Voltage-step Transient in Redox Systems II. 1D Approximation (revisited)

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2010

Research Report ICPF No. 2010 / 6

Institute of Chemical Process Fundamentals ASCR, v.v.i., 165 02 *Prague 6 - Suchdol*

Voltage-step transient in redox systems II. 1D approximation (revisited).

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Date: August 2010

Reviewer(s):

Revision: March 2011

Abstract

The voltage-step transient experiment can provide, via the well-known Cottrell asymptote, data on bulk concentration and diffusion coefficient of working depolarizer, essential in the liming-current techniques. However, the Cottrell asymptote cannot be directly applied in an early stage of the voltage-step transient process. There are three additional transport resistances that cannot be neglected at extremely high initial currents: Faradaic resistance at surface of working electrode, Ohmic losses in the electrolytic, and the galvanometric constraint in the outer circuit (galvanometer, current follower, potentiostat).

Non-linear effect of these additional transport resistances on the transient current for a finite voltage step is analyzed in a 1D approximation, i.e. assuming uniform accessibility of the working electrode. The Faradaic resistance is considered assuming reversible behavior of a redox couple $O + ne = R$ according to Butler-Volmer kinetics. The concept of galvanometric constraint is introduced and analyzed probably for the first time.

Využitím obecně známé Cottrellovy asymptoty může potenciostatický přechodový experiment poskytnout data o koncentraci a difuzivitě pracovního depolarizátoru, které jsou podstatné v experimentech založených na režimu limitních difuzních proudů. Nicméně, Cottrellova asymptota není přímo použitelná v rané fázi přechodového experimentu. Tam se uplatňují přídavné transportní odpory, které nelze zanedbat při extrémně vysokých proudových hustotách: Faradaický odpor při povrchu pracovní elektrody, Ohmické ztráty v její bezprostřední blízkosti, jakož i galvanometrické omezení (galvanometr, sledovač proudu, potenciostat) ve vnějším obvodu elektrochemické cely.

Vliv těchto přídavných transportních odporů na přechodový průběh proudů při větším celkovém konstantním přepětí je počítán v rámci nelineární 1D aproximace (zjednodušující předpoklad rovnodostupnosti povrchu elektrody jako v původním Nernstově modelu). Faradaický odpor je uvažován pro vratnou redox dvojici podle Butler-Volmerovy kinetiky. Pojem galvanometrického omezení je použit a analyzován pravděpodobne vůbec poprvé.

Key words

Voltage-step transient; Cottrell asymptote; Ohmic loss; Faradaic resistance; Galvanometric constraint; Butler-Volmer kinetics;

Potenciostatický přechod; Cottrellova asymptota; Ohmická ztráta; Faradaický odpor; Galvanometrické omezení; Butler-Volmerova kinetika.

Acknowledgements

This report is a part of the grant project, supported by GAČR (Grant Agency of the Czech Republic) under contract GACR 104/08/0428.

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Nomenclature

A	Electrode area, m^2
a_C	Cottrell coefficient, Eq. (12)
B	$\equiv D_O^{1/2} c_O^B / D_R^{1/2} c_R^B$, transport parameter of the Cottrell asymptote
$b_{1,2}$	coefficients in long-time asymptote, Eqs. (40ab)
c; $c_{O,R}^{B,W}$	molar concentration of depolarizers; specific boundary values
D; $D_{O,R}$	coefficient of diffusion; values for the components
$\mathbf{d}_T^{-1/2}$	semiintegral, Eq. (3)
E, $E_{O,R}[N]$	= Exp[P], Exp[$P\beta(1-\mu N)$], Exp[$-P(1-\beta)(1-\mu N)$]
f_{NP}	= $(E-1)/(E+B)$
G	= i_G/i_C, normalized galvanometric constraint
I	electric current, A
I_C	= $+U/R_C$, Ohmic current in the cell, A
I_G	galvanometric threshold, A
i	= I/A, current density, A m^{-2}
i_{BV}	exchange current density in Butler-Volmer kinetics of charge transfer, Eqs. (4, 5), A m^{-2}
i_S	= $\mu i_C = (\mu M) i_{BV}$, starting current density, Eqs. (16, 18), A m^{-2}
k_{BV}	rate constant in Butler-Volmer kinetics of charge transfer, Eq. (5)
L_C	equivalent resistor length, Eq. (6)
M	$\equiv i_C/i_{BV}$
n	number of electrons in the charge transfer per 1 mole of the working depolarizer
N	$\equiv i/i_S$, normalized flux, Eq. (19)
N_L	solution to the linearized transport equation, Eq. (28)
N_A	= $N_L[\psi^{-2}\theta]$, value of $N(\psi^{-2}T)$ in the diving point $\theta = \pi/4$
N_G	Galvanometric constraint
O, R	Oxy- and Red- forms of a redox couple, $O + ne^- = R$
P	$\equiv -U\,\boldsymbol{nF/RT}$, normalized overvoltage; $\boldsymbol{F}$ = 95608 C mol^{-1} Faraday constant; $\boldsymbol{R}$ = 8.313 J $K^{-1}mol^{-1}$, universal gas constant; $\boldsymbol{T}$ - absolute temperature, K
R_C	Ohmic resistance of the cell
T	time from the initial voltage step
t_S	$\equiv (a_C/i_S)^2$, lag time, s
T	$\equiv t/t_s$, normalized time, Eq.(17)
U	constant overvoltage
Y	coefficient in long-time asymptote, Eqs. (33, 34)
W	normalized concentration driving force, Eq. (15)
z	normal distance to the working electrode
β	symmetry coefficient in Butler-Volmer kinetics of charge transfer, Eqs. (4), (5)
$\Lambda[N]$	local equilibrium term in the normalized BV equation (24)
∂_T	partial derivative with respect to T
μ	$\equiv i_S/i_C$
η	overpotential, [V], Eq. (6)
κ	specific conductivity of the bulk solution, [$\Omega^{-1}m^{-1}$]
ψ	coefficient in short-time asymptote, Eqs. (30, 31)
BV	Butler-Volmer (charge-transfer kinetics)
NP	Nernst-Petersen (concentration overpotential)
VST	Voltage-step transient
B,W	compositions of the solution at *Bulk*, *Wall*
O, R	*Oxy-*, *Red-* forms of the redox couple
S	starting value
C, *G*	Ohmic cell resistance, Galvanic constraint

1. Introduction

The transient process, which takes place after switching on an electrochemical cell with a non-moving electrolyte solution, can be of some interest both for studying kinetics of electrode reactions [1-3] and for measuring the diffusion coefficients of the depolarizers [4-5]. Such a process is commonly taken as a potentiostatic one, i.e. with neglected additional transport resistances in the electrochemical cell and outer circuits. Such an assumption cannot be strictly right [1, 6-7], as it tacitly assumes infinite current at the start. In other words, other transport mechanisms should play dominating role in an early stage of the voltage-step (VS) process.

There are several transport mechanisms that can control the transient current at a given overvoltage, even with neglected transport resistances at the counter electrode and in bulk solution of the cell:

- Cottrellian transient diffusion, which includes equilibrium at the working electrode
- Ohmic losses in an intimate neighborhood of working electrode
- Faradaic losses on working electrode due to electrode kinetic limitations
- Galvanometric constraint due to limitations in the supplying outer circuit

In the present work, all these simultaneous transport resistances are accounted for, with an arbitrary constant overvoltage U between the working and counter electrode.

2. Problem statement

Transient diffusion of a species in a motionless solution at a constant concentration c^B in the bulk, i.e. at a large distance ($z \to \infty$) from the transport-active surface, can be described using either the Fick law in its differential form (so called 2nd Fick law), $\partial_t c = D\partial_{zz} c$, with corresponding initial and boundary conditions, or the semiintegral equation [8], which interrelates the diffusion flux with the wall concentration c^W.

2.1. Transport equations

In particular, for a couple of the redox depolarizers O, R with the diffusion fluxes linked through the stoichiometry of electrode reaction, $O + ne^- = R$, i.e. according to the Faraday law,

$$i/nF = D_O \partial_z c_O|_{z=0} = -D_R \partial_z c_R|_{z=0}, \tag{1ab}$$

the corresponding semiintegral formulation [8] can written as

$$\mathbf{d}_t^{-1/2} i(t)/nF = D_O^{1/2}(c_O^B - c_O^W(t)) = -D_R^{1/2}(c_R^B - c_R^W(t)), \tag{2ab}$$

where

$$\mathbf{d}_t^{-1/2} F(t) \equiv \pi^{-1/2} \int_0^t (t-s)^{-1/2} F(s)\,\mathrm{d}s\,. \tag{3}$$

It should be noted that the electrochemical system is kept, until the start at $t = 0$, in the equilibrium state, $i = 0$, $c_{O,R}^W = c_{O,R}^B$. To a given problem with three unknown fields $i(t)$, $c_{O,R}^W(t)$ and a given course of the electrode overpotential, $\eta = \eta(t)$, the closing constraints follow from kinetic equations of the charge transfer at surface of the working electrode. In particular, for the Butler-Volmer kinetics:

$$\frac{i}{i_{BV}} = \frac{c_O^W}{c_O^B}\,\mathrm{Exp}[-\beta\frac{\eta nF}{RT}] - \frac{c_R^W}{c_R^B}\,\mathrm{Exp}[(1-\beta)\frac{\eta nF}{RT}], \qquad \frac{i_{BV}}{nF} = k_{BV}(c_O^B)^{1-\beta}(c_R^B)^{\beta}. \tag{4), (5}$$

For including the effect of Ohmic losses let us assume the Ohmic resistance of the cell is constant and given by an effective thickness L_C and electric conductivity κ of the solution in bulk. If the electrodes (working, counter, and eventually reference one) are made from the same material ($i = 0$ and $\eta = 0$ at $U = 0$), then the effect of Ohmic losses on η can be expressed as

$$\eta = -U + i\,L_C/\kappa = -U + i\,R_C = -U(1 - i/i_C). \qquad (6)$$

With neglected Ohmic losses, the cell voltage is equal to overpotential of the working electrode, $\eta = -U$. At constant η, the voltage-step transient problem simplifies to the potentiostatic one. If, in addition, also Faradaic resistance is negligible, $i_{BV} \to \infty$, the transient process is controlled only by the transient diffusion of the depolarizers under the Nernst-Petersen equilibrium boundary conditions at surface of the working electrode. The corresponding simplified linear theory provides a well-known Cottrell solution [2].

In the present work, the transient process is analyzed by considering all the four transport resistances at a finite overvoltage, including the limiting diffusion current conditions, $|U| \to \infty$. In such cases, the Ohmic loss introduces into Eq. (4) a substantial non-linearity, which has been analyzed for very small overvoltage [1, 2], or for negligible Faradaic losses, $i/i_{BV} \to 0$, see [6]. Our results about the combined Ohmic and Faradaic resistances, published in Russian [7], provide only qualitative estimates of limited relevance. The effect of additional resistance in the outer circuit is analyzed here for the first time.

2.2. Cottrell asymptote

With negligible Ohmic and Faradaic losses, $i/i_{BV} \to 0$, $i/i_C \to 0$, the transient process is driven only by the concentration overpotential $\eta = -U$, with the diffusion resistance according to Eq. (2) under local equilibrium at the electrode interface (Nernst-Petersen),

$$0 = E\,(c_O^W / c_O^B) - (c_R^W / c_R^B), \qquad E = \mathrm{Exp}[P], \qquad P = -U\,nF/RT, \qquad (7), (8), (9)$$

which follows from Eq. (4) in an obvious way.

Solution of this simplified problem according to Eqs. (2), (7) with constant c_B^W, c_O^W, known as the *Cottrell problem*, see [1], can be written down as

$$i(t) = a_C\,(\pi t)^{-1/2}, \qquad D_O^{1/2}(c_O^B - c_O^W) = -D_R^{1/2}(c_R^B - c_R^W) = a_C / nF\,. \qquad (10), (11)$$

The Cottrell coefficient a_C depends both on the overvoltage U and solution properties

$$a_C / nF = f_{NP}\,D_O^{1/2} c_O^B = B f_{NP}\,D_R^{1/2} c_R^B, \qquad (12)$$

$$f_{NP} = \frac{E-1}{E+B} = -B^{-1}\,\frac{E^{-1}-1}{E^{-1}+B^{-1}}, \quad B = \frac{D_O^{1/2} c_O^B}{D_R^{1/2} c_R^B}. \qquad (13),(14)$$

In the cases $|P| \to \infty$, a cathodic ($P \to \infty$, $E \to \infty$) or anodic ($P \to -\infty$, $E^{-1} \to \infty$) regime of limiting diffusion currents is achieved. These asymptotes are fully controlled by transient diffusion of the working depolarizer to surface of working electrode. For cathodic reduction, it is $f_{NP} = 1$, $c_O^W = 0$, $c_R^W / c_R^B = 1 + B^{-1}$. For anodic oxidation, it is $f_{NP} = -B^{-1}$, $c_B^W = 0$, $c_O^W / c_O^B = 1 + B$. With a normalized concentration driving force of the process,

$$W \equiv (1 - c_O^W / c_O^B)/f_{NP} = -(1 - c_R^W / c_R^B)/(B f_{NP}), \qquad (15)$$

the Cottrell asymptote can be characterized simply as $W = 1$. Effect of the other transport resistances decreases W (it is always $0 \le W \le 1$).

2.3.Normalization to the problem

The normalized flux N and normalized time T are introduced in such a way, that

(i) the starting value of N (diffusion resistance negligible) is the unit, $N \to 1$ for $T \to 0$,

(ii) the long-time asymptote is in the common Cottrell form, $N \to (\pi T)^{-1/2}$ for $T \to \infty$.

Such a specification is fulfilled by the settings:

$$N = i/i_S, \qquad T = t/t_S, \qquad t_S = (a_C/i_S)^2, \tag{16, 17, 18}$$

where i_S stands for an unknown starting current density. The analyzed problem can be now formulated in the following form of a single non-linear integro-differential equation for unknown transient course of $N = N(T)$:

$$\mathbf{d}_T^{1/2} N(T) = W(T) = \Lambda[N(T)], \tag{19}$$

$$\Lambda[N] = \frac{E_O[N] - E_R[N] - \mu M N}{f_{NP}(E_O[N] + B E_R[N])} = \frac{E^{\beta(1-\mu N)} - E^{(\beta-1)(1-\mu N)} - (E^{\beta(1-\mu)} - E^{(\beta-1)(1-\mu)})N}{f_{NP}(E^{\beta(1-\mu)} + BE^{(\beta-1)(1-\mu)})}, \tag{20ab}$$

$$E_O[N] \equiv \mathrm{Exp}[P\beta(1-\mu N)] = E^{\beta(1-\mu N)}, \quad E_R[N] \equiv \mathrm{Exp}[-P(1-\beta)(1-\mu N)] = E^{(\beta-1)(1-\mu N)}, \tag{21ab}$$

$$\mu = i_S/i_C, \qquad M = i_C/i_{BV}. \tag{22, 23}$$

2.4. Starting current density

Immediately after switching on the cell, the diffusion resistance is always negligible in comparing with the other transport resistances, i.e. $c_{O,R}^W \to c_{O,R}^B$ and $W \to 0$. In such the case, the starting current, $i \to i_S = \mu i_C$ for $t \to 0$, is given by solving the system of Eqs. (4), (6), (7), which can be expressed as $0 = W(T{=}0) = \Lambda[1]$, or:

$$\mu M = E_O[1] - E_R[1] = E^{\beta(1-\mu)} - E^{-(1-\beta)(1-\mu)}. \tag{24ab}$$

For negligible Faradaic resistance in comparison with Ohmic one, $M = 0$, it is $\mu = 1$, in the opposite case, $M = \infty$, it is $\mu = 0$ but $\mu M \equiv i_S/i_{BV} = E^{\beta} - E^{-(1-\beta)}$. In all other cases it is $0 < \mu < 1$.

Under some circumstances, in particular for automated electrochemical instrumentations with a current follower in outer circuit, there is a threshold of current that cannot be passed over. In such the case, the early stage of transient process constant current (i.e. of galvanostatic nature) is accompanied with concentration changes at the electrode surface. On contrary to common potentiometric methods [2], these changes cannot be monitored in the two-electrode cells (no reference electrode), but they strongly affect the currents below the threshold in later stages of the transient process.

2.5. Useful symmetry

Within the normalized formulation, there are four independent parameters $\{P, B, \beta, M\}$ to the problem. For a given electrodes an a given solution, only the normalized overvoltage is variable, $P \in (-\infty; +\infty)$. The transformation

$$\{P \to -P, B \to B^{-1}, \beta \to 1 - \beta, M \to M\}, \tag{25}$$

which physically corresponds to the change from a cathodic to anodic polarization in a given electrolytic cell, guarantees that any actual case can be studied with a positive P. In particular, for the special symmetry case $\{B = 1, \beta = (1-\beta) = 0.5\}$, the problem is invariant with respect to polarity change, $P \to -P$.

3. Analytic approximations

3.1. Special cases and asymptotes in the space {*P*, *M*}

At the start of the VST, the diffusion resistance is negligible in comparison with Ohmic and/or Faradaic ones. At large time the Cottrellian diffusion resistance dominates. The asymptotic solution at $T \to \infty$ is known as the Cottrell asymptote,

$$N(T) = (\pi T)^{-1/2}. \tag{26}$$

At ***negligible Ohmic loss***, $\{M \to \infty, \mu \to 0, \mu M = E^{\beta} - E^{-(1-\beta)}\}$, the boundary-value constraint (20) simplifies to

$$\Lambda[N] \approx 1 - N. \tag{27}$$

There is a known analytic solution for this special case:

$$N(T) = N_L[T] \equiv \mathrm{Exp}[T]\ \mathrm{Erfc}[T^{1/2}], \tag{28}$$

$$N(T) \approx \begin{cases} 1 - 2(T/\pi)^{1/2}(1 + \frac{2}{3}T + ...) + (T + \frac{1}{2}T^2 + ...); & T \to 0 \\ (\pi T)^{-1/2}(1 - \frac{1}{2}T^{-1} + \frac{3}{4}T^{-2} - \frac{15}{8}T^{-3} + ...); & T \to \infty \cdot \end{cases} \tag{29ab}$$

At ***small overvoltage*** [1, 2], $P \to 0$, and a fixed M, the initial condition (24) simplifies to $\mu \to 0$ and the constraint (24) can be again linearized to the form (27) with the corresponding result (28).

Assumption of ***negligible Faradaic resistance*** $\{M \to 0, \mu \to 1, \mu M \to 0\}$ does not provide an analytic solution for $N(T)$.

At ***small voltage***, $P \to 0$, the constraint (29) simplifies again to (27), $\Lambda[N] \approx 1 - N$.

At ***large voltage***, $P \to \infty$, there is a finite lag-time period, $0 < T < \theta$, with negligible diffusion resistance, $W = \Lambda[1] = 0$, and constant starting current, $N = 1$. The $P \to \infty$ asymptote on the other hand gives $W = \Lambda[N] = 1$ for any finite (1-N). There is another analytic solution to this singular case, the ***extended Cottrell*** asymptote, see Eq. (42) in Chapter 3.4. A survey of all asymptotic sub-cases is given in the following Table 1, see also Fig. 1.

Table 1. *Asymptotic sub- cases*: *starting conditions*

	Case	*P*	*M*	$\varepsilon \to 0$	μ	*N(T)*
0	aCot	Finite	∞	-	0	Cottrell
1	aLowU	$\to 0$	Any	$\frac{P}{M + P(1 - M(\beta - \frac{1}{2}))}$	$0 + \varepsilon$	Linear
2	aNoFar	Any	$\to 0$	$\frac{M}{P + M(1 + P(\beta - \frac{1}{2}))}$	$1 - \varepsilon$	Num Eq. (29)
3	aHghU	$\to \infty$	$1 < M << E^{\beta}$	$\frac{\mathrm{Ln}(M)}{\beta P + 1}$	$1 - \varepsilon$	ExtCott Eq. (42)
4	aNoOhm	$1 < E^{\beta} << M$	$\to \infty$	$\frac{E^{\beta} - E^{\beta-1}}{M + P(\beta E^{\beta} + (1-\beta)E^{\beta-1})}$	$0 + \varepsilon$	Linear
5	aNum	Finite	Finite	Numerical	$0 < \mu < 1$	Num

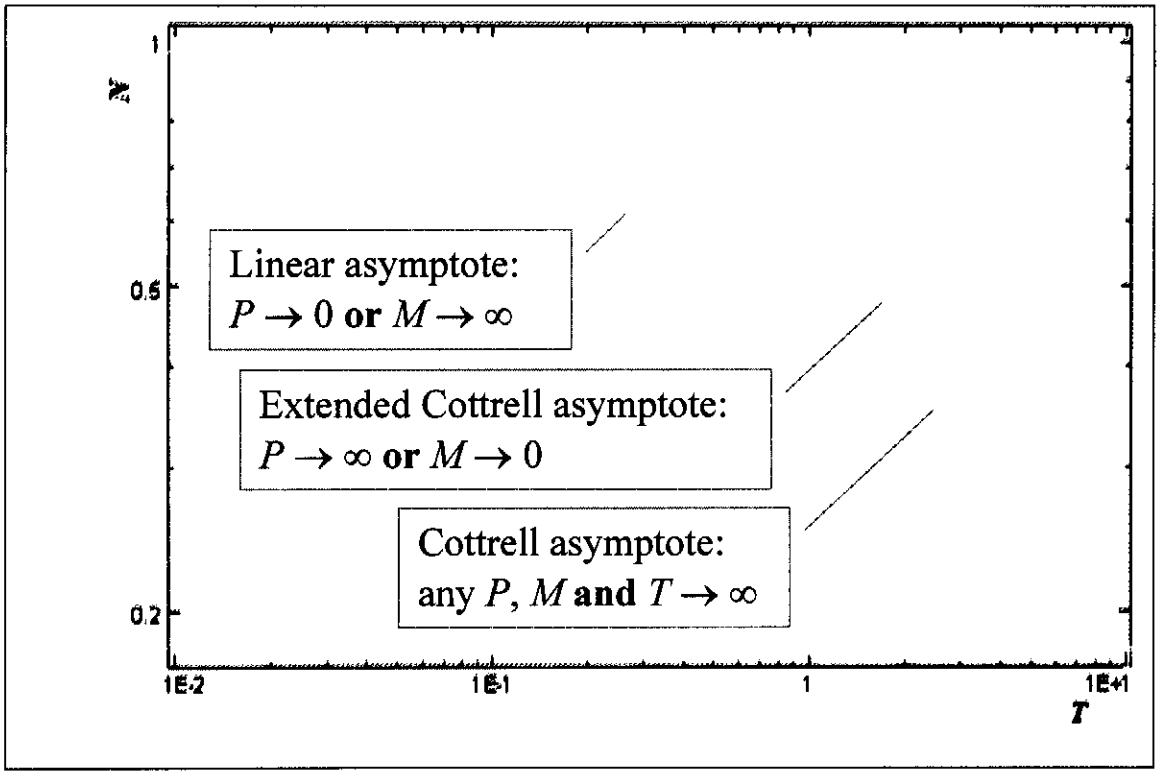

Fig. 1. Global asymptotes in the $\{M, P\}$ space.

3.2. Short-time asymptote

Immediately after the start, $T \to 0$, the flux is close to its starting value, $N \to 1$. The related concentration driving force $W(T) = \Lambda[N(T)]$ according to Eq. (20) can be linearized:

$$W = \Lambda[N] \approx \psi\,(1\text{-}N) + O(1\text{-}N)^2, \tag{30}$$

$$\psi = \frac{E+B}{E-1}\,\frac{E(1+\beta\mu P) - E^{\mu}(1-(1-\beta)\mu P)}{E+B\,E^{\mu}}. \tag{31}$$

The corresponding solution to (19) has a simple analytic representation:

$$N(T) = N_L[\psi^{-2}T]. \tag{32}$$

Survey of asymptotic sub-cases is given in the following Table 2.

Table 2. Parameters of *short-time and long-time asymptotes* for ψ (Eq. 31) *and* Y (Eq. 34)

	Case	*P, M*	ψ	Y
1	aLowU	$P \to 0$	$1-\frac{P^2(B-\beta-\beta B)}{(1+B)M}$	$1+\frac{P^2(B-\beta-\beta B)}{(1+B)M}$
2	aNoFar	$M \to 0$	$\frac{P}{f_{NP}(1+B)}\left(1+M(\beta-\frac{1}{1+B})\right)$	$\frac{(P-M)E(1+B)}{(E-1)(E+B)}+\frac{ME^{1-\beta}}{E-1}$
3	aHghU	$P \to \infty$	$\frac{P}{f_{NP}(1+B)}\left(1-\frac{\varepsilon P(1-\beta(1+B)}{1+B}\right)$	$\frac{P}{E-1}\left(\frac{(1+B)(1-\varepsilon E)}{E+B}+\varepsilon E^{1-\beta}\right)$
4	aNoOhm	$M \to \infty$	$1+\frac{f_{NP}(\beta(E+B)-B)}{1+\beta(E-1)+E^{1-\beta}M/P}$	$1+\frac{PE^{\beta}\left(\frac{1+B}{E+B}-E^{-1}(1-\beta)-\beta\right)}{M+PE^{\beta}\left(E^{-1}(1-\beta)-\beta\right)}$

3.3. Long-time asymptote

Long time after start, $T \to \infty$, the flux is small, $N \to 0$, merging to the Cottrell asymptote. The related concentration driving force W according to Eq. (20) can be approximated as

$$W = \Lambda[N] \approx 1 - Y N + O(N^2), \tag{33}$$

$$Y = ((E-E^{\mu})/ E^{\beta\mu} + \mu PE(1+B)/(E+B)) / (E-1). \tag{34}$$

The corresponding approximation to the transport equation (19), however, must take account also for the initial course of $N(T)$ for $T < \theta$, e.g. according to (32), $N(T) \approx N_L(\psi^2 T)$, to calculate a consistent approximation to the semi-integral for $T \to \infty$:

$$\mathbf{d}_T^{-1/2} N(T) \approx \int_0^{\theta} \frac{N(S)\,\mathrm{d}S}{\pi^{1/2}(T-S)^{1/2}} + \int_{\theta}^{T} \frac{N(S)\,\mathrm{d}S}{\pi^{1/2}(T-S)^{1/2}}, \tag{35}$$

$$\int_0^{\theta} \frac{N_L(\psi^{-2}S)\,\mathrm{d}S}{\pi^{1/2}(T-S)^{1/2}} \approx \sqrt{\frac{T}{\pi}} \int_0^{\theta/T} N_L(\psi^{-2}T\,s)(1+\tfrac{1}{2}s+\tfrac{3}{4}s^2\ldots)\,\mathrm{d}s \approx (\pi T)^{-1/2}(c_1 + c_2 T^{-1}), \tag{36}$$

$$\begin{aligned} c_1 &= \psi(1-\psi\,(1-N_L[\psi^{-2}\theta])), \\ c_2 &= \tfrac{1}{8}\pi\psi\,(\tfrac{1}{3}+\psi\,N_L[\psi^{-2}\theta]-\tfrac{1}{2}\psi^3(1-\psi\,(1-N_L[\psi^{-2}\theta])) \end{aligned} \tag{37ab}$$

Assuming the long-time approximation in the form

$$N(T) \approx (\pi T)^{-1/2}(1 + b_1 T^{-1} + b_2 T^{-2} + b_3 T^{-3}\ldots), \tag{38}$$

$$\int_{\theta}^{T} \frac{N(S)\,\mathrm{d}S}{\pi^{1/2}(T-S)^{1/2}} \approx 1 + (\pi T)^{-1/2}(C_1 + C_2 T^{-1} + \ldots), \tag{39a}$$

$$C_1 = \frac{16 b_2 + \pi 12 b_1 - 3\pi^2}{3\pi^2}, \quad C_2 = \frac{48 b_2 - \pi 12 b_1 - \pi^2}{24\pi}, \tag{39bc}$$

the solving of Eq. (19) with $\Lambda[N] \approx 1 - Y N$ and the choice $\theta = \pi/4$, $N_A = N_L[\psi^{-2}\theta]$ gives:

$$b_1 \approx \frac{\psi^3(1-\psi(1-N_A))}{2(Y-2)} + \frac{\pi(9(Y-\psi^2)-8(1-\psi)+6\psi^2 N_A)}{24(Y-2)}, \tag{40a}$$

$$b_2 \approx \frac{3\pi\psi^2(\pi-\pi Y-2\psi^2)N_A}{16(Y-2)} - \frac{3\pi(1-\psi)\psi^3}{8(Y-2)} - \frac{\pi^2(4+6Y^2-Y(9-6\psi+6\psi^2)-\psi(4-3\psi))}{32(Y-2)}. \tag{40b}$$

The third coefficient is calculated to satisfy the condition of continuous matching the short-time asymptote in the dividing point $T = \theta$. For the asymptotic cases, listed in Table 2, the values of b_1, b_2 are given below:

Table 3. *Asymptotic cases for the long- time expansion parameters*

	Case	b_1	b_2
1	aLowU	-1/2	+3/4
2	aNoFar	$+\pi/24$	$+3\pi^2/640$
3	aHghU	$+\pi/24$	$+3\pi^2/640$
4	aNoOhm	-1/2	+3/4

3.4. Galvanometric constraint

With a finite threshold $i \le (I_G/A)$ in the outer circuit, the initial current cannot overcome this limit. As a result, normalized current in an early stage is constant, $N(T) = G$, $G \equiv (I_G/A)/i_S < 1$, and $W(T)$ developing in the galvanostatic regime according to Eq. (19),

$$W(T) = \mathbf{d}_T^{-1/2} G = G\frac{2}{\pi}(\pi T)^{1/2}, \tag{41a}$$

This regime lasts until $W(T)$ increases to the threshold value W_G at a time T_G according to the constraints following from Eq. (19):

$$W_G = W(T_G) = G\frac{2}{\pi}(\pi T_G)^{1/2} = \Lambda[G], \tag{41b}$$

After passing the singular point $T = T_G$, the transient process continues in a normal way, according to Eq. (19).

If the Faradaic resistance and Ohmic loss are negligible at given galvanometric constraint, i.e. $G = 1$, there is a simple analytic solution to the problem with $T_G = \theta$:

$$N(T) = \begin{cases} 1; & T < \theta \\ \frac{2}{\pi}\,\mathrm{ArcCot}\left(\sqrt{T/\theta - 1}\right); & T > \theta \end{cases}. \tag{42}$$

Obviously, this solution provides a short-time extension to the long-time Cottrell asymptote. For $G = 1$, the solution (42) represents the extended Cottrell asymptote, noted in Chapter 3.1.

3.5. Long-time asymptote under galvanometric constraint

Analysis of this asymptotic case is analogous to that in Chapter 3.3 but slightly simpler, as the short-time increment for $T < T_G$ is known, $N(T) = G$. Trial form according to Eq. (38) results in:

$$b_1 \approx T_G \frac{18Y + 15GT_G - 32\sqrt{T_G/\pi}}{12(Y - 4T_G)}, \tag{43a}$$

$$b_2 \approx T_G^2 \frac{18Y + 9GT_G - 16\sqrt{T_G/\pi} - 6Y(GT_G + Y)/\sqrt{T_G/\pi}}{4\,(Y - 4T_G)}. \tag{43b}$$

4. Numerical analysis

The applied numerical scheme is based on a discrete representation of the course $N(T)$ with a constant-step grid but differs from the older one [5] both in several aspects:

- Instead of R2 algorithm [3], the semi-integral is calculated using the new R3 algorithm (an analogue to Simpson rule).
- Instead of its inverse form [5], the transport equation (19) is solved in its direct form, $\mathbf{d}_T^{-1/2} N(T) = \Lambda[N(T)]$.
- Instead of a relaxation procedure, the resulting non-linear problem is solved using the direct Newton iteration.

4.1. An iterative solving of the NC equation

Semiintegral of a function $F(T)$ can be transformed, using the linear transformation $T = K\,\Delta T$, $s = i\,\Delta T$, to the form

$$d_T^{-1/2} F(T) \equiv \pi^{-1/2} \int_0^T \frac{F(s)\mathrm{d}s}{(T-s)^{1/2}} = (\Delta T/\pi)^{1/2} \int_0^K \frac{F(i\Delta T)\mathrm{d}i}{(K-i)^{1/2}}. \tag{44}$$

If the function $F(T)$ is specified only in the discrete points of a homogeneous 1D grid, $F_i = F(T_i)$, $T_i = i\,\Delta T$, $i = [0..K]$. Its semiintegral can be approximated by a suitable discrete linear formula:

$$d_T^{-1/2} F(T) \approx (\Delta T/\pi)^{1/2} \sum_{i=0..K} S_{K,i} F_i\,. \tag{45}$$

Starting with a known discrete representation $N(T_i) = N_i$ for $i < K$, the discrete form of NC equation for unknown $N(T_K) = N_K$ can be written as

$$(\Delta T/\pi)^{1/2} \left(\sum_{i=0..K-1} S_{K,i} N_i + S_{K,K} N_K \right) = \Lambda[N_K]. \tag{46}$$

This non-linear equation can be solved efficiently and with no trouble, e.g. by *regula falsi* method using common first trial $N_K = N_{K-1}$.

4.2. R2-algorithm: the Trapezoidal rule

The coefficients $S_{K,i}$ in (42) can be constructed following various approximation schemes. Oldham and Spannier [8] suggested the formula R2, based on a "ramp" local approximations of $F(T)$, used also in [6, 7]. On a *segment* $T_{i-1} < T < T_i$ with two dividing points $\{L, H\} = \{ i\text{-}1, i\}$, and node values $\{F_L, F_H\} = \{F_{i-1}, F_i\}$, the linear interpolation, $F(s) \approx a_0 + a_1\,s$, is identified as

$$a_0 = F_L, \quad a_1 = F_H - F_L. \tag{47}$$

The contribution to overall semiintegral from a segment:

$$\int_L^H \frac{(a_0 + a_1 i)\mathrm{d}i}{(K-i)^{1/2}} = Q_L F_L + Q_H F_H\,, \tag{48}$$

$$Q_L = \tfrac{2}{3}\left(2\,(K-i)^{3/2} - \sqrt{K+1-i}\,(2K-2i+1)\right), \tag{49a}$$

$$Q_H = \tfrac{2}{3}\left(2(K+1-i)^{3/2} - \sqrt{K-i}\,(2K-2i+3)\right). \tag{49b}$$

The final coefficients, in agreement with [8]:

$$S_{k,i}=\tfrac{4}{3}\left((K-1-i)^{3/2}+2(K-i)^{3/2}-(K+1-i)^{3/2}\right), \tag{50a}$$

$$S_{k,0}=\tfrac{4}{3}\left(2(K-1)^{3/2}-(2K-3)(K)^{1/2}\right), \qquad S_{k,k}=\tfrac{4}{3}. \tag{50bc}$$

4.3. R3-algorithm: the Simpson rule

Let us consider an improved approximation, based on local quadratic interpolation (like in Simpson rule) of the function $F(T)$.

On a *full segment* $T_{i-2} < T < T_i$ with the dividing points $\{L, M, H\} = \{i\text{-}2, i\text{-}1, i\}$, and node values $\{F_L, F_M, F_H\} = \{F_{i-2}, F_{i-1}, F_i\}$, the parabolic interpolation, $F(s) \approx a_0 + a_1 s + a_2 s^2$, is identified as

$$\begin{aligned} a_0 &= \tfrac{1}{2}(F_L M H + F_H L M - 2F_M L H), \\ a_1 &= -\tfrac{1}{2}(F_L(M+H) + F_H(L+M) - 4F_M M), \\ a_2 &= \tfrac{1}{2}(F_L + F_H - 2F_M) \end{aligned} \tag{51}$$

Simpson-like contribution to overall semiintegral from a full or upper-half segment:

$$\int_L^H \frac{(a_0+a_1 i+a_2 i^2)\mathrm{d}i}{(K-i)^{1/2}} = Q_L F_L + Q_M F_M + Q_H F_H, \quad \int_M^H \frac{(a_0+a_1 i+a_2 i^2)\mathrm{d}i}{(K-i)^{1/2}} = R_L F_L + R_M F_M + R_H F_H, \tag{52ab}$$

$$Q_L=\tfrac{1}{15}\left(-\sqrt{K-i}\,(2K(4K+5)-2i(8K+5)+8i^2)+\sqrt{K+1-i}\,(2K(4K+3)-2-2i(8K+3)+8i^2)\right), \tag{53a}$$

$$Q_M=\tfrac{1}{15}\left(\sqrt{K-i}\,(8K(2K+5)-8i(4K+5)+16i^2)-\sqrt{K+2-i}\,(8K(2K+3)-16-8i(4K+3)+16i^2)\right), \tag{53b}$$

$$Q_H=\tfrac{1}{15}\left(-\sqrt{K-i}\,(2K(4K+15)+30-2i(8K+15)+8i^2)+\sqrt{K+2-i}\,(2K(4K+11)+12-2i(8K+11)+8i^2)\right), \tag{53c}$$

$$R_L=\tfrac{1}{15}\left(-\sqrt{K-i}\,(2K(4K+5)-2i(8K+5)+8i^2)+\sqrt{K+1-i}\,(2K(4K+1)+2-2i(8K+1)+8i^2)\right), \tag{54a}$$

$$R_M=\tfrac{1}{15}\left(\sqrt{K-i}\,(8K(2K+5)-8i(4K+5)+16i^2)-\sqrt{K+1-i}\,(16K(K+2)-14-32i(K+1)+16i^2)\right), \tag{54b}$$

$$R_H=\tfrac{1}{15}\left(-\sqrt{K-i}\,(2K(4K+15)+30-2i(8K+15)+8i^2)+\sqrt{K+1-i}\,(2K(4K+13)+18-2i(8K+13)+8i^2)\right). \tag{54c}$$

Note that these coefficients reduce, for $K \to \infty$, to common ones for the Simpson rule,

$$\sqrt{K}\{Q_L,Q_M,Q_H\} \to \{\tfrac{1}{3},\tfrac{4}{3},\tfrac{1}{3}\}, \quad \sqrt{K}\{R_L,R_M,R_H\} \to \{-\tfrac{1}{12},\tfrac{8}{12},\tfrac{5}{12}\}. \tag{55ab}$$

The semiintegral is calculated as a sum of contributions from full segments, Eq. (52a). For odd values of upper limit K is this sum completed by additional contribution from the upper-half segment, Eq. (52b).

As shown in another report [9], the R3 algorithm can be easily programmed and provides slightly better approximation than the R2 algorithm.

4.4. Simulation program

A computing program in Delphi-Pascal is available for numeric simulations. It calculates the $N(T)$ and $W(T)$ courses for a set of basic parameters or $\{B, P, \beta, M, G\}$, see Nomenclature, where M can be replaced with μ, see Eq. (24). Some output data are available as tables in *.txt (Excel-compatible) files or plots in *.emf files.

The program, with the source code written in an old Borland Object Pascal (Delphi4), is free available at http://home.icpf.cas.cz/wein. as **VST2010.EXE** file.

5. Results

Normalized form of the VST problem in 1D approximation results in a non-linear semi-integral equation with a local constraint, $W = \Lambda[N]$, Eqs. (19, 20). The courses of normalized flux, $N(T)$, and driving force, $W(T)$, depend on four parameters $\{B, \beta, P, M\}$. Additional parameter $G < 1$ reflects possible galvanometric constraint. The simulation program VST2010.EXE computes the N, W courses numerically, using an equidistant difference scheme. Analytic asymptotes, mentioned in Chapter 3, are included in the text output, as well.

5.1. Cottrell asymptotes: diffusion resistance and Nernst equilibrium only

With negligible Faradaic resistance, $M = 0$ (i.e. $\mu = 1$), the local constraint (20) reduces to the Nernst-Petersen surface equilibrium condition (24), i.e. $\Lambda[N] = 1$, and the kinetic parameters β, k_{BV} become irrelevant. The effect of Ohmic loss, under no galvanometric constraint, $G = 1$, is included in the normalized formulation by a suitable choice of the normalizing parameter t_S. In particular, for a fixed finite Cottrell coefficient a_C and $i_S = i_C \to \infty$, it is $t_S \equiv (a_C / i_C)^2 \to 0$ and, hence, $T \to \infty$ for any non-zero fixed t. This case, known as the Cottrell asymptote, is not a correct solution to a well-posed VST problem, but it yields just the asymptote, $W(T) \approx 1$, $N(T) \approx (\pi T)^{-1/2}$, discussed thoroughly in Chapter 2.2.

Galvanometric constraint provides the *extended Cottrell asymptote*, see Eq. (42), by introducing a finite threshold for the transient currents, $i_S \to (I_G/A)$, $i_C \to \infty$. By including this G-constraint, also the cases with negligible Ohmic loss can be treated in a regular way, over a full span of normalized time T. This asymptote corresponds to a plain constraint $G = 1$ in the remaining 3-parametric space $\{B, P, G\}$. The extended Cottrell asymptote is compared with the other important asymptotes in Fig.1.

5.2. Effect of varying voltage (*P*)

A set of transient fluxes is shown in Fig. 2. for the transport symmetric case $B = 1$, $\beta = ½$ and negligible Ohmic loss, $M = 0$. Remind that the parameter P is a normalized overvoltage. Remind also that the value $P = 50$ under common laboratory conditions for a reversible redox couple of depolarizers corresponds to $|U| = 1250$ mV, the value close to decomposition voltages for aqueous solutions.

Thin dashed gray curves correspond to the *Equilibrium*, *Cottrell*, and *Extended Cottrell* asymptotes, respectively, as suggested in the pilot Fig. 1. For $P < 1$, ($U < 25$ mV), the transient courses are very close to the equilibrium asymptote, $P = 0$. The cases for $P > 50$ are very close to the extended Cottrell asymptote.

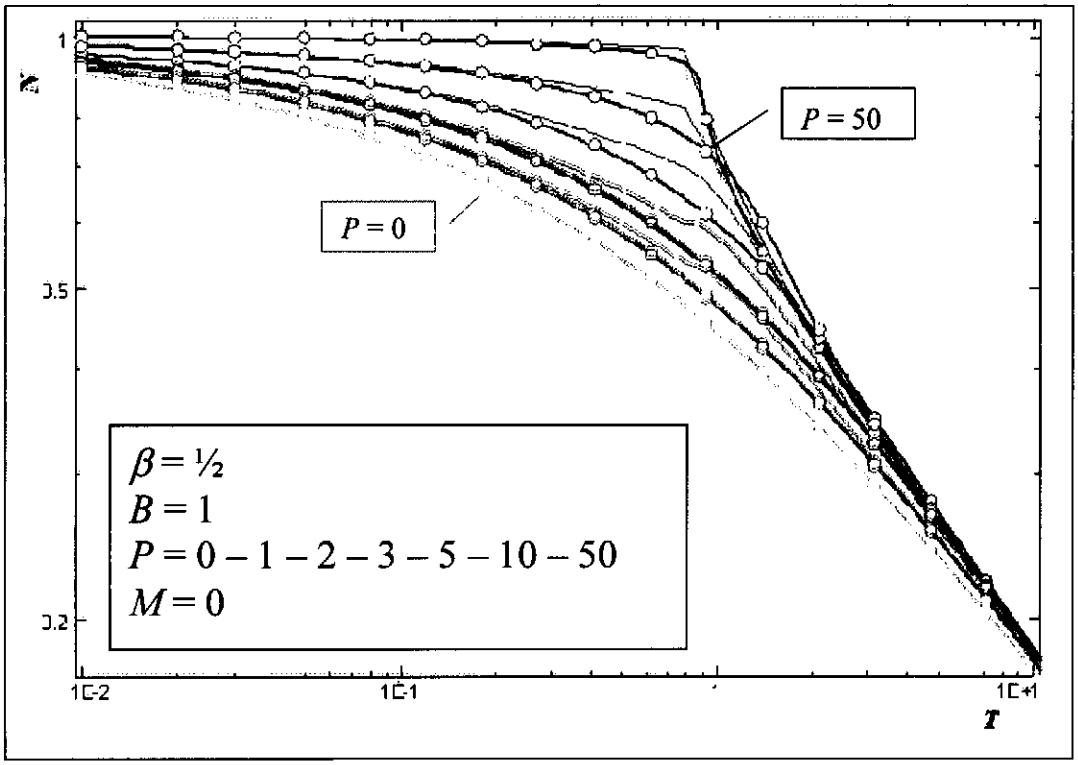

Fig. 2. Normalized transient currents for negligible Ohmic loss, effect of overvoltage .

5.3. Effect of varying composition (*B*)

Even for the equimolar solutions, $c_O^B = c_R^B$, the value of B can slightly differ from 1 due to different values of the diffusion coefficients of a given redox couple. For the ferri-/ferro-cyanides couple, the diffusion coefficient of the *R*- form is by 20% lower. Anyway, the normalized course $N(T)$ deviates from the symmetric case $B = 1$ only at very high B, see Fig. 3.

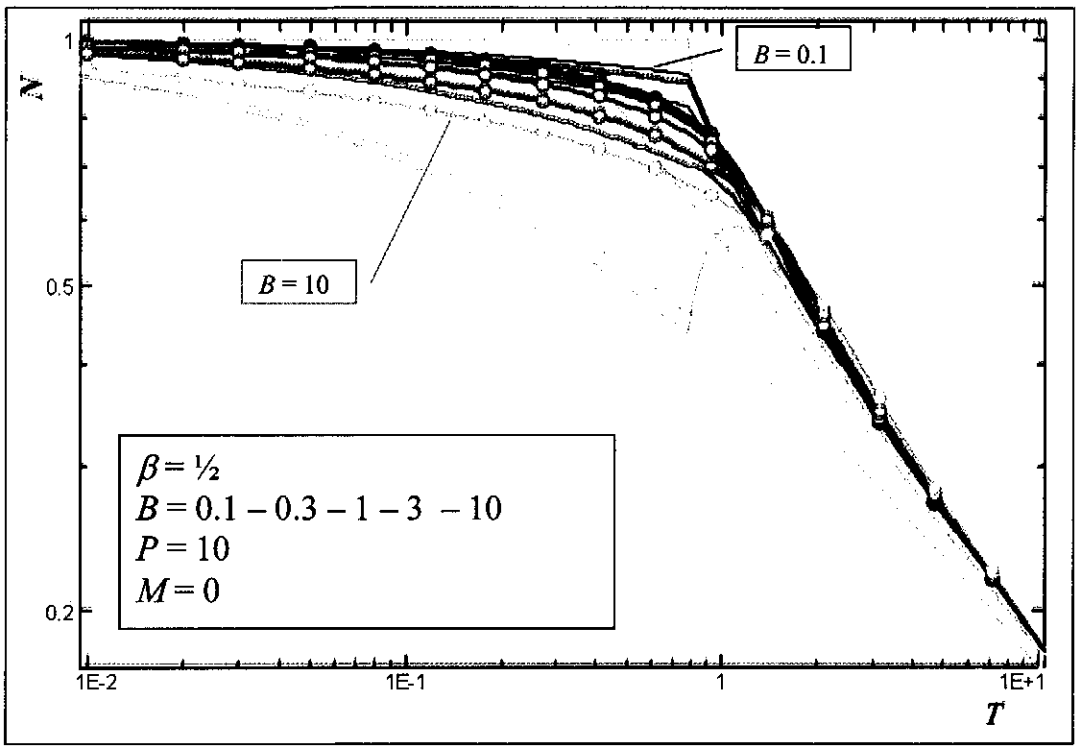

Fig. 3. Normalized transient currents for negligible Ohmic loss, effect of composition.

5.4. Effect of simultaneous Faradaic and Ohmic resistance (*M*)

The relative importance of the Faradaic and Ohmic resistance is represented by the single parameter *M*. Its effect is shown in Fig. 4a for a medium overvoltage, $P = 10$, and in Fig. 4b for an extremely high overvoltage, $P = 50$, commonly applied in the limiting-diffusion measurements.

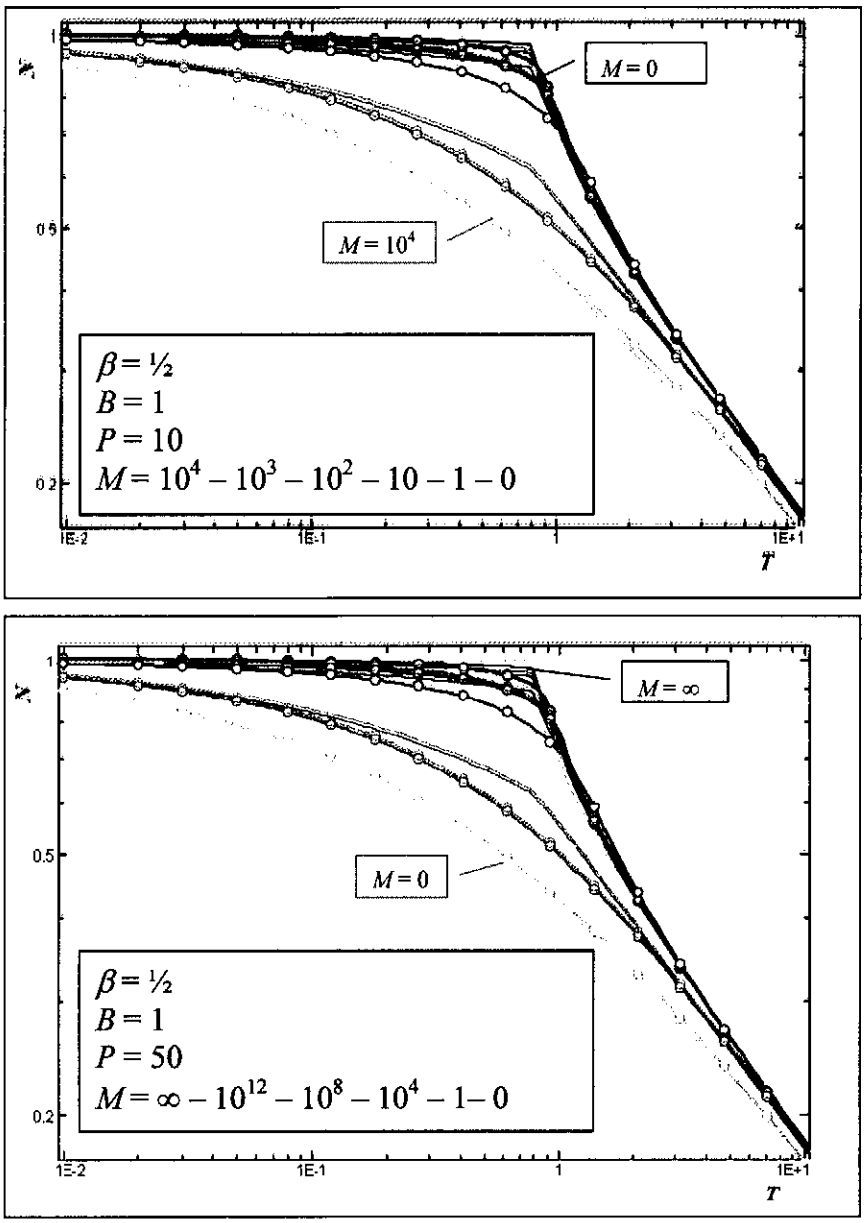

Fig. 4. Normalized transient currents, effect of Ohmic and Faradaic resistance.

5.5. Effect of galvanometric constraint (*G*)

With no galvanometric constraint, the default value is $G = 1$. For $G < 1$, the starting normalized current N cannot be higher than 1, and the process is controlled galvanostatically. The effect of this prehistory on the further course o $N(T)$ is shown in Fig. 5 for the symmetric case $B = 1$, $\beta = ½$, and high overvoltage, $P = 50$, assuming no additional Ohmic loss, $M = \infty$.

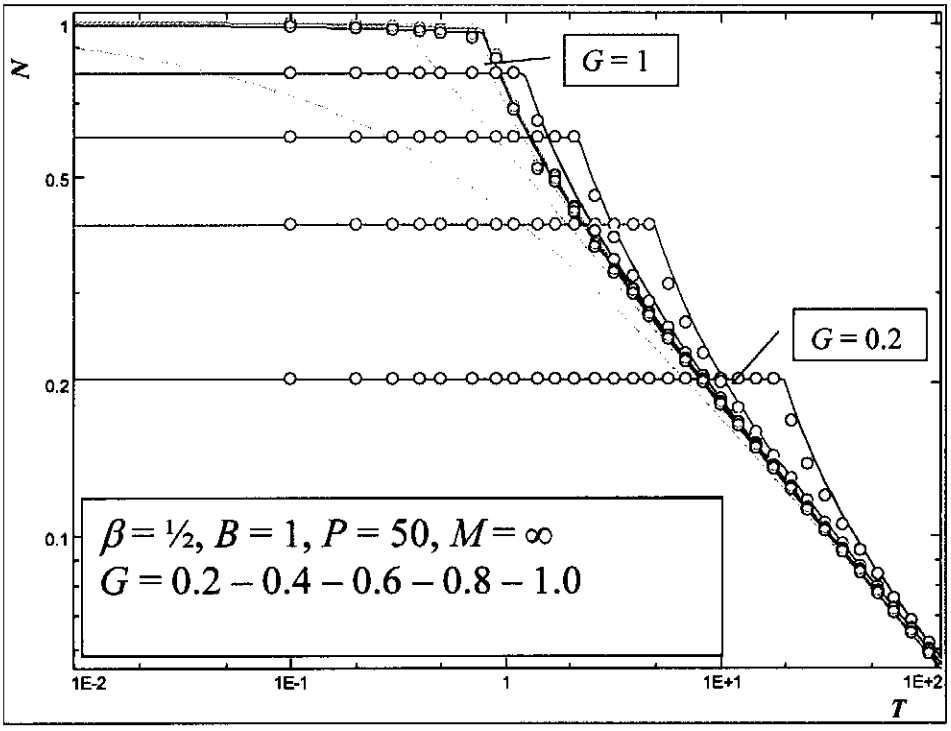

Fig. 5. Normalized transient currents for negligible Ohmic and Faradaic loss, effect of galvanometric constraint.

6. Conclusions

A computer program is available for numerical simulating the normalized VST curves $N(T)$ in a 1D approximation under a broad range of conditions, represented the by the set of five normalized parameters $\{\beta, B, P, M, G\}$, which correspond to :

- kinetics of electrode reaction, $\{k_{BV}, \beta\}$
- transport properties in a bulk of electrolyte solution $\{c_O^B, c_R^B, D_O, D_R\}$,
- overvoltage P,
- ED cell geometry $\{A, L_c\}$ and the bulk conductivity κ,
- Galvanometric constraint of the outer circuit, I_G.

While the numerical simulation of $N(T)$ is accurate and fast enough, the suggested analytic approximations over the multidimensional space $\{\beta, B, P, M, G; T\}$cover only narrow regions with uncertain accuracy.

The report will be published in the *Journal of Applied Electrochemistry* during 2011.