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# Can the Tafel equation be derived from first principles?

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## Abstract

A century ago, Tafel disapproved the attempts to derive the empirical equation named after him by thermodynamic methods. He noted that his observations referred to irreversible electrochemical reactions, where thermodynamics is inapplicable. This statement seems to remain valid until today. Indeed, it is impossible as yet to predict the kinetic parameters for chemical processes by determining rate constants and reaction orders from “first principles”, unless strictly specialized and, to a great extent, artificial models are developed.

Nevertheless, in this paper an attempt to derive the kinetic law of mass action from “first principles” is made in macroscopic formulation. It has turned out to be possible owing to the methods of thermodynamics of irreversible processes that were unknown in Tafel’s time.  
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## 1. Introduction

By combining measurements of current with the analysis of overpotentials for electrochemical reactions of hydrogen evolution (where the rate-determining step is the chemical combination of hydrogen atoms), Tafel (1905) empirically discovered

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the first formulation of the electrochemical kinetics law—Tafel's equation showing an exponential relation between the electrochemical reaction rate  $i$  and the overpotential  $\eta$  [1]:

$$\eta = a + b \log i, \quad (1)$$

where  $a$  and  $b$  are characteristic constants of the electrode system that were named Tafel constants.

Although Tafel emphasized the empirical basis of this equation, numerous attempts were made to derive a similar equation from thermodynamic considerations. It was even asserted that this equation could be derived from the Nernst equation. However, Tafel noted that his observations were particularly studied in irreversible electrochemical reactions, where thermodynamics is inapplicable. Thus, Tafel's studies were the first to separate electrochemical kinetics from thermodynamics, which enabled systematic studies of irreversible reactions [2,3].

This statement of Tafel seems to retain its importance until today. In fact, Tafel meant common thermodynamics related to reversible processes and equilibrium states, because at that time non-equilibrium thermodynamics had not been created as yet. Unfortunately, during the following 100 years researchers did not pay attention to this remark preferring not to reflect on the issue whether the equations of chemical and electrochemical kinetics have a sufficient theoretical basis.

## 2. Empiricism of kinetic equations

In fact, until now all handbooks on chemical kinetics and chemical thermodynamics start the description of kinetics with so called *kinetic law of mass action* given below by Eq. (2), which is a basic *postulate* of chemical kinetics. Long ago, Guldberg and Waage [4] proposed this generic law to describe their observations on the rate of chemical reactions as a linear function of concentrations  $c_i$  of substances:

$$J = k_f c_f - k_r c_r, \quad (2)$$

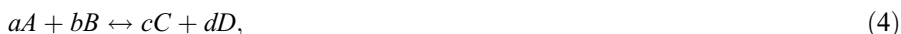
which can also be presented as follows:

$$J = k_f \prod_{j=1}^q c_j^{-v_j} - k_r \prod_{j=q+1}^n c_j^{v_j}, \quad (3)$$

where  $k_f$  and  $k_r$  are rate constants of the forward and reverse reactions, respectively;  $c_j$  are concentrations of reactants ( $j = 1, \dots, q$ ) and products ( $j = q + 1, \dots, n$ );  $v_j$  is a stoichiometric coefficient of  $j$ th component of the reaction ( $v_j < 0$  for reactants and  $v_j > 0$  for products).

Eq. (3) represents the most general form of the kinetic law of mass action, which has had only an empirical basis until now, in contrast to the classical law of mass action for chemical equilibrium rigorously derived in chemical thermodynamics from equilibrium condition [5]. Although, apparently, the first published experimental observation of the linear dependence of the chemical reaction rate (inversion of sucrose) on the concentrations of reagents was made in 1850 by Wilhelmy [6], at about

the same time Guldberg and Waage carried out their work on the “law of mass action” and derived an equilibrium equation on the basis of assumed empirical kinetic equations [4]. They studied chemical affinity (“forces”) and tentatively suggested that the rates of reactions might be proportional to the forces which are proportional to concentrations [7]. Thus, for the reaction



the force in the left-to-right direction should be proportional to  $[A]^a[B]^b$ , and the force from the right to the left is proportional to  $[C]^c[D]^d$ . It was assumed that if the forces in a system were equal and oppositely directed, chemical equilibrium was reached with the equilibrium constant:

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}. \quad (5)$$

However, Eqs. (2) and (3) were *only postulated* on the basis of experimental observations, because they could not be obtained by any method of chemical thermodynamics concerned with equilibrium processes while chemical reactions are essentially irreversible processes. Therefore, equilibrium thermodynamics can give an answer to the question whether a spontaneous reaction is possible, but cannot determine the reaction rate.

Incidentally, it should be noted that this postulate, side by side with the empirical Arrhenius law, served the basis for the well-known derivation of the principal kinetic equation of the transition overpotential by Erdey–Gruz and Volmer. They assumed that the transition rate and, hence, the current should be proportional to the components concentrations at the electrodes surface and to Boltzmann’s exponent involving the activation energy [8]. It is noteworthy that at high anodic and cathodic overpotentials it acquires the form of the Tafel’s equation, but, of course, it cannot serve as its theoretical substantiation, since it is based on empirical dependences.

### 3. Nernst equation for electrochemical equilibrium

An implicit aspiration for solving this problem has existed for many years, which is confirmed by an unsuccessful attempt to depart from the equilibrium state by introducing the notion of the *reaction quotient* suggested in recent years by several authors (e.g., [9]) for solving equilibrium problems. So called “reaction quotient”  $Q$  is written for non-equilibrium concentrations, but exactly in the same way as the equilibrium constant  $K$  in Eq. (5):

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}. \quad (6)$$

If  $Q$  is less than  $K$ , more products will be formed (forward reaction); if, however,  $Q$  is greater than  $K$ , more reactants will be formed (reverse reaction), and if  $Q = K$ , no changes occur. Thus, the difference between  $K$  and  $Q$  can only point out the direction

of the reaction like the second law of classic thermodynamics, but it cannot say anything about the reaction rate. Although the traditional method of determining the equilibrium concentration of chemicals in a reaction at a given equilibrium constant and initial concentration of chemicals involves the determination of the reaction quotient, it has been demonstrated that this step may be eliminated, thereby simplifying the algorithm of solving such problems [10].

We can show that the reaction quotient  $Q$  proves to be unnecessary not only for equilibrium problems, but also for non-equilibrium reactions, on the example of the derivation of the Nernst equation. It can be derived from ordinary chemical thermodynamics, because the general Nernst equation correlates the Gibb's free energy  $\Delta G$  with the electromotive force of an electrochemical system known as a galvanic cell. For a non-equilibrium redox reaction, the equation represents definite amounts of reactants forming definite (as well) amounts of products, and Gibb's free energy  $\Delta G$  is a negative value of the maximum possible electric work in this reaction:

$$\Delta G = -zF\Delta\varphi, \quad (7)$$

where the number ( $z$ ) of electrons in such reaction equation is related to the amount of charge transferred when the reaction is completed,  $F$  is the Faraday constant and  $\Delta\varphi$  is the maximum potential difference (the electromotive force, or cell voltage [9]) determined by the nature of the reactants and electrolytes.

For example, in the non-equilibrium reaction similar to Eq. (4) the Gibbs free energy is:

$$\Delta G = \Delta G^0 + RT \ln \frac{(a_C)^c (a_D)^d}{(a_A)^a (a_B)^b} = \Delta G^0 + RT \ln Q, \quad (8)$$

where  $\Delta G^0$  is related to a standard state,  $R$  and  $T$  are the gas constant and temperature, respectively,  $a_A$ ,  $a_B$ ,  $a_C$ , and  $a_D$  are the activities of the acting components A, B, C and D, and the reaction quotient  $Q$  is written with the activities. Apparently, the latter provides convenient abbreviations in symbols, but does not introduce anything new.

For example, in the reaction with “ $z$ ” electrons transferred and the oxidized components placed in right-hand side of the redox equation, the activity  $(a_Z)^z$  substitutes for  $(a_D)^d$  in Eq. (4). Thus, it follows formally [9] from Eqs. (7) and (8) that:

$$\Delta\varphi = \Delta\varphi_0 - \frac{RT}{zF} \ln Q = \Delta\varphi_0 - \frac{RT}{zF} \ln \frac{(a_C)^c (a_Z)^z}{(a_A)^a (a_B)^b}, \quad (9)$$

where  $\Delta\varphi_0$  is a value of the cell voltage when all activities  $(a_i)^i = 1$  or  $(a_C)^c (a_Z)^z = (a_A)^a (a_B)^b$ .

However, although the cell voltage obtained by such formalistic speculation depends on acting (non-equilibrium) activities the reaction quotient  $Q$  has nothing to do with the rate of non-equilibrium reactions. Therefore, Eq. (9) and the reaction quotient  $Q$  are unnecessary for electrochemical kinetics.

Nevertheless, when a system is in equilibrium, we can write  $\Delta\varphi = 0$  (i.e.,  $\Delta G = 0$ ) and the equilibrium potential difference is:

$$\Delta\varphi_0 = \varphi_0 - \varphi^0 = \frac{RT}{zF} \ln \frac{(a_C)_e^c (a_Z)_e^z}{(a_A)_e^a (a_B)_e^b} = \frac{RT}{zF} \ln K, \quad (10)$$

where the subscripts e denote equilibrium activities,  $\varphi_0$  is the equilibrium potential and  $\varphi^0$  is the standard potential. It is known as the Nernst equation for equilibrium potentials which is necessary for the definition of overpotentials serving as driving forces in electrochemical kinetics.

Note that although Eq. (9) has been obtained for a non-equilibrium reaction using the methods of equilibrium thermodynamics, nevertheless, it does not allow us to determine this reaction rate remaining within the frames of equilibrium thermodynamics. Tafel [1] attracted attention to the electrode reaction as a rate process and not as appendix to the Nernst electrode potential.

#### 4. Arrhenius and Eyring equations in chemical kinetics

In 1889, Arrhenius analyzed temperature dependence of measured reaction rates according to the equation which is now called the Arrhenius equation. However, it would be fair to emphasize that this equation was certainly first suggested by van't Hoff in 1884 [11]. Indeed, van't Hoff analyzed the temperature dependence of the equilibrium constant (now it is called the van't Hoff equation) and of the forward and reverse reaction rates. The effect of temperature on the reactions rates  $k$  was found by Arrhenius empirically as a linear relationship between  $\log k$  and  $1/T$ . In fact, the relationship is of the same form as the one in van't Hoff analysis:

$$\frac{\partial \ln k}{\partial (1/T)} = -\frac{E_a}{R}, \quad (11)$$

where  $E_a$  is an empirical calorimetric parameter called the *activation energy*,  $k$  is the observed reaction rate. More specifically, Arrhenius did not consider a temperature dependence of the energy  $E_a$  and therefore adopted van't Hoff's simpler equation:

$$k = A \exp\left(-\frac{E_a}{RT}\right), \quad (12)$$

where  $A$  is a pre-exponential term expressed in the same units as  $k$ . An assumption inherent in most applications of the Arrhenius equation to kinetic analysis is that this energetic term has some inherent meaning and correlates with the enthalpic activation barrier for the process under study. It turns out that this is a reasonable assumption, at least for reactions that are characterized by large ( $> 10$  kcal/mol)  $E_a$  values. Similarly, the pre-exponential factor  $A$  is often qualitatively correlated with the entropic component of the activation barrier.

The introduction of a value  $E_a$  having the dimension of energy and called activation energy (strictly speaking, a better name would be *experimental activation energy*) gives rise to many speculations. Note, by the way, that the term activation energy implies overcoming certain energetic barrier, which is obvious in models of the collision theory and of the transition state theory [12], but is never obvious in the

Arrhenius law. One of such speculations can be demonstrated as the “derivation” of the Tafel’s equation from the Arrhenius equation assuming  $E_a$  to be a linear function of overpotential. Obviously,  $E_a$  becomes clearly defined only in case of its application to a specific physical model of a barrier process, which, however, is usually far from the actual pattern of the reaction. Therefore, experimentally measured  $E_a$  values often contain little information about the process mechanism, except cases of characteristically differing  $E_a$  values (for instance, for diffusion or chemical activation).

At the same time, Arrhenius gave an original interpretation of energy barrier: he suggested that the equilibrium is established between normal and active molecules of the reactant, which are able to form products without further addition of energy. Later, this suggestion formed the basis of the modern transition state theory and Eyring equation, which is a theoretical construct based on *transition state* model. In 1917, Trautz and Lewis independently proposed that the rate of reaction is determined by the frequency of molecular collisions. This is now known as the collision theory of chemical reaction kinetics [12].

Finally, in 1935 Eyring developed a statistical treatment called the theory of absolute reaction rates or transition state theory, according to which the reaction occurs in two steps: (a) equilibrated conversion of the reactant(s) into an activated complex; (b) decomposition of the complex (which occurs at a definite rate) [12]. However, he was forced to use Eq. (3), i.e. postulate. Both the Arrhenius and Eyring equations described the temperature dependence of the reaction rate. Strictly speaking, the Arrhenius equation can be applied only to gas reactions. It is founded on the empirical observation that conducting a reaction at a higher temperature increases the reaction rate. The Eyring equation is used in the study of gas, condensed and mixed phase reactions—all cases where a simple collision model is not very helpful [12]. The collision model of the reaction rate assumes that the rate constant is written as Eq. (12) with  $A = pZ$ , where  $Z$  is the collision rate,  $p$  is the steric factor. If we consider this equation in terms of changing temperature, the steric factor clearly does not depend on temperature.  $Z$  turns out to be only magnitude weakly dependent on temperature: varying  $T$  from 500 to 600 K changes  $Z$  by less than 10%. It is, therefore, a reasonable approximation to assume that the  $pZ$  part of the above equation is constant, and we come to the Arrhenius equation again.

The Eyring equation is derived in the theory of absolute reaction rates using linear rate-concentration dependences of Eq. (3) type as a postulate ([12], pp. 12–13) and introducing a specific rate (rate constant) in the form:

$$k_c = \frac{k_B T}{h} \exp\left(-\frac{\Delta F^+}{RT}\right), \quad (13)$$

where  $k_B$  and  $h$  are Boltzmann and Planck constants, respectively, and  $\Delta F^+$  is the free energy of activation. Further replacement of the exponent with its equivalent in terms of the partition functions of the species using the methods of statistical mechanics expands and complicates the analysis, but does not change the fact that the mentioned postulate underlies it.

## 5. It is possible to proceed without postulates and activation energy

Meanwhile, classic thermodynamics using the Gibbs formulation of the condition for chemical equilibrium can give the *classic law of mass action* strictly enough only for the equilibrium constant, but *not for the reaction rate*.

Since the basic equation of chemical kinetics given by Eq. (3) is until today only postulated, but not derived theoretically, a basic question arises: what is it—empiricism or self-consistent theory in chemical kinetics? The answer is evident: unless the *kinetic law of mass action* would be derived strictly on the basis of fundamental laws, the chemical kinetics will not be based on self-consistent theory. Hence, the problem is to find a way for deriving the kinetic law of mass action without any postulates. To solve this problem, we must apply *thermodynamics of irreversible processes* because we are dealing with irreversible chemical reactions.

However, the conviction that the use of basic Eq. (3) as a postulate confirmed only empirically is inevitable is so deep-rooted with the researchers that even when describing chemical reactions in non-equilibrium thermodynamics, authors usually refer to Eqs. (2) and (3) as a postulate [5]. Thus, even in non-equilibrium thermodynamics they proceed from the idea that it is accepted from the experiment in chemical kinetics that the kinetic law of acting masses, i.e. Eq. (3), is valid for reactions in ideal gases or in dilute solutions. Then this equation is used as a postulate for deriving the kinetic equation in the form of the reaction rate dependence on chemical affinity [5]. Thus, the problem of substantiation of the kinetic equation calls for a solution.

Therefore, we are forced to revise this approach and suggest a different way. Making attempts to derive the kinetic law of mass action from the first principles, we have to resort to a different approach and use a fundamental transport law which is well proven in non-equilibrium thermodynamics by statistical methods. In non-equilibrium thermodynamics, generalized forces (in chemistry they imply the reaction affinity  $\tilde{A}$  as its driving thermodynamic force) are connected with generalized fluxes (in chemistry they imply the reaction rate  $J$ ) and their action produces entropy with the rate  $\partial S/\partial t = JA/T$ . The function is  $J = f(\tilde{A}/RT)$ , in general, an *unknown law of chemical kinetics*.

For the sake of simplicity and clarity, let us analyze a simple chemical reaction, where the substance 1 turns into 2 under the conditions of a stationary regime. These conditions are satisfied if the height of the barrier to be overcome greatly exceeds the difference of chemical potentials corresponding to these states and almost all the molecules are distributed between the initial and the final state of the present reaction. Intermediate products on the top of the barrier are unstable and decompose into the initial and final product. Thus, there is no product accumulation along the reaction path  $x$ , and therefore the flux is constant everywhere.

To find the reaction rate  $J$ , we subdivide the reaction path along its  $x$ -coordinate into a finite number of segments  $\Delta x_i$  with chemical potential differences  $\Delta\mu_i$  corresponding to these segments ( $\sum_i \Delta\mu_i = \Delta\mu$ ) [13]. Then the total reaction may be represented as a chain of consecutive substance transformations proceeding in consecutive  $i$  partial reactions with respective chemical affinity  $A_i = -\Delta\mu_i$ , the value

$\sum_i \tilde{A}_i = \tilde{A}$  representing the affinity of the total reaction. On sufficiently small segments ( $\tilde{A}_i \ll RT$  is achievable, since the number of segments is arbitrary) the unknown function  $J_i = f(\tilde{A}_i/RT)$  can be linearized for small arguments (according to the physical sense  $J_i = 0$ , if  $\tilde{A}_i = 0$ ):

$$J_i = \tilde{A}_i \left( \frac{\partial J_i}{\partial \tilde{A}_i} \right)_{\Delta x_i \rightarrow 0} = - \left( \frac{k_i \Delta x_i}{RT} \right)_{\Delta x_i \rightarrow 0} \frac{\partial \mu_i(x)}{\partial x} = -L_i \text{grad } \mu, \quad (14)$$

where we have used  $[\Delta \mu_i / \Delta x_i]_{\Delta x_i \rightarrow 0} = \partial \mu_i(x) / \partial x$ , and  $k_i$  and  $L_i$  are certain constants. The linear form of this equation is invariant for all transport phenomena (diffusion, electric current, heat conduction, filtration, migration, etc.). Summing-integrating the entropy production along the total reaction path in stationary conditions  $J = J_i$ , we obtain for the reaction on the whole:

$$T \frac{\partial S}{\partial t} = T \sum_i \frac{\partial S_i}{\partial t} = - \sum_i J_i \frac{\partial \mu_i(x)}{\partial x} \Big|_{\Delta x_i} \Big|_{\Delta x_i \rightarrow 0} = -J \int_1^2 \frac{\partial \mu(x)}{\partial x} dx = -J \Delta \mu = J \tilde{A}, \quad (15)$$

where integration is carried out over the entire reaction path from the initial (1) to the final (2) state.

Thus, the general form of the entropy production in the course of a chemical reaction is valid for chemical reactions described by any non-linear kinetic law. A linear phenomenological equation in the invariant form of the transport equation (resulting from the entropy production calculation) approximates the reaction rate near the equilibrium state or at sufficiently small  $\Delta x_i$  segment of the reaction path. Of course, this does not necessarily mean the existence of a linear dependence of the reaction rate on the total affinity of the entire reaction consisting of several slow sequential partial reactions for which the linearization is possible.

To find unknown kinetic law,  $J = f(\tilde{A}/RT)$  let us write a standard expression of chemical potential through the activity  $a(x)$ :

$$\mu(x) = RT \ln a(x) + \mu^0(x), \quad (16)$$

where  $\mu^0(x)$  is a standard value for every point  $x$  (i.e., a profile of the standard chemical potential along  $x$ -coordinate). Substituting into the general transport equation, one obtains:

$$J(x) = -L(x) \frac{\partial \mu(x)}{\partial x} = - \frac{RTL(x)}{a(x)} \exp \left[ - \frac{\mu^0(x)}{RT} \right] \frac{\partial}{\partial x} \exp \frac{\mu(x)}{RT}. \quad (17)$$

Subdividing this equation as follows:

$$J(x) \frac{a(x) \exp \frac{\mu^0(x)}{RT}}{L(x)} = -RT \frac{\partial}{\partial x} \exp \frac{\mu(x)}{RT} \quad (18)$$

and integrating along  $x$  from the initial state (1) to the final (2) state with the account for the conditions of a stationary regime  $J(x) = J$  over the entire path from 1 to 2, one obtains:



$$J = \frac{RT \exp \frac{\mu_2}{RT}}{\int_1^2 \frac{a(x)}{L(x)} \exp \frac{\mu^0(x)}{RT} dx} \left( \exp \frac{\mu_1 - \mu_2}{RT} - 1 \right), \quad (19)$$

where subscripts 1 and 2 are related to chemical potentials and activity in the states 1 and 2, respectively. Denoting the constant quantity by

$$L = \frac{\exp \frac{\mu_2}{RT}}{\int_1^2 \frac{a(x)}{L(x)} \exp \frac{\mu^0(x)}{RT} dx}, \quad (20)$$

we obtain the general kinetic law:

$$J = RTL \left( \exp \frac{\mu_1 - \mu_2}{RT} - 1 \right) = RTL \exp \left( \frac{\tilde{A}}{RT} - 1 \right) = k \exp \left( \frac{\tilde{A}}{RT} - 1 \right), \quad (21)$$

that in linear approximation for  $\tilde{A} \ll RT$  (near equilibrium state) transforms into the linear form of transport equations:

$$J = L\tilde{A} = -L \text{grad } \mu. \quad (22)$$

Now we can rigorously derive the kinetic law of mass action in the form which was earlier only postulated from experimental observations. Let us denote:

$$k_r = \frac{RT \exp \frac{\mu_2}{RT}}{\int_1^2 \frac{a(x)}{L(x)} \exp \mu \frac{\mu^0(x)}{RT} dx} \quad \text{and} \quad k_f = k_r \exp \left( -\frac{\mu_2^0 - \mu_1^0}{RT} \right). \quad (23)$$

Substituting Eqs. (23) into the general kinetic law (21), we rigorously obtain the kinetic law of mass action in the form of Eq. (2):

$$J = k_f a_1 - k_r a_2 = k'_f c_1 - k'_r c_2 \quad (24)$$

and the classic law of mass action:

$$K \equiv \frac{k_f}{k_r} = \exp \left( -\frac{\mu_2^0 - \mu_1^0}{RT} \right) = \frac{a_2^{\text{eq}}}{a_1^{\text{eq}}}, \quad (25)$$

where  $k_f$  and  $k_r$  are the rate constants of the forward and reverse reactions, respectively; superscript eq denotes the activity in the equilibrium state with the equilibrium constant  $K$ . Unfortunately, usually an opposite situation takes place, namely, a kinetic equation in the form of Eq. (21) (see, e.g., [5], etc.) is obtained from the empirically obtained and then postulated Eq. (2). We, however, derive the kinetic Eq. (21) without resorting to empirical Eq. (2) and, in the long run, obtain Eq. (2) rigorously from the first principles.

Passing to electrochemical kinetics, it is necessary to replace the chemical potential in Eq. (16) with the electrochemical potential:

$$\tilde{\mu} = RT \ln a + \mu^0 + zF\varphi \quad (26)$$

and the activity  $a$ —with electrochemical activity [13]:

$$\tilde{a} = a \exp \frac{zF\varphi}{RT}. \quad (27)$$

Analyzing, for simplicity, the redox reaction  $\text{red} = \text{ox}^{+ze} + ze$  (e.g., metal dissolution  $\text{Me} = \text{Me}^{+ze} + ze$ ) and dividing the electrochemical affinity into two parts for anodic (forward) and cathodic (reverse) reactions using common anodic and cathodic transfer coefficients  $\alpha$  and  $\beta$ , respectively (taking into the account for the negative sign of cathodic potential), Eq. (27) can be rewritten for these partial reactions:

$$\tilde{a}_a = a_{\text{red}} \exp \frac{\alpha z F \varphi}{RT} \quad \text{and} \quad \tilde{a}_c = a_{\text{ox}} \exp \left( -\frac{\beta z F \varphi}{RT} \right), \quad (28)$$

where  $a_{\text{red}}$  and  $a_{\text{ox}}$  are ordinary activities of the species in reduced and oxidized forms, respectively. Substituting electrochemical activities (28) into Eq. (24), we obtain the net reaction rate without resorting to the notion of activation energy in contrast to the approach [14] generally accepted in electrochemical kinetics:

$$J = z\bar{i} = k_f \tilde{a}_a - k_r \tilde{a}_c = k_f a_{\text{red}} \exp \frac{\alpha z F \varphi}{RT} - k_r a_{\text{ox}} \exp \left( -\frac{\beta z F \varphi}{RT} \right) \quad (29)$$

and in the case of equilibrium ( $i = 0$ ), equilibrium potential will be established:

$$\varphi_0 = \frac{RT}{zF} \ln \frac{k_r a_{\text{ok}}}{k_f a_{\text{red}}} = \varphi^0 + \frac{RT}{zF} \ln \frac{a_{\text{ok}}}{a_{\text{red}}}, \quad (30)$$

where the standard potential is:

$$\varphi^0 = \frac{RT}{zF} \ln \frac{k_r}{k_f}. \quad (31)$$

Note that the right-hand side of Eq. (30) coincides with the Nernst Eq. (10) obtained by a purely thermodynamic method from the condition of the equilibrium of chemical potentials. Therefore, the left-hand side of Eq. (30) obtained from a kinetic analysis makes it possible to reveal the physical meaning of the standard potential in Eq. (10) as a ratio of chemical rate constants of forward and reverse reactions. Introducing, as usual, the overpotential  $\eta = \varphi - \varphi_0$  and the exchange current density  $i_0$  from the equilibrium condition  $i = 0$ , one obtains from Eq. (29) the Butler–Volmer equation:

$$i = i_0 \left[ \exp \frac{\alpha z F \eta}{RT} - \exp \left( -\frac{\beta z F \eta}{RT} \right) \right], \quad (32)$$

where the exchange current density is:

$$z\bar{i}_0 = k_r a_{\text{ox}} \exp \left( -\frac{\beta z F \varphi_0}{RT} \right) = k_f a_{\text{r}} \exp \frac{\alpha z F \varphi_0}{RT} = k_r^\alpha k_f^\beta a_{\text{ok}}^\alpha a_{\text{red}}^\beta. \quad (33)$$

Assuming, in a particular case, that  $\alpha = 1$  and  $\beta = 0$  (asymmetrical distribution of applied potential) and combining Eqs. (29) and (30), we obtain the equation in the form analogous to that of Eq. (21) used in non-equilibrium thermodynamics of chemical reactions:

$$i = i_0 \exp \left( \exp \frac{zF\eta}{RT} - 1 \right) = i_0 \exp \left( \exp \frac{\tilde{A}}{RT} - 1 \right), \quad (34)$$

where the electrochemical affinity  $\tilde{A} = zF\eta$  shows the role of overpotential  $\eta$  as a measure of thermodynamic motive force for a non-equilibrium electrochemical reaction. If it is far enough from the equilibrium ( $zF\eta \gg RT$ ), the general kinetic law (21) transforms through Eq. (34) into the Tafel Eq. (1) and reveals the meaning of Tafel's constants  $a$  and  $b$  from the first principles.

## 6. Conclusions

The kinetic law of mass actions is derived rigorously from non-equilibrium thermodynamics using invariant properties of the transport law applied to the elementary steps along the reaction path. Therefore, all non-linear equations of chemical kinetics become rigorously grounded, and theoretical derivation of the Tafel equation becomes possible without an empirical basis or models using postulates and activation energy.

## References

- [1] J. Tafel, *Z. Phys. Chem.* 50 (1905) 641.
- [2] K. Müller, *J. Res. Inst. Catal., Hokkaido Univ.* 17 (1969) 54–75.
- [3] Biography of J. Tafel compiled by E. Katz. Available from: <<http://chem.ch.huji.ac.il/~eugeniik/history/tafel.html>>.
- [4] C.M. Guldberg, P. Waage, *Forhandlinger I Videnskabs Selskabet I Cristiana* (1864) 35–40, 92–94, 111–120.
- [5] R. Haase, *Thermodynamics of Irreversible Processes*, Addison-Wesley, London, 1969, p. 509.
- [6] L. Wilhelmy, (*Poggendorff's Ann. Phys. Chem.* 81 (1850) 413–433, 499–526.
- [7] C.M. Guldberg, P. Waage, *J. Prakt. Chem.* 19 (1879) 69–114.
- [8] T. Erdey-Gruz, M. Volmer, *Z. Phys. Chem.* 150A (1930) 203.
- [9] R.M. Hanson, S.M.E. Green, *Introduction to Molecular Thermodynamics*, Integrated Graphics, Northfield, 2003, p. 342.
- [10] P.S. Matsumoto, *J. Chem. Educat.* 82 (3) (2005) 406.
- [11] J.H. van't Hoff, *Etudes de dynamique chimique*, F. Muller, Amsterdam, 1884.
- [12] S. Glesston, K. Laidler, H. Eyring, *The Theory of Rate Processes*, McGraw-Hill Book Comp., N.-Y., 1941, p. 611.
- [13] E.M. Gutman, *Mechanochemistry of Materials*, Cambridge International Sci. Publ., Cambridge, 1998, p. 212.
- [14] K.J. Vetter, *Electrochemical Kinetics*, Academic Press, N.-Y., 1967, pp. 789.

Corrigendum

Corrigendum to “Can the Tafel equation  
be derived from first principles?”  
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I regret the misprints in the Eqs. (14), (23) and (33).

The corrected Eq. (14) is as following:

$$J_i = \tilde{A}_i \left( \frac{\partial J_i}{\partial \tilde{A}_i} \right)_{\Delta x_i \rightarrow 0} = - \left( \frac{k_i \Delta x_i}{RT} \right)_{\Delta x_i \rightarrow 0} \frac{\partial \mu_i(x)}{\partial x} = -L_i \text{grad} \mu_i(x) \quad (14)$$

The corrected first equation of Eqs. (23) and (33) are, respectively:

$$k_r = \frac{RT \exp \frac{\mu_2^0}{RT}}{\int_1^2 \frac{a(x)}{L(x)} \exp \frac{\mu^0(x)}{RT} dx} \quad (23)$$

$$i_0 = k_r a_{\text{ox}} \exp \left( - \frac{\beta z F \varphi_0}{RT} \right) = k_r a_r \exp \frac{\alpha z F \varphi_0}{RT} = k_r^\alpha k_f^\beta a_{\text{ok}}^\alpha a_{\text{red}}^\beta \quad (33)$$

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