

ELECTRODE THERMOKINETICS

Károly OLÁH

Department of Physical Chemistry
Technical University of Budapest
H-1521 Budapest, Hungary

Received: Feb. 21, 1997

Abstract

A thermodynamic interpretation of the kinetics of processes taking place on equilibrium and polarized electrodes is given using the new theory 'Thermokinetics', a nonlinear general kinetic theory of physicochemical processes. In the introductory parts the observations of Tafel and the interpretation given by Erdey-Gruz and Volmer are shortly summarized. In the next section the methodology and some important results of Thermokinetics, e.g., the principle of the general macroscopic reversal symmetry are discussed. In the next part some new results of electrode kinetics provided by the application of Thermokinetics are presented. Last, taking into account the carried heat transport, the mass-heat cross effect is discussed, demonstrating the general reciprocity relation of Thermokinetics. In the linear range, the consistency with the Onsagerian irreversible thermodynamics is shown.

Keywords: electrochemistry, electrode kinetics, thermodynamics, thermokinetics, processes.

1. Introduction

Electrochemistry is known to be the most instructive part of physical chemistry and thermodynamics. Conductance measurements provide valuable information about transport phenomena, nonideal behaviours and cross effects of electrolyte solutions. Equilibrium measurements on galvanic cells permit the evaluation of the affinity, the temperature dependences, and the calculation of the enthalpy and entropy changes of electrochemical processes; Concentration dependences led to the evaluation of chemical potentials, activities and cross effects between mass and charge transport, and diffusion potentials. And last but not least, studies on polarization phenomena have yielded a series of instructive examples for nonequilibrium thermodynamics, not only for Onsagerian irreversible thermodynamics but also for modern nonlinear kinetic theory, 'Thermokinetics'. Electrode kinetics can be deservedly called a precursor of thermokinetics, which, developed later into a general theory, made important steps in completing the theoretical interpretation of electrode processes.



Fig. 1. Overpotential of H₂ evolution on various cathode metals

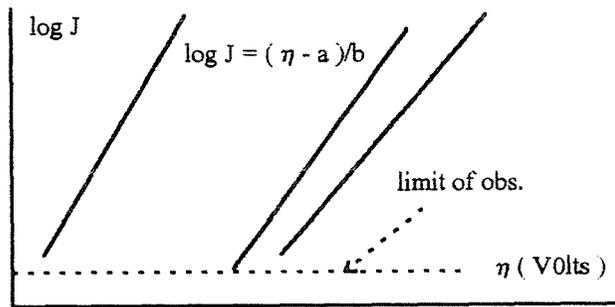


Fig. 2. Tafel plots

2. Overpotential. Tafel

The deposition of ions or evolution of gases, e.g. hydrogen on a metal surface occurs to an appreciable extent only at potentials exceeding the zero current cell potential. This difference is called 'overpotential' (η).

TAFEL [1] in 1905 investigated the current densities vs. voltages in galvanic cells and observed that the overvoltages vary approximately proportionally to the logarithm of the current density (J)

$$\eta = a + b \cdot \log J \quad (1)$$

parameter a varies with the material of the electrode and with its surface properties and measures the overpotential.

Parameter b is nearly the same (0.11–0.12)

These experiments suggest that the same electrochemical process, e. g. evolution of hydrogen gas, begins to rise at a distinctly different voltage than it would be expected from thermodynamic calculations. It was hard to understand that the (apparently) zero current voltage may vary with the electrode material which does not take part in the chemical process.

Table 1
Overpotential of H₂ evolution on different electrodes

Electrode material	Overpotential in volts
Pt (platinized)	0.005
Pt (smooth)	0.08
Ni (spongy)	0.05
Ni (smooth)	0.21
Pb	0.64
Hg	0.78

Table 2
Tafel's parameter *b* for H₂ evolution

Electrode material	<i>b</i> in volts
Pt	0.120
Ni	0.115
Pb	0.125
Hg	0.119

3. Erdey-Gruz and Volmer

These authors [2] (1930) made a great progress in interpreting the experiments. The basic statements of this interpretation are:

- a) The current measured by the ammeter in series with the cell is really a 'net' current, the difference of two opposite currents flowing at the electrode surface, individual 'anodic' (j^+) and 'cathodic' (j^-) 'absolute' partial currents:

$$J = j^+ - j^- \quad (2)$$

- b) The zero current potential is in all cases the same, it is determined only by the electrode process and does not vary with the electrode material. The current at the apparent zero potential is not zero but immeasurably small.
- c) At equilibrium the absolute currents equalize but do not vanish

$$J_{eq} = 0; \quad j_{eq}^+ - j_{eq}^- = j^0, \quad (3)$$

where j^0 is the so-called 'exchange current'.

- d) The absolute currents are exponential functions of the voltage, in the whole range. Near the equilibrium the net current-voltage function is

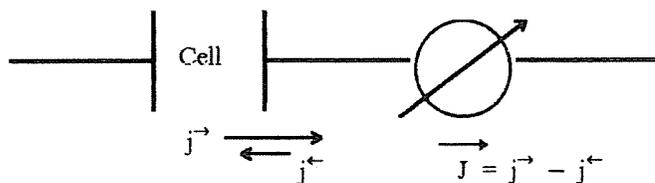


Fig. 3. Absolute and net (measured) currents

linear (Ohmic)

$$J \cong j^0 (zF/RT) \cdot \eta \quad \text{if } J \ll j^0 \quad (4)$$

and far from the equilibrium it is of exponential character

$$J \cong j^- \quad \text{if } j^- \ll j^+,$$

$$\ln j^- = \ln j^0 + [(1 - \alpha) \cdot z \cdot F/RT] \cdot \eta(\text{anodic}), \quad (5a)$$

$$\ln j^+ = \ln j^0 + [(-\alpha) \cdot z \cdot F/RT] \cdot \eta(\text{cathodic}), \quad (5b)$$

where α is the transfer coefficient,

F is the Faraday charge (96 500 C/mol),

z is the number of elementary charges passing the electrode surface.

The process can be symbolized as involving the electrons as a participant

$$\sum_k \nu_{k,red} \cdot A_k \rightleftharpoons \sum_k \nu_{k,ox} \cdot A_k. \quad (6)$$

The charge balance is

$$\sum_k \nu_{k,red} \cdot z_k = \sum_k \nu_{k,ox} \cdot z_k, \quad (7)$$

where z_k is the charge number of the k -th ion, ν_k is the number of the k -th participant taking part in the process, j^0 is a function of T and the concentrations of the participants (C_k). Tafel's constants are in this respect

$$a = \log j^0 \cdot b, \quad (8a)$$

$$b = 2.3026 \cdot RT/(\alpha \cdot zF) = 0.059/\alpha (T = 298K). \quad (8b)$$

(If $\alpha = 0.5$ and at $1 \mu\text{A}$ $\eta = 0.5\text{V}$, then $b=0.118$ and $j^0 = 0.58 \cdot 10^{-10}\text{A}$).

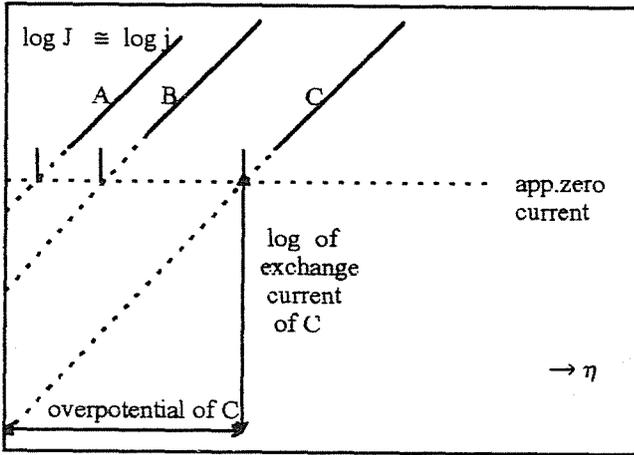


Fig. 4. Plot of $\log j$ vs. η

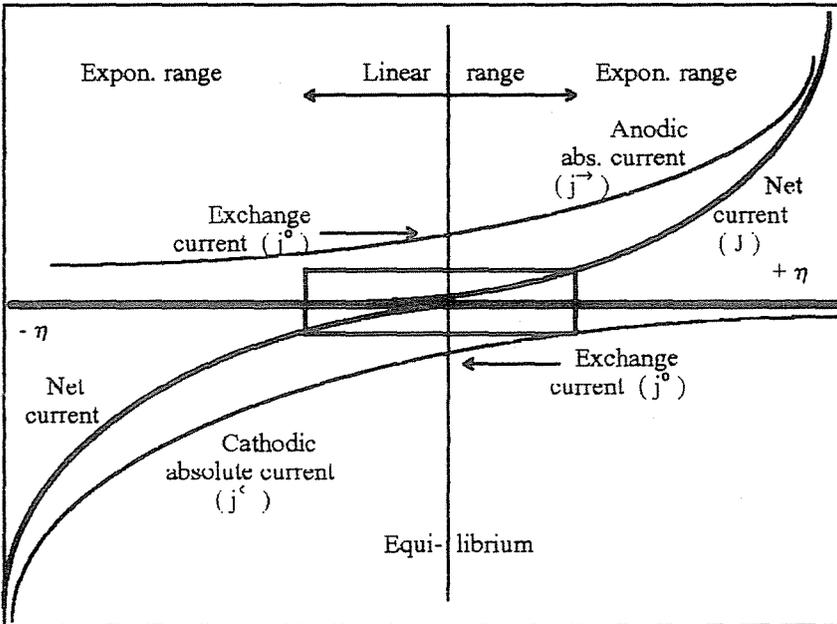


Fig. 5. Anodic, cathodic and net currents

Taking into account the dependence on the temperature and the activities of the chemical species taking part in the process [3]

$$j^- = k_{red} \cdot T^{n_{red}} \cdot \exp\left(-\frac{\Delta H_{red}^\#}{RT}\right) \cdot \Pi a_k^{\nu_{k,red}} \exp\left(\frac{(1-\alpha) \cdot z \cdot F}{RT} \cdot \eta\right), \quad (9)$$

$$j^+ = k_{ox} \cdot T^{n_{ox}} \cdot \exp\left(-\frac{\Delta H_{ox}^\#}{RT}\right) \cdot \Pi a_k^{\nu_{k,ox}} \exp\left(-\frac{\alpha \cdot z \cdot F}{RT} \cdot \eta\right)$$

The first three factors include the temperature-dependence, the next one the concentration-dependence and the last one the variation with the electric potential. In general,

$$j = j(T, C_k, \eta).$$

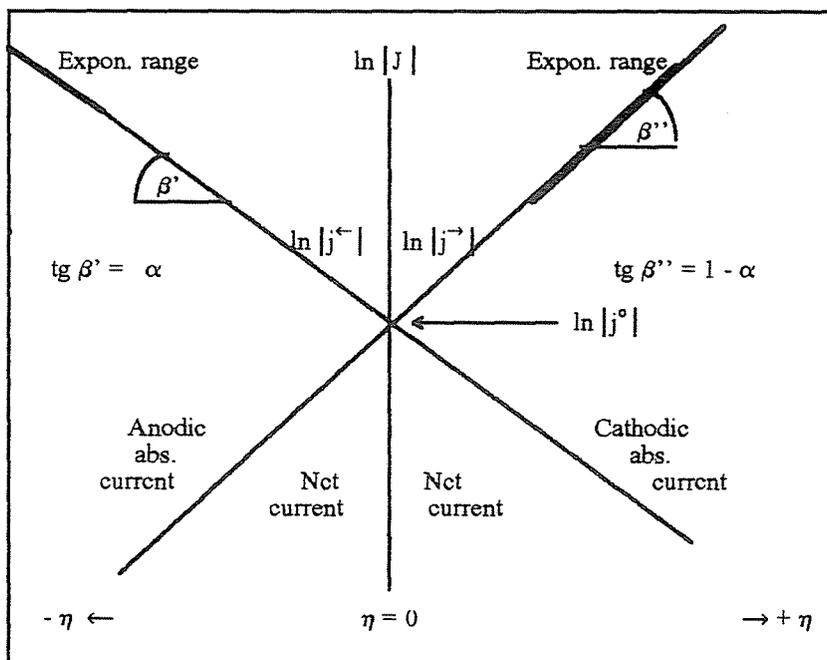


Fig. 6. $\ln |J|$, $\ln |j^-|$ and $\ln |j^+|$ vs. η

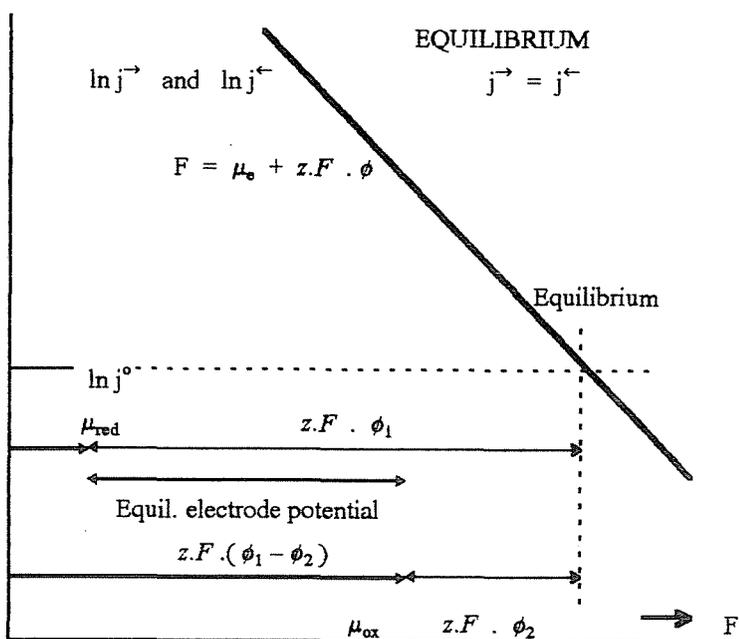


Fig. 7. The anodic/cathodic common $j(F)$ plot. Equilibrium

4. Thermokinetics

According to a modern kinetic theory [4,5] the kinetic properties of the electrode processes form a prototype of a more general kinetics. This theory was developed mainly in the last two decades and led to important consequences which permitted further developments in electrode kinetics. Its basic statements are as follows:

4.1 Absolute Process Rates

A thermodynamic system differs from a mechanical one in that it consists of a great number of similar elements (particles). Thermodynamic processes are carried by motions or transformations of these elements in space and time. All these processes have some kind of duality. Any elementary process may take place in the opposite direction. Such reverse process pairs are in time-reverse relation with each other. In the kinetic theory the 'absolute' process rates play dominant roles.

This general feature of thermodynamic processes has been put into words by FOWLER (1924) [6]: *any one process of exchange acting in a particular direction must be invariable accompanied by an analogous reverse process*. It can be expressed as follows:

any 'net' process rates (J_i) are differences
of a 'forward' (j_i^{\rightarrow}) and a 'backward' (j_i^{\leftarrow}) 'absolute' process rate:

$$J_i = j_i^{\rightarrow} - j_i^{\leftarrow}. \quad (10)$$

Examples: chemical reaction 'from left to right' and 'from right to left', evaporation and vapor condensation, in gases the fluxes of particles in directions $+x$ and $-x$ and, last but not least, the anodic and cathodic exchange current on electrode surfaces according to the interpretation given by Erdey-Gruz and Volmer. The Onsagerian 'irreversible thermodynamics' (IT) always deals with 'net' fluxes (J_i) [7].

4.2 The Dynamic Equilibrium. Law of Detailed Balance

First Ludwig BOLTZMANN [8], later KLEIN and ROSSELAND (1921) [9], KRAMERS and MILNE (1923) [10] studied the collisions of atoms or ions with electrons. FOWLER (1924) comments their results: 'It seems quite certain that the law of distribution of the velocities of free electrons must be the same... it follows that any one process of exchange acting in a particular direction must be invariable *accompanied by an analogous reverse process*.' And, analysing the three-level energy exchanges, 'we have *ruled out the possibility of the cyclic process* $1 \rightarrow 2, 2 \rightarrow 3, 3 \rightarrow 1$. I cannot any convincing a priory reason to believe that such cycles are not permissible' Paul DIRAC (1924) [11] formulated the new general law: 'It seems plausible to suppose that *all atomic processes are reversible*, or, more exactly, that if after any encounter all the velocities are reversed, then the whole process would just repeat itself backwards, the system finally leaving the scene of action being the same as the original systems in the first process and having the reverse velocities. With this assumption to which *there are no known exceptions*, each kind of encounter must be just as likely to occur as its converse in which every velocity has changed sign, the whole process taking place backwards, since there is now perfect symmetry between past and future time.... This *principle of detailed balancing* of atomic encounters with their reverse encounters has been used... by Kramers and Milne.'

Saying this, Dirac has raised the basic pillar of the thermokinetic theory. The new, general kinetic law writes: in equilibria cycles are not

permissible, or, all partial processes are balanced ('in all details')

Principle of Detailed Balance, 'DB'

$$j_{ieq}^{\rightarrow} = j_{ieq}^{\leftarrow} \quad (i = 1, \dots, n) \quad (11)$$

4.3 The Absolute Rate Equations

a) Mass-Action Law (MA)

This law was declared by GULDBERG and WAAGE in 1872 [12]. In brief MA asserts that *the rate of a process is proportional to the number density of the participants*. The factor of proportionality is called the *rate constant of the process* (k). The rate equation in the sense of the MA law can be written as

$$j = k_{(T)} \cdot \Pi_k \cdot C_k^{\nu_k}, \quad (12)$$

where k is the rate constant (in general temperature-dependent), C_k is the concentration (number density) of the k -th participant, ν_k is the stoichiometric coefficient of the k -th participant. The type of the MA rate equation is then

$$j = j(T, C_k). \quad (13)$$

The law, though it was not declared, was employed since the first half of the 19th century, first of all, for chemical processes. Boltzmann, Maxwell, Einstein, Tolman, Onsager and many others up to now, all calculated with rate equations of MA type. The meaning of the law seems to be clear and self-evident, although, in more instances problems arose. One example: a number of processes take place in non-ideal mixtures. Here, the thermodynamic consistency requires 'activities' instead of concentrations. It has turned out that the problems came from the inconsequent choice of the participants. These problems were solved recently by the author [13]. A 'pure' representation would be the expression which contains only densities of extensive quantities, e. g.

$$j = j(C_U \cdot C_k), \quad (14)$$

where C_U is the density of the internal energy. The practical applications would be much more problematic than that of (13). Up to this point the classical electrode kinetics of Erdey-Gruz implies all statements of Thermokinetics listed above. Now follow the new consequences.

b. Potential-Action (PA) Rate Equations

PA type rate equations will be called relationships where the absolute process rates are expressed in terms of the potentials F_i ($1/T$, $-\mu/T$, etc.) [14].

$$j_i(F_1, \dots, F_n), \quad (15)$$

where the variables F_i form the set of *independent* potentials. (15) is in close relation with the Onsagerian 'Ohmic' rate equations (net fluxes in terms of the forces there).

Though this form of rate relations is not so generally used, (an exception is the thermal radiation law, $j_{rad} = \sigma \cdot T^4$), in kinetic theories its use is inevitable.

A result, which may have a wide-spread practical use, is the following law.

4.4 The Time-Reversal Symmetry

Time reversal symmetries are known for mechanical motions. All mechanical, quantum-mechanical kinetic relations show such symmetry as the DB. The time reverse symmetry of other laws of physics are well known. Many signs suggest that time reverse symmetry might be a general property of natural processes. A general symmetry law has always been expected to be valid in thermodynamic systems, too. As we have seen in the former paragraph, two criteria are realized in any equilibrium (at any values of potentials) simultaneously:

$$F_{i,eq}^I = F_{i,eq}^{II}, \quad i = 1, 2, \dots, n, \quad (16)$$

$$\overline{j_{i,eq}} = \overline{j_{i,eq}}, \quad i = 1, 2, \dots, n, \quad (17)$$

The combination of these relations leads to an important consequence [15]. *The PA type rate equations of the reverse absolute rate pairs are always identical, not only their mathematical forms but all constant parameters as well.*

$$j_i^-(F_1^I, \dots, F_n^I) \equiv j_i^-(F_1^{II}, \dots, F_n^{II}) \quad (18)$$

Law of the Reversal Symmetry (RS)

4.5 Carriers and Carried Quantities. Charges

All physico-chemical processes are originated from the motions of elementary constituents of the material system (atomic particles, ions, quasipar-

ticles, electrons, photons, phonons, elementary chemical transformations). Let the absolute rate of such elementary processes be denoted by j_z^* .

These processes may represent (carry) one or more different entities (mass, energy, electric charge, momenta, etc.) [16]. In this case the appropriate process j_i exists as well. The i -th quantity carried by a unit process rate j_z^* will be denoted by Q_{zi} called i -th 'charge' of the z -th process

$$j_i = \sum_z Q_{iz} \cdot j_z^*, \quad (19)$$

$$Q_{iz} = \left(\frac{\partial j_i}{\partial j_z^*} \right), \quad (20)$$

In electrochemistry: if a particle carries an electric charge of $z_k F$, then the absolute fluxes of mass and electric current are closely connected. The flux of the ions (j) carry

$$j_e = j \cdot (z \cdot F) \quad (21)$$

electric current. The charge here is

$$Q = z \cdot F.$$

The charges play a double role in thermokinetics. To any potential (or force field) belongs an appropriate charge. The i -th force field acts upon j_z^* if and only if $Q_{iz} \neq 0$. Here, on the flux of a particle acts, in addition to the chemical potential, the electric force (φ) if and only if it carries $z \cdot F$ electric charge. (And, on it acts the temperature gradient to an extent proportional to its 'thermal charge'. And what thermal charge really is, we will show later). In general, denoting the resultant potential acting on the z -th particle flow by F_z^* ,

$$dF_z^* = \sum_i Q_{zi} \cdot dF_i \quad (22a)$$

and the alternative definition of Q is

$$Q_{zi} = \left(\frac{\partial F_z^*}{\partial F_i} \right). \quad (22b)$$

For the cross effect a new interpretation is now given: *A cross effect exists if one carrier flux carries two or more different charges.*

4.6 The Entropy-Dissipation (D_S)

'Entropy-Dissipation' [17] is the name for the product-sum defined as

$$D_S \equiv \sum_i j_i \cdot F_i. \quad (23)$$

The exact differential of D_S is in general

$$dD_S = \sum_i F_i \cdot dj_i + \sum_i j_i \cdot dF_i = dD_S^j + dD_S^F. \quad (24)$$

The first derivatives are

$$F_i = \left(\frac{\partial D_S^j}{\partial j_i} \right); \quad j_i = \left(\frac{\partial D_S^F}{\partial F_i} \right). \quad (25)$$

The Dynamic Fundamental Equations

For energy and mass transport, the dynamic fundamental equations are [18]

$$dD_S^j = (1/T) \cdot dj_U + \sum_k (-\mu_k/T) \cdot dj_k + (\varphi/T) \cdot dj_e \quad (26)$$

$$D_S^j \equiv (1/T) \cdot j_U + \sum_k (-\mu_k/T) \cdot j_k + (\varphi/T) \cdot j_e \quad (27)$$

$$dD_S^F = j_U \cdot d(1/T) + \sum_k j_k \cdot d(-\mu_k/T) + j_e \cdot d(\varphi/T) \quad (28)$$

As seen, D_S^F is a Legendre-transformed of D_S^j . As D_S^j is the principal dynamic quantity of the *dynamic (j) space*, D_S^F is the same for the *potential-space* both connecting potentials and absolute rates.

The Electrochemical Potential (μ_e)

The particle fluxes and the electric current are not independent because no other kind of electric charge transport occurs. Consequently, the chemical potentials and the electric potential are not independent either: in equilibrium neither the chemical potentials, nor the electric potential equilibrate

independently of each other. In such cases, the appropriate potentials are to be modified in the sense that the entropy dissipation, i.e., the product-sum

$$D_S = \sum_i j_i \cdot F_i$$

be invariant.

Here, F_i denotes the i -th entropic potential ($-\mu/T$ or η/T)

$$j \cdot (-\mu/T) + j_e \cdot (\eta/T) = j \cdot (-\mu - zF\eta)/T = j \cdot (-\mu_e/T)$$

Instead of the chemical potential and the electric potential the *electrochemical potential* (μ_e) is to be applied.

$$\mu_{k,e} \equiv \mu_k - z_k F \cdot \eta. \quad (29)$$

Stoichiometric constraints mean further modifications. The independent potentials are then for the forward (\rightarrow) and backward (\leftarrow) processes:

$$F^{\rightarrow} = -\left(\sum_k \nu_{k,red} \cdot \mu_{k,e}\right)/T; \quad F^{\leftarrow} = -\left(\sum_k \nu_{k,ox} \cdot \mu_{k,e}\right)/T. \quad (30)$$

The condition of equilibrium is the equilibration of the *independent* potentials

$$F_{eq}^{\rightarrow} = F_{eq}^{\leftarrow}.$$

4.7 The General Rate Equation

Analysis of various types of elementary physicochemical rate equations (chemical reactions, phase transfer processes, e.g., evaporation and vapor condensation, heat and mass diffusion) shows that they exhibit a very similar mathematical form if expressed in a consistent way keeping some rules:

- a) The rates should be the absolute and not the net rates.
- b) The rates are to be expressed in terms of the potentials (PA type).
- c) The set of potentials should be the set of independent ones.

The General Rate Equation writes:

$$-R \cdot d \ln j_z^* = \sum_i Q_{zi} dF_i. \quad (31)$$

Together with the balance equation 19 the (nonlinear) rate relations can be constructed.

5. Electrode Thermokinetics

Many works (c.g. KJELSTRUP and BEDEAUX [19, 20] and others have dealt with electrode kinetics, using results of the Onsagerian Irreversible Thermodynamics. Thermokinetics was first applied by the author [21]. It was shown that electrode kinetics can be developed further by applying Thermokinetics.

5.1 PA Type Equations of the Charge Transfer Process

First, one has to transform rate equations (8) into the form $j(F)$. Knowing that

$$d \ln T = -T \cdot d(1/T),$$

$$R \cdot \ln a_k = \frac{\mu_k - \mu_k^0}{T},$$

$$\mu_{k,e} = \mu_k + z \cdot F \cdot \eta,$$

$$H = \left(\frac{\partial \frac{\mu_k^0}{T}}{\partial \frac{1}{T}} \right).$$

The top of the energy barrier in the activation Gibbs function varies with the electric potential. The top of the energy barrier consists of a fixed potential energy $E^\#$ and a term proportional to the applied overvoltage. The barrier of the anodic process is lowered by $(1 - \alpha)z \cdot F \cdot \eta$.

But because the enthalpy of the oxidized species is lowered by $(z \cdot F \cdot \eta)$, too, $\Delta H^\#$ of the backward (cathodic) process increases by $(\alpha \cdot z \cdot F \cdot \eta)$.

$$\Delta H^\#_{\rightarrow} = [E^\# - (1 - \alpha) \cdot zF] - H_{red}, \quad (32a)$$

$$\Delta H^\#_{\leftarrow} = [E^\# + \alpha \cdot zF] - H_{ox}, \quad (32b)$$

Let us denote

$$\mu_{red,e} \equiv \sum_k \nu_{k,red} \cdot \mu_{k,e}, \quad (33a)$$

$$\mu_{ox,e} \equiv \sum_k \nu_{k,ox} \cdot \mu_{k,e}, \quad (33b)$$

$$\begin{aligned} -Rd \ln j^- &= -n_{red} R d \ln T + d([E^\# - (1 - \alpha) \cdot zF\eta - H_{red}]/T) + \\ &+ d\left(\sum_k \nu_{k,red} [\mu_k^0 - \mu_{k,e}]/T\right) + (1 - \alpha) \cdot zF d(\eta/T) = \end{aligned}$$

$$\begin{aligned}
&= (n_{red}RT + E^\#)d(1/T) - (1 - \alpha) \cdot zFd(\eta/T) - \\
&- H_{red} \cdot d(1/T) + d\mu_{red}^0/T - d(\mu_{red,e}/T) + (1 - \alpha)zFd(\eta/T) \\
&- Rd \ln j^{\rightarrow} = d[-(\mu_{red,e}/T)] + (n_{red}RT + E^\#)d(1/T) \quad (34)
\end{aligned}$$

In a similar way

$$\begin{aligned}
&-Rd \ln j^{\leftarrow} = -n_{ox}Rd \ln T + d([E^\# + \alpha \cdot zF\eta - H_{ox}]/T) + \\
&+ d\left(\sum_k \nu_{k,ox}[\mu_k^0 - \mu_{k,e}]/T\right) - \alpha \cdot zFd(\eta/T) = \\
&= (n_{ox}RT + E^\#)d(1/T) + \alpha \cdot zFd(\eta/T) - H_{ox} \cdot d(1/T) + d(\mu_{ox}^0/T) \\
&-d(\mu_{ox,e}/T) - \alpha zFd(\eta/T) - Rd \ln j^{\leftarrow} = d[-(\mu_{ox,e}/T)] + (n_{ox}RT + E^\#)d(1/T) \quad (35)
\end{aligned}$$

(34) and (35) are of the form

$$-R \cdot d \ln j^{\rightarrow} = dF^{\rightarrow} + Q_q \cdot dF_q, \quad (36a)$$

$$-R \cdot d \ln j^{\leftarrow} = dF^{\leftarrow} + Q_q \cdot dF_q. \quad (36b)$$

In a general form,

$$-R \cdot d \ln j = dF + Q_q \cdot dF_q \quad (37)$$

where the potentials are

$$F^{\rightarrow} = -\mu_{red,e}/T; \quad F^{\leftarrow} = -\mu_{ox,e}/T \quad (38)$$

$$F_q = \left(\frac{1}{T}\right) \quad (39)$$

(The temperature is first taken as equal for the reactants and the products)

Because in equilibrium at *any* temperature and any set of concentrations if

$$dF_{eq}^{\rightarrow} = dF_{eq}^{\leftarrow} \quad \text{and} \quad T^{\rightarrow} = T^{\leftarrow} = T, \quad (40)$$

then

$$d \ln j_{eq}^{\rightarrow} = d \ln j_{eq}^{\leftarrow} \quad (41)$$

follows that

$$j^{\rightarrow}(F) \equiv j^{\leftarrow}(F)$$

and it follows that *all constant parameters* ($E^\#, n$) *are the same in the forward and backward rate equation when the formulation is executed in a regular way.* For the mass transfer

$$Q^{\rightarrow} = Q^{\leftarrow} = 1 \quad (42)$$

and the heat transfer

$$Q_q^{\rightarrow} = Q_q^{\leftarrow} \tag{43}$$

consequently, $E^\#$ is common (follows from its physical interpretation) and

$$n_{red} = n = n_{ox} \tag{44}$$

which is not plausible. We have seen the generalized equation as a typical form

$$-R \cdot d \ln j_z = \sum_i Q_{zi} \cdot dF_i.$$

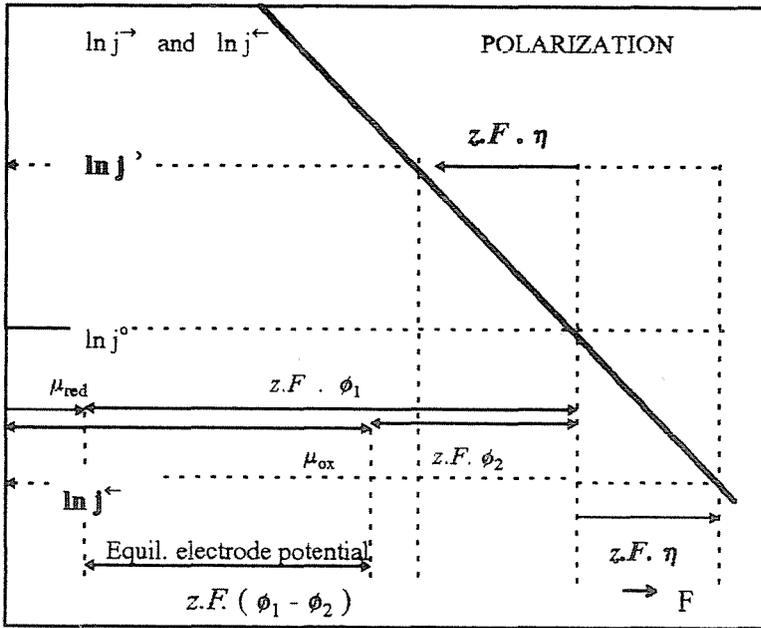


Fig. 8. The anodic/cathodic common $j(F)$ plot. Polarization

5.2 Heat Flux

The process studied above has a temperature-dependent term, consequently carries energy (heat) and, therefore, there exists a heat flux beside the material/electric charge complex transfer. If the energy transport were carried only by the latter process, it had be included in the complex potential of a single process. However, an independent, conductive heat transfer is not excluded (carried by motion of particles or phonons, the flux of these

carriers cannot be taken into account due to lack of information), so that an independent heat flux will be taken as an additional process (see SIENU-TYCZ, [22]). Its rate equation consists of a carried and a conductive term. As it follows from (33), the heat carried, the 'thermal charge', can be calculated knowing the temperature dependence [23]

$$Q_q = E^\# + n \cdot RT. \quad (45)$$

The process balance (14) states that

$$j_q = j \cdot Q_q + j_{\text{cond}}. \quad (46)$$

Let us denote the heat (absolute) flow rate by j_q . Then

$$-R \cdot d \ln j = 1 \cdot dF + Q_q \cdot dF_q, \quad (47)$$

$$-dj = (j/R) \cdot dF + (j \cdot Q_q/R) \cdot d(1/T), \quad (48a)$$

$$-dj_q = (j \cdot Q_q/R) \cdot dF + (j/R) \cdot L_{qq} \cdot d(1/T), \quad (48b)$$

where

$$L_{qq} = Q_q^2 + R \cdot \frac{\partial Q_q}{\partial(1/T)} + \frac{R}{j} \cdot \frac{\partial j_{\text{cond}}}{\partial(1/T)} \quad (49)$$

the reciprocity can be observed (not confined to linear $j - F$ relations !)

If operation d means a small difference, (45) expresses the relations between net fluxes and forces and becomes an Onsagerian set of linear rate equations.

$$-dj \cong J, \quad -dj_q \cong J_q, \quad dF \cong X, \quad d(1/T) \cong X_q \quad (50)$$

In the matrix form

$$\begin{bmatrix} J \\ J_q \end{bmatrix} = \frac{j}{R} \cdot \begin{bmatrix} 1 & Q_q \\ Q_q & L_{qq} \end{bmatrix} \cdot \begin{bmatrix} X \\ X_q \end{bmatrix} \quad (51)$$

with the reciprocity of the cross coefficients. In a generalized form

$$-R \cdot dj_z^* = \sum_i j_x^* \cdot Q_{zi} \cdot dF_i. \quad (52)$$

At last it must be emphasized again that because of the very high value of the last term in (49) X_q is immeasurably small, and, consequently, the Onsagerian method cannot be applied. One of the most valuable achievements of Thermokinetics is that it calculates with T . instead of its difference. The temperature dependence of the electrode process rates can be measured, the (very small) X can be evaluated and the heat flow processes can be investigated. For chemical processes a similar problem has been investigated by the author [23].

References

1. TAFEL, J.: *Z. physik. Chemie*, Vol. 50., p. 641.
2. ERDEY-GRUZ, T. – VOLMER, M.: *Z. physik. Chem.* Vol. 150.A, p. 203. (1930)
3. VETTER, K. J.: Elektrochemische Kinetik, eng. transl. Acad. Press (1967).
4. OLÁH, K.: Thermokinetics. An Introduction. *Periodica Polytechnica, Ser. Chem. Eng.* Vol. 31, pp. 19–27 (1987).
5. OLÁH, K.: Thermostatitics, Thermodynamics and Thermokinetics, *Acta Chimica Hungarica*, Vol. 125., pp. 117–130 (1988).
6. FOWLER, R. H.: *Phil. Mag.*, Vol. 47, p. 257 (1924).
7. ONSAGER, L.: Reciprocal Relations in Irreversible Processes I-II. *Phys. Rev.* Vol. 37, p. 405, Vol. 38, p. 2265 (1931).
8. BOLTZMANN, L.: *Wien. Sitz.*, Vol. 66, p. 275 (1872).
9. KLEIN, O. – ROSSELAND, S.: *Zeitschrift für Physik*, Vol. 4, p. 46, (1921).
10. KRAMERS, H. A. – MILNE, E. A.: *Phil. Mag.* Vol. 46, p. 386 (1923), Vol. 47, p. 209 (1924).
11. DIRAC, P. A. M.: *Proc. Roy. Soc.*, Vol. 106. A. pp. 581–596 (1924).
12. GULDBERG, C. M. – WAAGE, P.: Etudes sur les affinités chimiques, Brogger & Christie (1867).
13. OLÁH, K.: *Hung. J. Ind. Chem.* Vol. 21. pp. 287–301 (1993).
14. OLÁH, K.: The Entropy Production. New Aspects. in: Second Law Analysis of Energy Systems. Ed. E. Sciubba and M. J. Moran, Roma, pp. 165–179 1995.
15. OLÁH, K.: Progress in Understanding the Concepts: Reversibility, Balances and Cross Symmetry, in 'Thermodynamics: History and Philosophy': Ed: Martinus. World Scientific, Singapore, London, pp. 228–238 (1991).
16. OLÁH, K. – BÓDISS, J. – FARKAS, H.: Thermodynamic Charges, *Acta Chimica Hungarica*, Vol. 137. p. 783 (1990).
17. OLÁH, K. – FARKAS, H. – BÓDISS, J.: The Entropy Dissipation Function, *Periodica Polytechnica, Ser. Chem. Eng.* Vol. 33, pp. 125–139 (1989).
18. OLÁH, K.: Lecture on the Symp.: *Recipr. Relns. and Non-Linear Thermodyn.* Balatonvilágos, 22–25. Sept. 1996.
19. BEDEAUX, D. – KJELSTRUP RATKJE, S.: *J. of the Electrochem. Soc.*, Vol. 143, pp. 767–779 (1996).
20. KJELSTRUP RATKJE, S. – BEDEAUX, D.: *J. of the Electrochem. Soc.* Vol. 143, pp. 779–789 (1996).
21. OLÁH, K.: Electrode Kinetics, Lecture Notes in Phys. Chem. VII. Ed. Techn. Univ. Budapest, Dept. Phys. Chem. (in Hungarian), 1993.
22. SIENUTYCZ, S. – RATKJE, K.: *Int. J. Heat Mass Tr.*, Vol. 39, pp. 3293–3303 (1996).
23. OLÁH, K.: *Acta Chim. Hung.* Vol. 127, pp. 135–147 (1990).