THE APPLICATION OF THE RELAXATION METHOD IN THE STUDY OF ELECTRODE KINETICS: RELAXATION THEORY OF THE SIMPLE CHARGE-TRANSFER PROCESS

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The paper presents the relaxation theory of a simple charge-transfer electrode process; the derived equations provide the basic kinetic parameters. The range of applicability of the presented theory will be given in an experimental paper under preparation.

The problem of measuring rates of very fast electrode reactions is one of the most important targets of the electrode kinetics. Many so-called "relaxation techniques" have been developed for this purpose. The upper limit of rate constants obtainable by various experimental techniques according to[1] is 10 cm s^{-1} and may be increased to 100 cm s^{-1} by the increase of the mass transportation[2].

However, the description of such methods as potential step[3], voltage step[4], galvanostatic methods[5], galvanostatic pulse[6], coulostatic techniques[7], faradaic impedance[8] and faradaic rectification[9] as "relaxation techniques" is not fully justified. In all these methods, the indicator electrode response is measured simultaneously during its polarization.

In chemical kinetics a relaxation method is a procedure in which the studied reaction, being initially at equilibrium, is slightly displaced from equilibrium by sudden application of a short perturbation followed by a free return back to equilibrium. Only the free return back to equilibrium need to be traced. The application of the relaxation methods in chemical kinetics made it possible to increase the magnitude of the measured rate constants by many orders[10].

The idea to apply the relaxation method to the study of fast electrode processes has been formulated only recently in the study of molten salts electrode reactions[11]. In the derived theory the anodic dissolution of metal into pure molten halide has been considered and the theory was then verified experimentally on silver − molten silver chloride electrode reaction[12]. The relaxation method, however, may be used for the determination of the rate constants of fast electrode processes also in aqueous and similar systems. This paper presents the relaxation theory of a simple charge-transfer process.

THEORETICAL

Let us regard an electrode process

$$R \; \underset{k_c^*}{\overset{k_a^*}{\rightleftarrows}} \; O + ne \qquad\qquad (A)$$

being at equilibrium on an inert Pt electrode. Here k_a^* and k_c^* are the surface or pseudo-
-first order anodic and cathodic rate constants (dimension s^{-1}). The concentrations
of the reduced (R) and oxidized (O) forms are much higher than in the usual dif-
fusional electrode kinetics and the high supporting electrolyte concentration should
also reduce the electrolyte resistance. Such high concentrations of the reactants are
needed to avoid any diffusional control of the overall electrode process.

The rate of the electrode reaction (A) may be written:

$$dN_O/dt = k_a^* N_R - k_c^* N_O , \qquad\qquad (1)$$

where N_O and N_R are the concentrations of the oxidized and reduced ionic species
in the reaction layer of thickness μ (ref.[13]). According to the IUPAC convention, the
anodic current is taken as positive[14].

At equilbrium

$$dN_O/dt = 0 , \quad k_a^* N_R^e - k_c^* N_O^e = 0 , \qquad\qquad (2),(3)$$

where N_R^e and N_O^e are the equilibrium concentrations.

Let us apply to the electrode (reaction (A) being at equilibrium) a sudden, small
anodic perturbation (galvanostatic or potentiostatic). As a result the concentrations
N_R and N_O change slightly to new values:

$$N_O = N_O^e + \Delta N , \quad N_R = N_R^e - \Delta N . \qquad\qquad (4),(5)$$

According to (4) and (3):

$$dN_O/dt = d(\Delta N)/dt = 0 \qquad\qquad (6)$$

and substituting equations (4), (5), and (6) into (1) one obtains:

$$d(\Delta N)/dt = k_a^*(N_R^e - \Delta N) - k_c^*(N_O^e + \Delta N) . \qquad\qquad (7)$$

Using the equilibrium condition (3), Eq. (7) becomes:

$$d(\Delta N)/dt = -(k_a^* + k_c^*) \Delta N \qquad\qquad (8)$$

which after integration gives the final result:

$$\Delta N = \Delta N_0 \exp\left[-\left(k_a^* + k_c^*\right) t\right] . \tag{9}$$

The surface or pseudo-first order rate constants k_a^* and k_c^* are expressed in s^{-1}. It follows from[9] that the decay of the applied perturbation, ΔN_0, is, as in all relaxation methods, a first order process[10].

The evaluation of the sum $\left(k_a^* + k_c^*\right)$ of rate constants involves the registration of the decay function (9) and this in turn depends upon the type of perturbation.

Galvanostatic Perturbation

Before application of the perturbation the electrode reaction (A) is in equilibrium and the electrode potential is given by the Nernst's equation:

$$E(t' = 0) = E_c^0 - \frac{RT}{nF} \ln \frac{N_R^e}{N_O^e} , \tag{10}$$

where E_c^0 is the formal standard potential and other symbols have their usual meaning.

Let us apply to this electrode a sudden constant anodic (positive) current through time $t' = t_a'$. It will displace the equilibrium potential to a new, close, value given by the equation:

$$E(t' = t_a') = E_c^0 - \frac{RT}{nF} \ln \frac{N_R^e - \Delta N}{N_O^e + \Delta N} . \tag{11}$$

At the end of the perturbation $(t' = t_a', t = 0)$ we have

$$\Delta E = E(t' = t_a') - E(t' = 0) = \frac{RT}{nF} \ln \frac{N_R^e(N_O^e + \Delta N)}{N_O^e(N_R^e - \Delta N)} . \tag{12}$$

For equal initial equilibrium concentrations

$$N_R^e = N_O^e = N^0 \tag{13}$$

equation (12) simplifies to:

$$\Delta E = \frac{RT}{nF} \ln \frac{1 - \left(\Delta N/N^0\right)}{1 + \left(\Delta N/N^0\right)} . \tag{14}$$

The ratio $\Delta N/N^0$ should be much less than unity and use can be made of McLaurines expansion[15]:

$$\ln \frac{1 + x}{1 - x} \cong 2x ; \tag{15}$$

equation (14) becomes:

$$\Delta E = \frac{RT}{nF} 2 \frac{\Delta N}{N^0} = \text{const.}\ \Delta N \tag{16}$$

and

$$\Delta N / \Delta N_0 = \Delta E / \Delta E_0 . \tag{17}$$

It follows from this equation that in this galvanostatic perturbation, which produces a small concentration change ΔN in the reaction layer, the free return back to equilibrium may be followed by the potential decay:

$$\Delta E = \Delta E_0 \exp\left[-(k_a^* + k_c^*)\ t\right], \tag{18}$$

where ΔE_0 is the electrode potential change at zero time (end of the perturbation pulse).

Potentiostatic Perturbation

To an electrode system (A) at equilibrium a sudden small constant anodic potential pulse is applied through time $t' = t_a'$. As a result of this perturbation a sudden current flows through the electrode interface and the initial equilibrium concentrations are slightly changed to the new values given by equations (4) and (5). Before the application of the potential pulse the current flowing through the indicator electrode surface of area A is zero:

$$I(t' = 0) = nFA(k_a^* N_R^e - k_c^* N_O^e) = 0 . \tag{19}$$

At the end of the perturbating pulse the current is:

$$I(t' = t_a') = nFA\left[k_a^*(N_R^e - \Delta N) - k_c^*(N_O^e + \Delta N)\right] . \tag{20}$$

Thus:

$$\Delta I = I(t' = t_a') - I(t' = 0) = -nFA(k_a^* + k_c^*)\ \Delta N \tag{21}$$

and

$$\Delta N = -\frac{\Delta I}{nFA(k_a^* + k_c^*)} = \text{const}.\ \Delta I . \tag{22}$$

The ratio:

$$\Delta I / \Delta I_0 = \Delta N / \Delta N_0 \tag{23}$$

may be thus used for the potentiostatic evaluation of the sum $(k_a^* + k_c^*)$ according

to the equation (9):

$$\Delta I = \Delta I_0 \exp\left[-(k_a^* + k_c^*)\,t\right],\qquad(24)$$

where ΔI_0 is the current response at zero time.

The Relationship between Heterogeneous (k_a, k_c) and Surface (k_a^*, k_c^*) Rate Constants

The rate of reaction (A) may be expressed in two ways: with the use of surface rate constants as given by equation (1) or with the use of heterogeneous rate constants k_a and k_c (ref.[14]):

$$dN_O/dt = k_a c_R - k_c c_O .\qquad(25)$$

Here c_R and c_O are volume concentrations at the electrode[13]. The concentrations N_R and N_O, expressed in mol . cm^{-2} are related to the volume concentrations c_R and c_O, expressed in mol . cm^{-3}:

$$N_R = \mu c_R , \quad N_O = \mu c_O \qquad(26),(27)$$

where μ is the reaction layer thickness[13]. The comparison of equations (1) and (25) with the use of Eqs (26), (27) gives the desired relationships:

$$k_a = \mu k_a^* , \quad k_c = \mu k_c^* .\qquad(28)$$

It is to be pointed out that the surface rate constants k_a^* and k_c^* are measured at equilibrium potential only. They can be, however, used for the evaluation of the exchange current density and the overall transfer coefficients.

The net current density j of the electrode reaction (A)

$$j = nF(k_a^* N_R - k_c^* N_O)\qquad(29)$$

at equilibrium is equal zero:

$$j = 0 .\qquad(30)$$

The exchange current density is thus given by the equation:

$$j^0 = nFk_a^* N_R^e = nFk_c^* N_O^e\qquad(31)$$

and with the assumption expressed by the equation (13) also the rate constants are equal[13]:

$$k_a^* = k_c^* .\qquad(32)$$

If there is a linear dependence:

$$N_R^e = a N_O^e \tag{33}$$

instead of equation (13), where $a \neq 1$ is a constant, then — as follows also from (31):

$$k_a^* = a k_c^* . \tag{34}$$

The individual rate constants k_a^* and k_c^* are thus available. The constant a in equation (33) should be choosen in such a way that the produced perturbation of the electrode potential does not exceed $10 \div 20$ mV.

The potential dependence of the surface rate constants may be written in a similar way to the heterogeneous rate constants[13,14,16]:

$$k_a^* = k_a^{**} \exp\left(\alpha_a f E\right) \quad \text{or} \quad k_a^* = k^0 \exp\left[\alpha_a f (E - E_c^0)\right] \tag{35}, (36)$$

and

$$k_c^* = k_c^{**} \exp\left(-\alpha_c f E\right) \quad \text{or} \quad k_c^* = k^0 \exp\left[-\alpha_c f (E - E_c^0)\right], \tag{37}, (38)$$

where $f = F/RT$, E_c^0 is the formal standard potential and k_a^{**}, k_c^{**}, k^0 are the corresponding rate constants at zero and standard potential, respectively.

By combining (31), (36) and the Nernst's equation one obtains:

$$j^0 = n F k^0 (N_R^e)^{[1 - (\alpha_a/n)]} (N_O^e)^{(\alpha_a/n)} . \tag{39}$$

By taking log of both sides of equation (39) and by differentiation, the overall transfer coefficients may be evaluated:

$$\left(\frac{\partial \ln j^0}{\partial \ln N_R^e}\right)_{N_O^e} = 1 - \frac{\alpha_a}{n}, \quad \left(\frac{\partial \ln j^0}{\partial \ln N_O^e}\right)_{N_R^e} = \frac{\alpha_a}{n}. \tag{40}, (41)$$

It is thus seen from the above equations that the relaxation method can provide the basic kinetic parameters of the charge-transfer electrode process. An experimental paper which will present the range of applicability of the presented theory in concentrated aqueous electrode systems will appear in this Journal in the near future.

REFERENCES

1. Bindra P., Brown A. P., Fleischmann M., Plecher D.: J. Electroanal. Chem. Interfacial Electrochem. *58*, 31 (1975).
2. Bernst Ch., Heindrichs N. A., Vielstich W.: J. Electroanal. Chem. Interfacial Electrochem. *87*, 81 (1978).

3. Gerischer H., Vielstich W.: Z. Phys. Chem. (Wiesbaden) *3*, 16 (1955).

4. Vielstich W., Delahay P.: J. Amer. Chem. Soc. *79*, 1874 (1957).

5. Berzins T., Delahay P.: J. Amer. Chem. Soc. *77*, 6448 (1955).

6. Gerischer H., Krauze M.: Z. Phys. Chem. (Wiesbaden), *10*, 264 (1957).

7. Delahay P., deLevie R., Guiliani A. M.: Electrochim. Acta *11*, 1141 (1966).

8. Randles J. E. B.: Discuss. Faraday Soc. *1*, 11 (1947).

9. Does K. S. G., Agarwal H. P.: Proc. Ind. Acad. Sci. *34A*, 266 (1951).

10. Laidler K. J.: *Chemical Kinetics*. McGraw-Hill, New Delhi 1979.

11. Kisza A.: Pol. J. Chem. *58*, 307 (1984).

12. Kisza A., Kaźmierczak J.: Electrochim. Acta *30*, 57 (1985).

13. Bard A. J., Faulkner L. R.: *Electrochemical Methods, Fundamentals and Applications*. John Willey, New York 1983.

14. Parsons R.: J. Pure Appl. Chem. *501* (1973).

15. *Mathematics at a Glance*. Bibliogr. Institut, Leipzig 1975.

16. Bockris J. O'M., Reddy, A. K. N.: *Modern Electrochemistry*. Plenum Publ. Corp., New York 1970.