can be seen in Figs. 5 and 6.

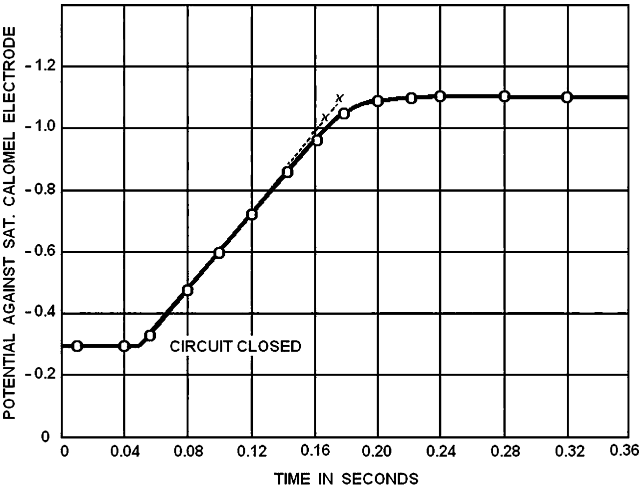

Fig. 5 The rise of potential as a function of time on passing a current density of 4×10^{-5} A cm^{-2}. Mercury electrode immersed in N/5 sulfuric acid freed from oxygen. A string galvanometer and a camera were used for the registration of the curve. From the paper of Bowden and Rideal [24]

Based on these and the results of their own measurements, T. Erdey-Grúz (Fig. 7), then visiting researcher in Germany, and the outstanding physical chemist, M. Volmer (Fig. 8), derived the respective relationships between the current density and the overpotential when the charge transfer is the rate-determining step in the case of hydrogen evolution. The recognitions of these scientists led to the development of the fundamental theory of electrode kinetics. Before discussing their paper, it is worth to have a look at the work of Bowden and Rideal entitled “The Electrolytic Behaviour of Thin Films. Part I. –Hydrogen” [24], which was cited by Erdey-Grúz and Volmer. Of course, the most important experimental results were the curves like that shown in Fig. 4. However, there were other remarkable points. They wrote that “The view most generally accepted is that this overpotential is due to an accumulation of electromotively active material on the electrode, and it has been suggested by various workers that it may consist of metallic hydrides, hydrogen atoms or negative hydrogen ions.” They referred to Heyrovský's paper in this respect [28]. They considered the accumulation of hydrogen atoms, and not the accumulation of hydrogen ions, i.e., a slow discharge process. (It should be mentioned that the state of hydrogen at the electrode surface is still not fully understood.) Nevertheless, they could explain their findings as follows: First, they assumed that “the relation between the solution pressure of the hydrogen P and the surface concentration of atoms C_H is given by the relation”:

$$P = kC_\mathrm{H}^m \qquad (33)$$

Then they applied the Nernst equation:

“It is generally assumed that the relation between the potential and the concentration of active hydrogen is given by the Nernst expression

$$-E = \frac{RT}{F}\log\frac{fC_\mathrm{H}}{fC_\mathrm{H}^+} \qquad (34)$$

where C_H is the concentration of active hydrogen on the cathode surface and fC_H^+ is the activity of hydrogen ions in the solution.” (Note that they used correctly “activity,” which was not a general practice in that time!)

Then, they assumed that “the relation between the electrode potential and the surface concentration of active material is a linear one, viz.,

$$-E = \beta\Gamma + \text{const} \qquad (35)$$

where E is the electrode potential and Γ is the true surface concentration of active hydrogen on the cathode surface.” Moreover, they stated that “the rate of decay, $-\mathrm{d}\Gamma/\mathrm{d}t$, of the active material is not proportional to Γ^2 as usually assumed, nor to Γ as supposed by Heyrovsky, but is an exponential function of the potential, viz.,”:

$$-\frac{\mathrm{d}\Gamma}{\mathrm{d}t} = k_1\mathrm{e}^{-k_2E} \qquad (36)$$

and thus, also the surface concentration

$$-\frac{\mathrm{d}\Gamma}{\mathrm{d}t} = k_1\mathrm{e}^{-k_3\Gamma} \qquad (37)$$

Taking into account that

$$-\mathrm{d}\Gamma/\mathrm{d}t = i \qquad (38)$$

they derived the Tafel relation.

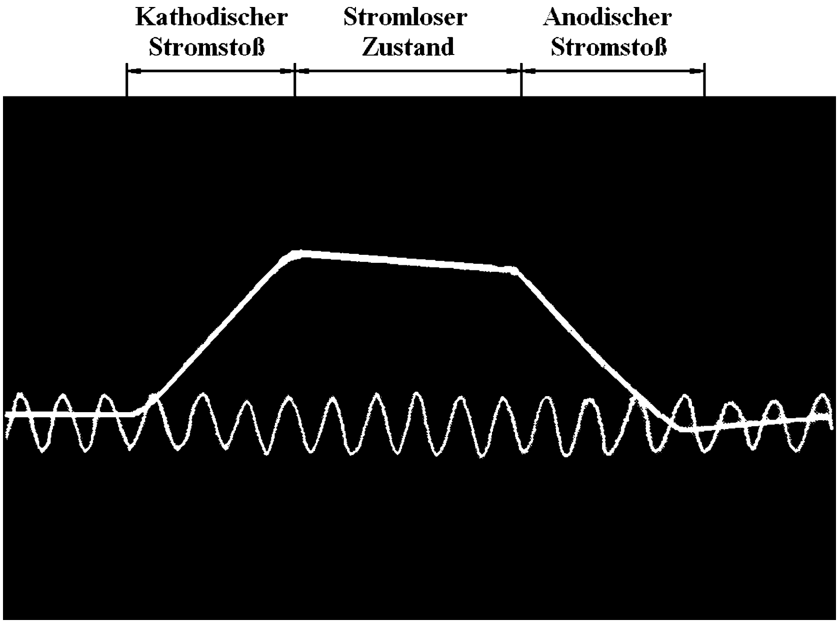

Fig. 6 Oscillogram obtained for a silver electrode in 1 M H_2SO_4. *X*-axis, 1 cm=0.008 s; *y*-axis= 0.028 V. From the paper of Erdey-Grúz and Volmer [27]

They arrived at the following important conclusion: “It is also significant that the rate of discharge of hydrogen is an exponential function of the potential.”

It is of importance that they corrected the *b* value given by Tafel: “the value of *b* is practically the same for mercury, for silver, and for smooth platinum, viz., 0.120. The value obtained by Tafel for mercury was 0.110.” It should also be mentioned that Bowden and Rideal emphasized the importance of the removal of the oxygen from the solution. An interesting aspect is that this work initiated the further studies of Gurney and Butler (see later).

Volmer also published an important paper in 1928 entitled “Zur Theory der Vorgänge an unpolarisierbaren Elektroden” [29].

Fig. 7 Tibor Erdey-Grúz (October 27, 1902; Budapest–August 16, 1976; Budapest, Hungary)

The breakthrough, the birth of the electrode kinetics

In their pivotal paper entitled “Zur Theory der Wasserstoffüberspannung” that appeared in 1930 [27], Erdey-Grúz and Volmer applied the laws of reaction kinetics and recognized that electrolytic hydrogen overpotential (on the electrodes characterized by large overpotential) was due to the slow neutralization of hydrogen ions which, in turn, was caused by the high activation energy of this process. As shown by Erdey-Grúz and Volmer, the energy of activation can be changed in a controllable manner by varying the potential. The transfer coefficient (α) introduced by them proved to be extremely useful. Based on this kinetic model, the relationship between the reversible (equilibrium) potential and the concentration of the species participating in the electrode reaction, i.e., the Nernst equation, were also derived, and the Tafel relationship was properly elucidated. The essential steps made by Erdey-Grúz and Volmer were as follows [27].

Fig. 8 Max Volmer (May 3, 1885; Hilden, Germany–June 3, 1965; Potsdam, Germany)

One of their useful ideas was the splitting of the terms involving the applied potential into two terms, for the anodic (oxidation) and cathodic (reduction) processes, respectively:

$$\frac{J}{F} = k_2 c_+ \mathrm{e}^{-\frac{\alpha EF}{RT}} - k_3 c_\mathrm{H} \mathrm{e}^{+\frac{\alpha EF}{RT}} \tag{39}$$

where J is current; F is the Faraday; constants k_2 and k_3, the rate constants of the neutralization of the hydrogen atom and the ionization of the hydrogen, respectively; c_+ and c_H are the concentrations of the hydrogen ions and the hydrogen at the electrode surface; E is the electrode potential; α is the transfer coefficient; R is the gas constant; and T is the thermodynamic temperature.

At equilibrium, i.e., at the reversible potential (E_r)

$$\frac{J}{F} = k_2 c_+ \mathrm{e}^{-\frac{\alpha E_r F}{RT}} - k_3 c_\mathrm{H} \mathrm{e}^{+\frac{\alpha E_r F}{RT}} \tag{40}$$

At overpotential η

$$J = Fk_2 c_+ \mathrm{e}^{-\frac{\alpha(E_r+\eta)F}{RT}} - Fk_3 c_\mathrm{H} \mathrm{e}^{+\frac{\alpha(E_r+\eta)F}{RT}} \tag{41}$$

A high negative η, $\eta > -0.03$ V

$$J = Fkc_+ \mathrm{e}^{-\frac{\alpha\eta F}{RT}} \tag{42}$$

It soon became clear that the relationships derived from the above concept for the hydrogen overpotential constitute the general basis of the theory of electrode processes with charge transfer as the rate-determining step.

This seminal paper can be considered as a landmark since the Nernstian equilibrium (osmotic) theory already hindered the development of electrochemistry.

Nowadays, in most books and papers, the following equation is called the Butler–Volmer equation:

$$j = j_\mathrm{o}\left\{-\exp\left[-\frac{\alpha_\mathrm{c} F\eta}{RT}\right] + \exp\left[\frac{\alpha_\mathrm{a} F\eta}{RT}\right]\right\} \tag{43}$$

which gives the description of the polarization curve when the charge transfer step is very sluggish, the standard rate coefficient, $k^{\ominus}$, and the exchange current density, j_o, are very small, and a large activation overpotential is needed to drive the reaction in any direction. In this case, the anodic and cathodic reactions are never simultaneously significant. This type of kinetics is called irreversible or quasi-reversible in electrochemistry. It is easy to recognize that a linear Tafel plot can be obtained only in this case. This equation is practically identical with the equation (6.13) in the Erdey-Grúz–Volmer paper [27] cited above as Eq. 41.

Although such terms as Butler–Volmer equation or Butler–Volmer kinetics are widely used in the literature, the name is questionable in the light of the historical facts [1, 30]. As it has been pointed out earlier, in Butler's mostly cited papers [21, 22], overpotential or current density was not used at all. The hindered charge transfer step was not considered. R. de Levie [30] wrote: “Erdey-Grúz and Volmer were the first to do this, in 1930, when they derived the corresponding rate expression in a paper on the kinetics of the hydrogen electrode. Recently, this basic law of electrode kinetics has become known as the Butler–Volmer equation. Butler was a leading British electrochemist, who had indeed attempted to find an answer to this question. Butler did not find it. In fact, in his 1940 book on electrocapillarity, Butler specifically refers to Erdey-Grúz and Volmer in this respect. The first time that the name of Erdey-Grúz was replaced by that of Butler appears to be in the 1970 textbook by Bockris and Reddy, but it may have an earlier origin. At any rate, subsequent textbook authors simply copied it…” It is somewhat surprising that Bockris–who recognized the the pioneering work of Erdey-Grúz and Volmer–started to use Butler's name and later left out Erdey-Grúz. In his book of 1967, Butler was not mentioned [31]. In his next work, Bockris mentioned that Butler made an attempt to use the kinetic approach regarding the potential dependence of current density (which is in fact incorrect, as we have mentioned earlier), but the adequate description appeared first in the paper of Erdey-Grúz and Volmer [32]. In 1977, Bockris used the expression that “Butler–Volmer– Erdey-Grúz theory” [33], which determined the post-nernstian electrochemistry. Most likely, three names were too many, and the name of the equation was simplified for Butler–Volmer equation, which was used by Bockris [34] and other authors later on. It is even strange that, in the book [34], the name of the chapter is “The Butler-Volmer Equation”; however, it starts as follows: “That an exponential relation exists between the shift of the electrode potential from that corresponding to equilibrium to that corresponding to a given rate was established experimentally by Tafel and rationalized properly for the first time by Erdey-Grúz and Volmer in 1930.”

In Russian books, the names of Erdey-Grúz and Volmer as well as Frumkin were mentioned in this respect [35]. In a book of French authors, the title of the respective chapter is as follows: “The Theories of Erdey-Gruz, Volmer and Audubert” [36].

In another widely used book, it is written that the “slow discharge theory was suggested by Erdey-Grúz and Volmer.” Butler was mentioned among the actors who contributed to the further developments; the authors cited a paper of Butler from 1936 [37]. Laidler [4] mentioned only the names Tafel, Erdey-Grúz, and Volmer at the early history of kinetics of electrode processes. Albeit such practice is not unique in the scientific literature, that is, theories, equations, and methods were named after scientists working in that field but did not play a real role in the establishment of the given achievements. Therefore, in this case, the usage of the name Erdey-Grúz–Volmer equation has to be proposed.

Erdey-Grúz and Volmer published another important paper in 1931 entitled “Zur Frage der elektrolytischen Metallüberspannung” [38]. In this paper, they applied the recognition made by them in the previous year, i.e., when the neutralization of the metal ions is the rate-determining step, the explanation that was given for the slow discharge of hydrogen ions is also valid, and the dependence of the overvoltage on the current density is the same. However, when the crystallization step is retarded, either the formation of two-dimensional nuclei or the three-dimensional nucleation or the mass transport by surface diffusion, the current–potential function will be different. They used the expressions derived by Volmer and Weber [39] for the energy of three-dimensional nucleation and also the crystal growth theory of I.N. Stranski [40]. For the two-dimensional nucleation, the equation derived for the current–potential function was as follows:

$$i = k_1 \exp\left[-\frac{\pi\rho^2 O}{RTzF\eta}\right] = k_1 \exp\left[-\frac{k_2}{z\eta}\right] \tag{44}$$

where ρ is the specific edge energy of the two-dimensional nucleus, O is its molar surface, and k_1 and k_2 are constants at constant temperature. The overpotential (η) logarithmically depends on the ratio p/p_∞, which is the measure of supersaturation, where p and p_∞ are vapor pressures of the nucleus and the crystal, respectively. Consequently,

$$\ln i = \ln k_1 - \frac{k_2}{z} \cdot \frac{1}{\eta} \tag{45}$$

For the three-dimensional nucleation,

$$i = k_4 \exp\left[-\frac{k_5}{z^2\eta^2}\right] \tag{46}$$

$$\ln i = \ln k_4 - \frac{k_5}{z^2} \cdot \frac{1}{\eta^2} \tag{47}$$

where the square of the overvoltage is in reverse ratio to the energy of three-dimensional nucleation, which depends on p/p_∞, as well as on the specific surface-free energy, on the molecular mass, and on the density.

They presented nice pictures about the crystal growth and demonstrated the effect of the current density and the composition of the solutions. Because the “microkinematographic” pictures and photos that appeared in the original publications could have been copied only in poor quality, I show the recent photos of three crystals prepared in the 1930s by Erdey-Grúz, very well preserved for illustration (Fig. 9).

Soon, several authors exploited the new ideas. The most notable achievements were done by A.N. Frumkin (Fig. 10) in the 1930s, who developed further the theory of slow discharge [41], suggesting that the α factor has the same origin as the fractional exponent in the Brönsted equation for general acid and base catalysis [42–44]. He introduced a correction–called the Frumkin correction–which described the effect of the double-layer structure on the kinetics of electrode processes [45, 46]. In 1940, Frumkin and his co-workers published a series on important papers on kinetics of processes on platinum electrode [47, 48], also dealing with the discharge of H^+ ions [48]. Frumkin's achievements and influence are discussed in another paper of this issue. We have to mention also the paper by C. Wagner and W. Traud [49], which substantially contributed to the understanding of corrosion, by the formation of a mixed potential when both anodic and cathodic processes occur at the same electrode. In the 1930s, new and very important theories appeared in chemical kinetics. M. Polanyi (Fig. 11) started to use contour maps for representing the potential energy of the species participating in chemical reactions. Polanyi and H. Eyring worked on the calculation of activation energy using this entirely new approach. In 1933, Polányi left Germany and became a professor of physical chemistry at

Fig. 9 Silver crystals deposited under different conditions. From left to right: 0.3 n Ag_2O+25% NH_3, 42×10^{-5} A cm^{-2}, 2 weeks; 0.2 n Ag_2O+25% NH_3, 5×10^{-5} A cm^{-2}, 1 week; 1 n $AgNO_3$+25% HNO_3, 1.3×10^{-5} A cm^{-2}, 3 days. (The author's property, who inherited the collection of silver crystals made by Erdey-Grúz in the 1930s.)

Fig. 10 Alexander Naumovich Frumkin (October 24, 1895; Kishinev, Russia (now Chişinău, Moldova)–May 27, 1976; Tula, USSR (now Russia))

University of Manchester. There and simultaneously in Princeton by Eyring, the transition state theory has been developed, which practically replaced the kinetic theory of collisions later on.

The understanding of the transfer coefficient

Erdey-Grúz and Volmer introduced the transfer coefficient in a heuristic way without giving a detailed explanation. We have mentioned that Brönsted introduced a relationship [42–44]:

$$k = k_0 (K/K_0)^{\alpha} \quad (48)$$

where k and k_0 are the rate constants and K and K_0 are the equilibrium constants in a series of homogeneous reactions.

Fig. 11 Michael (Mihály) Polányi (March 11, 1891; Budapest, Hungary–February 22, 1976; Oxford, UK)

It is easy to see–as Frumkin predicted–α is indeed the transfer coefficient. According to the transition state theory developed by Polányi and Eyring, respectively, the rate constant can be expressed as follows:

$$k = x \frac{kT}{h} \exp\left(-\frac{\Delta G^{\ddagger}}{RT} \right) \quad (49)$$

where k is the Boltzmann constant, h is the Planck constant, T is the temperature, $\Delta G^{\ddagger}$ is the Gibbs energy of activation.

It follows from the Brönsted equation that

$$\Delta G^{\ddagger} = \Delta G_0^{\ddagger} + \alpha \left(\Delta G^o - \Delta G_0^o \right) \quad (50)$$

where the ΔG^{o} and ΔG_0^o values are the standard Gibbs energies of the respective reactions.

For electrode reactions, the Gibbs energy includes the electric work, $nF\Delta\varphi$, where $\Delta\varphi$ is the Galvani potential difference; therefore,

$$\Delta G^{\ddagger} = \Delta G_0^{\ddagger} + \alpha n F \Delta \varphi \quad (51)$$

Polanyi with J. Horiuti could explain the physical meaning of the transfer coefficient (α) by the help of the transition state theory which was a milestone in the development of the kinetics of electrode processes [50]. In their paper entitled “Grundlinien einer Theorie der Protonübertragung” (outlines of a theory of proton transfer), they treated the ionization and charge transfer processes occurring in solutions and at the electrodes. They assumed that the mechanism in both cases is the same. They accepted the idea of Erdey-Grúz and Volmer, i.e., the rate of the electrode reaction is determined by the potential drop in the electrochemical double layer. Besides analyzing the proton transfer in solution, they treated the case of the nickel electrode immersed in aqueous solution in detail. It was assumed that the whole potential difference (ε) is between the electron surface of the metal and the adsorbed hydrogen ions, and the electric field is homogeneous. They also considered the case of dilute solutions and referred to Frumkin's works. The most important figure in their paper is that they plotted the electrode potential as the function of the heat of activation of the ionization/deionization processes and gave a generalized view, how the variation of the energy of the hydrogen ions, by changing the electrode potential, influences the activation energy (Fig. 12). Their explanation was as follows. Neglecting the dipole character of the Ni–H bond, any change of the electric field causes the increase or decrease of the energy of hydrogen ions; consequently, there will be a perpendicular shift of the parabola b; the horizontal shift is minimal and can be neglected. Therefore, it can be written

$$\Delta_1 Q' = \alpha \varepsilon \quad (52)$$

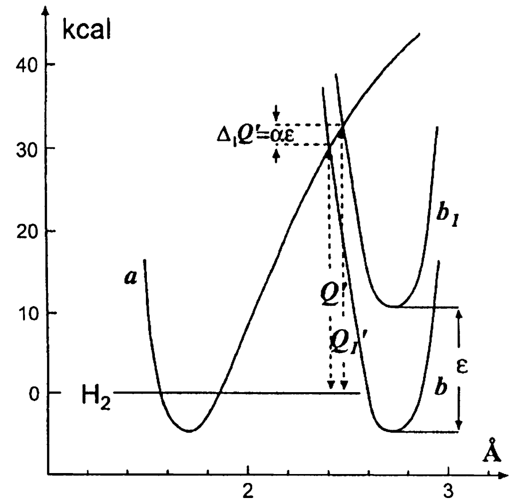

Fig. 12 The relationship between the electrode potential and the heat of activation of the ionization/deionization processes; $\Delta_1 Q' = \alpha\varepsilon$ és $\Delta_2 Q' = -(1-\alpha)\varepsilon$. From [50]

and

$$\Delta_2 Q = -(\varepsilon - \alpha\varepsilon) = -(1-\alpha)\varepsilon \tag{53}$$

(While they assigned earlier in this paper ε as the electrode potential, herein, seemingly, they used it as energy.) It follows that the difference of the anodic and cathodic partial currents can be expressed as:

$$\begin{aligned} i &= i_1 - i_2 \\ &= \mathrm{const}\left(\mathrm{e}^{-(\alpha\varepsilon)/FRT} - \mathrm{e}^{-((1-\alpha)\varepsilon)/FRT}\right). \end{aligned} \tag{54}$$

At high values of ε, the Tafel equation can be obtained

$$\log i = \frac{(1-\alpha)\varepsilon}{FRT} + const \tag{55}$$

(It should be mentioned that there is a mistake in these equations since if ε is potential, F should be in the numerator; if ε is energy, F is not needed at all.) They could explain also the observation that, at different metals, the energy of activation and, consequently, the overpotentials are different. They stated that this effect was due to the different adsorption energy of hydrogen (W); H^+ ions play no role. They also illustrated this situation (Fig. 13).

The quantum mechanics enters the electrochemistry

Not only the theory of the chemical kinetics developed in the 1930s, but it was the time of the introduction of quantum mechanics in chemistry. The first quantum-mechanical treatment of ion discharge by electron transfer is due to Gurney who published a paper entitled “The Quantum Mechanics of Electrolysis” in 1931 [51]. (It is interesting to note that Gurney's work was communicated by Lord Rutherford.) He noted that electrons in electrodes occupy a distribution of states according to Fermi-Dirac statistics as well as the fact that ions in solution occupy an electron transfer distribution of states due to their differing degrees of solvation, and that electron transfer must take place preferentially between states having the same energy. He also pointed out that the effect of the electrode potential was to decrease the electron work function of the metal. Gurney considered that the elementary act of electron transfer must take place so quickly that nuclei are effectively stationary; an essential condition for large current flow was that there must be a large overlap between the ionic and metallic orbitals. He showed that the mathematical formulation of electron transfer theory necessarily involves summations over joint distributions of ionic and electronic states. Butler made a comment on the paper of Gurney [52]. He wrote that “Dr. R.W. Gurney has calculated the rate of transfer of electrons between an electrode and dischargable ions in solution, and has developed on this basis a general theory of overvoltage.” “I made use of this concept in 1923….employing classical statistical mechanics....” Butler criticized Gurney that “the exponential term required by the experimental data was half that which appears in (1),” i.e., in [51]. Butler cited the equation deduced by Gurney:

$$i = kTe^{E_0 - E_1 + FV/\gamma RT} \tag{56}$$

where E_0 and E_1 are constants, and i is the current density for the potential difference V. He rewrote it, taking into account the concentration of hydrogen ions in the solution, and emphasized that “γ is a constant which is greater than unity; if its value is 2, the experimental findings are accounted for.”

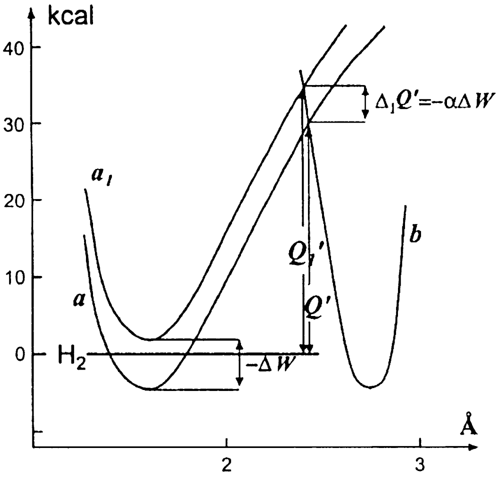

Fig. 13 The effect of the energy of adsorption of hydrogen on the activation energy. From [50]

In this paper, Butler used the exponential current–potential equation for both the cathodic and anodic processes and reported data based on the experiments that he carried out in collaboration with Mr. G. Armstrong. It is strange that, while he dealt with the hydrogen overvoltage, he referred to the paper of Erdey-Grúz and Volmer [38] but not to [27].

A good review entitled "The mechanism of hydrogen overvoltage and of the electrolytic oxidation of hydrogen" on the contemporary situation was written by L.P. Hammett in 1933 [53]. (In this paper and also in other English works, e.g., in [54], the name of Erdey-Grúz appeared as Erdey-Grusz, which is due to old spelling rules regarding the use of "esszet"; most likely, the typesetters thought that the name was a German one.)

Spreading of ideas of electrode kinetics and the expansion of electrochemistry

The recognition of the role and the importance of electrode kinetics has progressed surprisingly slowly. In the year of the founding of the International Society of Electrochemistry, i.e., in 1949 according to Bockris [55]: "The atmosphere and background of electrochemistry at this time was dominated by the dead hand of Nernst. Overpotential was regarded as a kind of disease suffered by gas electrodes. Erdey-Grúz and Volmer, whom I see as the fathers of electrode kinetics, and Frumkin, were seldom mentioned." "…people were suspicious of kinetic treatments as not exact. Models? But these could be wrong." "It was mainly in Moscow that spoke kinetics and the rest of the electrochemical world was thermodynamically inclined. The big change came with Vetter's Book of 1955."

Bockris was right. The changes of the attitude have started with the works of Russian researchers (besides Frumkin, M.I. Temkin, Z.A. Iofa, B.N. Kabanov, V.G. Levich, and later, V.S. Bagotzky, L.I. Kristhalik, O.A. Petrii, B.B. Damaskin, R.R. Dogonadze, A.M. Kuznetsov, Yu. V. Pleskov, and others), but from 1950, several works by R. Parsons, K.J. Vetter, D.M. Mohilner, P. Delahay, M. Salomon, J.E.B. Randles, J. Koutecký, J.O'M. Bockris, B. E. Conway, H. Gerischer, A.J. Bard, E. Gileadi, M.J. Weaver, W.R. Fawcett, and many other scientists were directed to elaboration of the advanced theories of electrode kinetics. Interestingly, one of the most-cited papers of the *Journal of Electrochemical Society*, with over 1,000 citations [ECS Interface (2009) 18:33], is entitled "Electrochemical Polarization. 1. Theoretical Analysis of the Shape of Polarization Curves" [56], which contained no really new results but was a very good compilation of the knowledge that has accumulated until the mid-1950s. This paper was especially influential among the researchers working in the area of corrosion for whom the kinetic approach was somewhat new since the thermodynamic treatment still dominated in that time.

The potentiostat and the new and more powerful electrochemical devices have become widely used from the 1960s. Time has gained its real importance. In the science, the study of fast and even faster reactions was the goal of the researchers, while in the industrial applications, the rate was a crucial factor. The quest for novel power sources, especially fuel cells, accelerated research in the area of electrochemical kinetics. Electrocatalysis became of primary importance, and many new ideas were adopted from the catalysis research, which has also progressed to a great extent. One of the most remarkable recognitions was the role of the state of the electrode surface. It became evident that, while the properties of the bulk phase of the metal are responsible for the thermodynamics, the surface state plays a determining role in the kinetics.

While polarography remained a standard technique until the 1970s and its new versions are still in use (see another review in this issue of this journal), cyclic voltammetry replaced it in the everyday laboratory practice. The basic equations were introduced independently by Ševčík and Randles in 1948 [57, 58]. The paper of Nicholson and Shain [59] gave new impetus, inasmuch as their derivation made possible the determination of the rates of charge transfer step and the accompanying homogeneous reactions from the scan rate dependence of the peak currents and peak potentials. Even in 1950s, the electrochemical techniques could be used to study reactions in millisecond regime and therefore were considered as suitable to study fast reactions; however, the fast spectroscopic techniques after the invention of laser overshadowed their glory. The use of microelectrodes [60] and ultramicroelectrodes as well as the advancement of electronics (fast response electronic circuitries) made it possible to work with very high scan rates and consequently the study of "very fast" reactions, at least in the nanosecond range [61, 62]. The elaboration of the theory and practice of rotating disk and ring disk electrodes considerably helped the understanding of the multistep, diffusion-coupled, and catalytic reactions [63–65].

Albeit the measurements of impedance of the cell (electrode) as a function of frequency of the alternating current has a long past, the real renaissance of this technique has started when the operational amplifiers, the analog-to-digital and the digital-to-analog converters, the fast Fourier transformation method, and eventually, the commercial impedance analyzers appeared. The small signal perturbation of the system from the equilibrium allows to obtain the wealth of information in a short time such as charge transfer resistance (exchange current), reaction rate coefficients, diffusion coefficients, double layer, and pseudocapacitances, etc. [66, 67].

The combination of transient electrochemical techniques and other methods like spectroscopies, radiotracer, etc. opened up new vistas in respect of the deeper understanding of multistep electrode reactions with a complex mechanism.

With the help of the radiotracer technique, the transfer of electrons has been proven in 1920 [68]. Even earlier, the first evidence of the underpotential deposition was discovered by this technique. The modern period has started in the 1950s when different isotopes, labeled compounds, and ions became easily available. These investigations have been providing direct information on the adsorption of ions and compounds, dissolution of metals, etc. [69–72].

The opportunity of measurements of the mass change at the electrode surface in the nanogram range even during electrolysis fascinated the electrochemists. The birth of this technique was due the development of the quartz technology from the 1950s, when they started to use properly cut quartz crystals in oscillators applied for several purposes such as in watches; therefore, those became easily accessible also for scientific research. Somewhat surprisingly, quartz crystals covered with a thin layer of metals can work also in a liquid environment, i.e., they can be used in electrolyte solutions even when current flows through the electrode [73–75]. While in the 1980s until the mid-1990s, only a limited number of groups could use this technique, since quartz crystal microbalances (nanobalances) were still home-made apparatuses; nowadays, those are available commercially, and at present, hundreds of papers appear from different groups in diverse topics including, e.g., ion adsorption, ionic exchange at polymer film electrodes, surface layer formation and dissolution, and corrosion. Albeit it is already a combined technique, further combinations with other techniques have appeared and proved to be very useful for the study of electrode reactions and other phenomena.

The application of ESR in electrochemistry has started when Geske and Maki designed an appropriate cell [76, 77]. This technique made it possible to detect the radical ions, which form after the first electron transfer in the case of the oxidation or reduction of organic compounds. It opened up new vistas concerning the study of the mechanism of multistep electrochemical processes. Later, it became a routine method for electrochemists. Similarly, the introduction of optically transparent electrodes by Kuwana et al. [78] revolutionized the in situ UV-vis spectroelectrochemistry, which allows the detection of the products, therefore to follow the kinetics of the electrode processes. Many spectroscopic [79] and optical techniques have been developed for the in situ investigation of the solution phase and also the electrode surface among others, Raman, resonance Raman, surface-enhanced Raman [80], Fourier transform infrared, Mössbauer spectroscopies, synchrotron techniques, ellipsometry, and probe beam deflection (mirage) techniques. The development and the importance of these methods are summarized in other papers of this issue.

Over the past years, the application of the scanning tunneling microscope (STM) has been applied almost routinely for the examination of the surface topography of conducting and semiconducting surfaces on the nanometer or even on the atomic level [81]. Similarly, by now, the atomic force microscope (AFM) becomes a standard method to characterize conducting and nonconducting surface structures [82–84]. Both techniques can be applied in situ, and therefore, they help to understand the nature of the events occurring during charge transfer. An alternative technique that was developed is scanning electrochemical microscopy (SECM) [85].

At the end of the 1970s, novel modified electrodes have appeared, which posed new challenges regarding the explanation of the kinetics of electrode reactions. New materials such as redox and electronically conducting polymers [86–89], different forms of carbon, composites, semiconductors, intercalation systems, etc. have opened up new vistas, since the electrochemists could make molecularly designed electrodes [90], and they are not restricted to certain metals or graphite anymore. The application of semiconductors [91–94], nonaqueous solvents, molten salts [95, 96], as well as the use of other materials formerly neglected by electrochemists, caused to arise new theoretical and practical questions that needed to be answered. New areas appeared such as photoelectrochemistry [97] or electrochemistry of immobilized particles [98].

The novel systems posed new theoretical questions, e.g., the simultaneous electron and ionic charge transport in polymer film electrodes or the solid–solid phase transition during the redox transformation of microcrystals attached to the metal surface.

The permanent development of instrumentation and techniques and later, from the 1990s, the computerization provided opportunities for obtaining a wealth of information on electrochemical systems in a short time, which was just unimaginable earlier. The advanced theories of the electron transfer have also been developed.

Electron transfer has been one of the challenging topics since J.J. Thomson confirmed the existence of the electron in 1897. Before it, obviously only ion transfer has been considered in electrochemistry. However, this situation lasted until ca 1950s because of the dominating role of Nernst's heritage. It hindered the development of electrochemistry, and even the interpretation of redox potential remained obscure. It is rather surprising since Hevesy and Zechmeister [68] already proved the existence of electron transfer in 1920. The remarkable progress in quantum mechanics including the discovery of the tunneling phenomena as well as in electrochemistry regarding the structure of double layer, solvation and interactions of ions, and homogeneous and heterogeneous redox reactions led to the development of the modern theory of electron transfer. The solvent fluctuation model introduced by R.A. Marcus (Fig. 14) in the mid-1950s has become the most widely accepted theory of electron transfer [99, 100]. Marcus published a series of papers entitled “On the Theory of Oxidation-Reduction Reactions Involving Electron Transfer,” in which he set forth his ideas in detail. Marcus got the Nobel Prize for his achievements in 1992. Other scientists who made important contributions to the development of the theory of heterogeneous electron transfer include Hush [101, 102], Dogonadze and Levich [103, 104], and, from the early period, Libby [105], Randles [106], and Weiss [107]. For instance, Randles understood that in the case of electron transfer (one part of) the reaction coordinate was the bond length of the inner solvation shell, not the distance from the electrode as was used by Polányi and several authors afterwards.

A very good review on the development and present state of the theory of electron transfer appeared in this journal recently [108]. It is impossible to survey all the results herein, since more than 20,000 research papers related to this topic have appeared [108]. We mention only one of the important consequences of these theories, namely, the dependence of charge transfer coefficient, α, on the overpotential, which can be expressed as follows:

$$\alpha_{\mathrm{a}} = \frac{1}{2}\left(1 - \frac{F\eta}{2\lambda_{\mathrm{m}}}\right) \tag{57}$$

$$\alpha_{\mathrm{c}} = \frac{1}{2}\left(1 + \frac{F\eta}{2\lambda_{\mathrm{m}}}\right) \tag{58}$$

where λ_{m} is the reorganization energy per mole. The reorganization energy represents the energy necessary to transform the nuclear configuration in the reactant and the solvent to those of the product state. It should be mentioned that, due to the temperature dependence of λ_{m}, the symmetry factor also depends on temperature. The phenomenological parameter α introduced by Erdey-Grúz and Volmer [27] is an experimental parameter that can be obtained from the current–potential curve, and it is simply the reciprocal Tafel slope in dimensionless form. The symmetry factor is related to a specific single step in a reaction sequence and depends on the shape of the energy barrier and the position of the activated complex along the reaction coordinate. In several cases, it may be assumed that the symmetry factor is equal to the charge transfer coefficient when only one electron is transferred.

There is still much work ahead because the experimental verification of these theories is rather difficult. For instance, the potential dependence of α is not too large; therefore, obtaining experimental evidences is not an easy task.

Fig. 14 Rudolph A. Marcus (July 21, 1923; Montreal, Canada)

The kinetics of electrode processes became an important chapter of all electrochemistry books. The first book devoted entirely to this topic appeared in the Soviet Union [109], and it has been followed by several other books and monographs, e.g., [110] there, e.g., the excellent book by Damaskin and Petrii [35]. Unfortunately, outside the Soviet Union and the so-called socialist countries, their impact was relatively minor due to the language problem, since most of these books were not translated from Russian. We have already mentioned Bockris's opinion concerning the influence of Vetter's book [111, 112] in the West. In the 1960s, a series of books were published on electrode kinetics such as by Delahay [113], Conway [114], Erdey-Grúz [115, 116], and it has continued since then, e.g., Gileadi [117].

Of course, we do not want to enlist all electrochemistry books which deal with electrode kinetics in detail; however, the book of Bard and Faulkner [118], the first edition of which appeared in 1980, has to be mentioned in that besides the fundamentals, a very detailed compilation and analysis can be found concerning the determination of kinetic parameters from the results of transient electrochemical and combined techniques.

Can we predict the future?

From the present trends, perhaps the near future can be predicted. A longer prognosis is impossible since, according to the history of science, the real breakthroughs have never been foreseen.

A rather trivial prediction is the further development of the techniques in connection with the progress in electronics, computerization, etc., and consequently, the electrochemists could further expand the limits concerning the time scale of the experiments and the spatial characterization of electrode surfaces.

At present, the usable potential limits are still narrow, albeit they have been substantially widened in the last two decades. The interval between −3 V and +3 V can be used almost routinely due to the introduction of aprotic solvents and appropriate supporting electrolytes as well as ionic liquids. We are close to the negative potential limit (ca −4.4 V), and a +6 V positive potential record (the theoretical maximum value is +7.6 V) is also remarkable.

The use of nitrogen and its compounds is very desirable since an abundant source is available. However, the electrode reactions of these molecules are hindered and therefore kinetically irreversible. It would be a nice task for researchers working in the field of electrode kinetics.

The author is sure that the enhancement of the rate of electroreduction of oxygen will be solved soon, and there will be no obstacle for the fabrication of efficient H_2–O_2 fuel cells. The future of the application of new, nanostructured, tailor-made materials seems to be also bright, if we extrapolate from the development that occurred in the first decade of this century. Semiconductors and photoelectrochemistry will still be in the foreground of interest in the next decades.

The more efficient computers will make the simulation of complex processes and structures possible and consequently will contribute to the theory and will help to construct new materials and devices.

Conclusions

At the end of a long journey through the history of the kinetics of electrode processes, we may conclude that our knowledge on the factors determining the rate of the electrode processes has been growing significantly. From the establishment of the relationship between current and overpotential by Tafel, its explanation by the pivotal work of Erdey-Grúz and Volmer, and also the contributions of Polányi, Frumkin, Levich, Gurney, Hush, Marcus, and others that were surveyed in this paper were the milestones along the road. Electrochemistry with its 210-year past became a well-established branch of science with deep, but certainly not final, understanding on the governing rules. It has met the requirements posed by the needs of the society during the last century. The knowledge accumulated on the area of electrode kinetics was the basis of the technologies directed to the development of more efficient current sources, electrolysis methods, and sensors when the acceleration of the charge transfer rate is crucial, concerning the economic competitiveness, but also slowing down the unwanted processes like in the case of corrosion protection. We may predict–without too much risk–that the electrode processes in the energy area will play an important role also in the future since the environmental concerns give an impetus to the cleaner energy sources such as H_2–O_2 fuel cells and batteries or solar energy conversion through photoelectrochemistry at semiconductors. The preparation and utilization of advanced materials with well-defined structures as well as the development of new methods will remain tasks of electrochemistry also in the next decades, in which the electrode kinetics will play an important role. Because both the electron transfer and ion transfer processes and their rates are of importance in the life sciences, the techniques of electrochemical kinetics can give a unique tool for gaining a deeper understanding of the processes occurring in biological systems.

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