

FLOW ELECTROLYZERS. VI.*

CALCULATION OF VOLTAGE AND CURRENT DENSITIES
FOR DIAPHRAGM FLOW ELECTROLYZERS

I. ROUŠAR, V. CEZNER and J. HOSTOMSKÝ

*Department of Inorganic Technology,
Institute of Chemical Technology, Prague 6*

Received December 4th, 1969

Criterion equations are derived enabling the calculation of voltage and local current densities for a monopolar type of diaphragm electrolyzer with current leads at the bottom or at the top, and for a bipolar diaphragm electrolyzer. The influence of the position of current leads on the terminal cell voltage and on local current densities is discussed in the case of a technically important electrolyzer for decomposition of hydrochloric acid solutions.

The present paper is concerned with the derivation of analytical expressions suitable for the calculation of parameters of diaphragm electrolyzers where the flow of electrolyte through the diaphragm is excluded.** For systems with a flow of electrolyte through diaphragms, the calculation of the rate of flow of electrolyte and of voltage distribution were performed by McMullin¹, Genin and Krongauz². Analogous expressions are known also for a number of diaphragmless electrolyzers either without formation of a gaseous phase^{3,4}, for fuel cells⁵, or for systems with formation of a gaseous phase at the electrodes⁶⁻⁸.

Model System

A diaphragm electrolyzer with plate-shaped electrodes consists of two channels separated by a diaphragm (Fig. 1). The electrodes are placed on the channel walls opposite each other, the remaining walls are made of an insulating material. The electrolyte flows into each channel at the bottom, while the mixture of bubbles and electrolyte gets out at the top. The thickness of the anode plate is denoted S_A , that of the cathode plate S_K . The spaces between the electrodes and the diaphragm have dimensions d_A , w , L and d_K , w , L , respectively. The thickness of the diaphragm is denoted as d_D . The origin

* Part V: This Journal 35, 2044 (1970).

** A similar paper (Funk J. E., Thorpe J. E.) based on numerical solution of the corresponding differential equations was presented at the conference of the Electrochemical Society in Boston, May 1968, see also J. Electrochem. Soc. 116, 48 (1969).

of the coordinate system is $P(0,0,0)$ for both models P with current lead at the top and Q with current lead at the bottom.

Mathematical Description of Model P

From the physical point of view the system is isothermal and both electrode processes are governed by the rate of electrode reaction. So far as the change of electrode potential with current density is large and the electrode distance small we can assume that the lines of force in the metal, electrolyte and diaphragm are perpendicular to the electrode surface. With these assumptions we can write the equation for the terminal voltage of the electrolyzer in the form

$$U = U_A + U_K + \varepsilon_A - \varepsilon_K + U_{MA} + U_{MK} + U_D \quad (1)$$

(for the meaning of symbols see p. 15). This equation is valid regardless of the value of the y coordinate. The potentials can be calculated from the Tafel equation

$$\varepsilon_A = a_A + b_A + b_A \ln i, \quad -\varepsilon_K = a_K + b_K \ln |i|. \quad (2), (3)$$

The current density is defined so that its positive value means anodic current and negative value cathodic current. According to our assumptions, the current density is the same for both electrodes in a given height; therefore we can use in further equations only the anodic (positive) current density.

We shall calculate the decrease of voltage along the electrodes under the assumption that the intensity of the electric field parallel to the x - and z -axes is negligible in comparison to that parallel to the y -axis. From the previous work^{6,7} we get the following expressions for the voltage losses in the electrodes:

$$U_A = i_p (\varrho_A / S_A) L^2 (y_r - \int_0^{y_r} \int_0^{y_r} i_r dy_r dy_r), \quad (4)$$

$$U_K = i_p (\varrho_K / S_K) L^2 (y_r - \int_0^{y_r} \int_0^{y_r} i_r dy_r dy_r). \quad (5)$$

The average current density related to the geometric surface area of the electrode, i_p , relative local current density, i_r , and relative length of electrode, y_r , are defined as

$$i_p = I_T / wL, \quad i_r = i / i_p, \quad y_r = y / L. \quad (6), (7), (8)$$

The voltage loss in the diaphragm is equal to the sum of the ohmic voltage drop and

of the diffusion potential U_{dif} :

$$U_D = id_D r_D \int_0^1 \varrho \, d\chi + U_{\text{dif}}. \quad (9)$$

The relative coordinate χ is defined as

$$\chi = (x - x_1)/d_D, \quad (10)$$

where $x_1 = S_A + d_A$. The dependence of ϱ on χ for diluted solutions of binary electrolytes in the absence of forced liquid flow through the diaphragm is given⁹ by

$$\varrho = \varrho_{\text{EK}} [\varrho_{\text{EK}}/\varrho_{\text{EA}} + \chi(1 - \varrho_{\text{EK}}/\varrho_{\text{EA}})]^{-1}. \quad (11)$$

We assume that this equation holds also for concentrated electrolyte solutions. Introducing Eq. (11) into (9) and integrating we obtain

$$U_D = id_D r_D \varrho_D + U_{\text{dif}}, \quad (12)$$

where for $\varrho_{\text{EA}} \neq \varrho_{\text{EK}}$

$$\varrho_D = [\varrho_{\text{EA}}\varrho_{\text{EK}}/(\varrho_{\text{EA}} - \varrho_{\text{EK}})] \ln(\varrho_{\text{EA}}/\varrho_{\text{EK}}). \quad (13)$$

For $\varrho_{\text{EA}} = \varrho_{\text{EK}}$ it follows from Eqs (11) and (9)

$$\varrho_D = \varrho_{\text{EA}} = \varrho_{\text{EK}}. \quad (14)$$

The U_{dif} value in Eq. (12) is known from thermodynamics¹⁰:

$$U_{\text{dif}} = (RT/F) \sum_j \int_{a_{j,\text{EA}}}^{a_{j,\text{EK}}} (t_j/z_j) \, d \ln a_j. \quad (15)$$

The voltage loss in the electrolyte is given as

$$U_{\text{MA}} = id_A \varrho_{\text{MA}}, \quad U_{\text{MK}} = id_K \varrho_{\text{MK}}. \quad (16), (17)$$

The specific resistance of the mixture of bubbles and electrolyte is calculated from the Maxwell or Tobias equation¹¹. As mentioned in the preceding communications^{6,7}, the Maxwell equation can be used for mixtures with a low volume fraction of the dispersed gaseous phase. For the anodic compartment we have

$$\varrho_{\text{MA}} = \varrho_{\text{EA}} [1 + 1.5\alpha_A/(1 - \alpha_A)]. \quad (18)$$

The volume fraction of the gas is calculated from the equation given by Zuber¹² for a streaming two-phase system, namely a liquid with dispersed particles, assuming that the motion of the bubbles is governed by laminar flow:

$$v_{GA} = v_{EA} + v_{RA}(1 - \alpha_A)^{3.5}. \quad (19)$$

The volume flow of anolyte, V_{EA} , and the volume flow of gas in the anodic compartment, V_{GA} , are given as

$$v_{EA} = V_{EA}/wd_A(1 - \alpha_A), \quad v_{GA} = V_{GA}/wd_A\alpha_A. \quad (20), (21)$$

Introducing Eqs (20) and (21) into (19) and rearranging we obtain an equation enabling to calculate α_A by iteration:

$$\alpha_A = V_{GA}/[V_{GA} + V_{EA} + wd_A v_{RA}(1 - \alpha_A)^{4.5}]. \quad (22)$$

The volume flow of anolyte is determined experimentally. The velocity of gas bubbles due to buoyancy is calculated according to the Stokes law from the mean bubble diameter determined experimentally:

$$v_{RA} = gd_{GA}^2/18v_{EA} \quad (23)$$

for $v_{RA}d_{GA}/v_{EA} = \text{Re}_{GA} \leq 1.9$, or from the empirical relation

$$v_{RA} = (4/3)^{5/7}(gd_{GA}/18.5)^{5/7}(d_{GA}/v_{EA})^{3/7} \quad (24)$$

for $\text{Re}_{GA} \in (1.9; 505)$. The volume rate of flow of the gas in a given place in the electrolyzer is calculated with the use of the Faraday law and of the equation of state of the ideal gas:

$$V_{GA} = [RT/(P_0 - P_s) F_1] (wLi_p/F) (\eta_A/n_A) (1 - \int_0^{y_r} i_r dy_r), \quad (25)$$

where F_1 , a correction for the hydrostatic pressure of the bubble-electrolyte mixture in the height L_{y_r} , is defined by the equation

$$F_{1A} = [P_0 - P_s + (0.9869 \cdot 10^{-6} L g s_A) (1 - 0.5\alpha_{A,\max} - 0.5\alpha_A)] / (P_0 - P_s), \quad (26)$$

Analogous equations can be derived also for α_K and K_{1K} . Introducing Eqs (22) and (25) into (18) and rearranging we obtain

$$\varrho_{MA} = \varrho_{EA} \left[1 + 1.5K_{3A} \left(1 - \int_0^{y_r} i_r dy_r \right) \right], \quad (27)$$

where

$$K_{3A} = V_{GA}^0 / [V_{EA} + wd_A v_{RA} (1 - \alpha_A)^{4.5}] \quad (28)$$

and V_{GA}^0 denotes the V_{GA} value for $y_r = 0$. For small α_A values the K_{3A} value can be considered as constant and α_A in Eq. (28) can be set equal to $\alpha_{A,max}$. The voltage loss in the anolyte is then given by

$$U_{MA} = id_A \varrho_{EA} \left[1 + 1.5K_{3A} \left(1 - \int_0^{y_r} i_r dy_r \right) \right]. \quad (29)$$

Analogous considerations lead us to the expression valid for the channel through which the catholyte flows:

$$U_{MK} = id_K \varrho_{EA} \left[1 + 1.5K_{3K} \left(1 - \int_0^{y_r} i_r dy_r \right) \right]. \quad (30)$$

For the calculation of the local current density from Eq. (1) it is suitable to linearize the logarithmic dependence of electrode potential on current density. By expanding the term $\ln i$ in series in the point $i = i_p$, the Tafel equation takes the form

$$\varepsilon_A = a'_A + b'_A F_2 i_p i_r, \quad -\varepsilon_K = a'_K + b'_K F_2 i_p i_r, \quad (31), (32)$$

where

$$a'_A = a_A - b_A + b_A \ln i_p, \quad (33)$$

$$a'_K = a_K - b_K + b_K \ln i_p, \quad (34)$$

$$b'_A = b_A / i_p, \quad b'_K = b_K / i_p, \quad (35), (36)$$

$$F_2 = (1 + \ln i_r) / i_r. \quad (37)$$

F_2 is an auxiliary function; if $F_2 = 1$, then the function $\ln i$ is linearized in the point $i = i_p$. Now the individual terms in Eq. (1) can be expressed from Eqs (4), (5), (12), (29)–(32). After rearrangement we obtain the relation

$$K_1 = i_r \left[1 + F_2 K_2 + 1.5K_3 \left(1 - \int_0^{y_r} i_r dy_r \right) \right] + K_4 \left(y_r - \int_0^{y_r} \int_0^{y_r} i_r dy_r dy_r \right), \quad (38)$$

whereby the criteria K_1 through K_4 are introduced:

$$K_1 = (U - U_{\text{dif}} - a'_A - a'_K)/i_p R_D, \quad (39)$$

$$K_2 = (b'_A + b'_K)/R_D, \quad K_3 = (d_A \varrho_{EA} K_{3A} + d_K \varrho_{EK} K_{3K})/R_D, \quad (40), (41)$$

$$K_4 = (\varrho_A/S_A + \varrho_K/S_K) L^2/R_D, \quad (42)$$

where

$$R_D = d_A \varrho_{EA} + d_K \varrho_{EK} + d_D \varrho_D r_D. \quad (43)$$

The accuracy of the Maxwell equation for the conductivity of heterogeneous mixtures decreases with increasing volume fraction of the dispersed phase. Therefore, for electrolyzers with a higher gas content in the electrolyte, it is better to calculate the voltage loss in the gas-electrolyte mixture from the equation derived by Tobias and Meredith¹¹. Thus, we define the following correction for systems with larger α_A and α_K values:

$$F_3 = [\varrho_{EA} d_A (4 + \alpha_A) (4 - \alpha_A) / 8(2 - \alpha_A) (1 - \alpha_A) + \\ + \varrho_{EK} d_K (4 + \alpha_K) (4 - \alpha_K) / 8(2 - \alpha_K) (1 - \alpha_K) + \\ + d_D \varrho_D r_D] / R_D [1 + 1.5 K_3 (1 - \int_0^{y_r} i_r dy_r)]. \quad (44)$$

Eq. (38) can be rearranged with the use of the mentioned correction into a form suitable for the calculation of the local current density:

$$i_r = [K_1 - K_4 (y_r - \int_0^{y_r} \int_0^{y_r} i_r dy_r dy_r)], \\ \cdot \{K_2 F_2 + F_3 [1 + 1.5 K_3 (1 - \int_0^{y_r} i_r dy_r)]\}^{-1}. \quad (45)$$

This equation is identical with Eq. (P-48) in reference⁷ not only formally but also so far as its physical meaning is concerned. The criterion K_1 characterizes the terminal voltage of the electrolyzer diminished by the diffusion overvoltage in the diaphragm and by the hypothetical terminal voltage in the currentless state relative to the voltage loss in the pure anolyte, catholyte and in the diaphragm. The criterion K_2 characterizes the slope of the polarization curves of both electrodes, K_3 the influence of the gas content in the anolyte and catholyte, and K_4 the influence of the specific resistance and electrode thickness. The unknown value of the criterion K_1 can be determined

from the condition that the current flowing through the electrode surface equals the total current flowing through the electrolyzer:

$$\int_0^1 i_r dy_r = 1. \quad (46)$$

Introducing Eq. (45) into (46) and integrating numerically, we obtain by iteration K_1 and from this the terminal voltage of the electrolyzer.

For electrolyzers with a small electrode height, small current density and high rate of flow of electrolyte, where the local current density does not differ appreciably from the average one, we may assume that $F_{1A} \approx K_{1K} \approx F_2 \approx F_3 \approx 1$ and $i_r \approx 1$. Then the first and second integrals on the right-hand side of Eq. (45) can be set approximately equal to $0.5y_r^2$ and y_r , respectively, and Eq. (45) can be simplified to

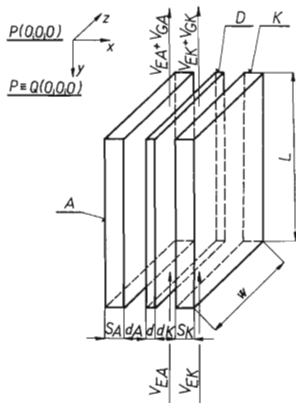


FIG. 1

Model Diaphragm Electrolyzer

A Anode; K cathode; D diaphragm; w electrode width; L electrode height; S_A , S_K thickness of anode and cathode; d_D thickness of diaphragm; d_A , d_K distance between diaphragm and anode or cathode; V_{EA} , V_{EK} volume rate of flow of anolyte or catholyte.

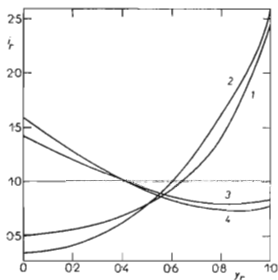


FIG. 2

Dependence of Relative Local Current Density on Relative Electrode Height for a Monopolar Diaphragm Electrolyzer

1 Current lead at the bottom, numerical solution; 2 current lead at the bottom, analytical solution; 3 current lead at the top, numerical solution; 4 current lead at the top, analytical solution.

$$i_r = [K_1 - K_4(y_r - 0.5y_r^2)]/[1 + K_2 + 1.5K_3(1 - y_r)]. \quad (47)$$

If this expression is introduced into Eq. (46), the integration can be performed analytically and the criterion K_1 can be expressed as function of the other ones as follows

$$K_1 = K_4K_5 - 0.5K_4K_5^2 + (0.75K_4 - 0.5K_4K_5 - 1.5K_3) \ln [(1 + K_2)/1.5K_3K_5], \quad (48)$$

where

$$K_5 = (1 + K_2 + 1.5K_3)/1.5K_3. \quad (49)$$

The latter equations enable us to calculate the distribution of voltage and current density also for a bipolar electrolyzer, if the electrode resistance is neglected. If $\varrho_A = \varrho_K = 0$, then $K_4 = 0$ and Eq. (48) enables to calculate the voltage for a bipolar electrolyzer with very well conducting electrodes, the electric current in parallel circuits being neglected.

Mathematical Description of Model Q

For electrolyzers with current lead at the bottom, we place the origin of coordinates again into the point $P(0, 0, 0)$. Also in this case the equations (1)–(3), (12), (29) and (30) hold. However, the equations (4) and (5) are changed as follows:

$$U_A = (i_p \varrho_A L^2 / S_A) (1 - y_r - \int_{y_r}^1 \int_{y_r}^1 i_r dy_r dy_r), \quad (50)$$

$$U_K = (i_p \varrho_K L^2 / S_K) (1 - y_r - \int_{y_r}^1 \int_{y_r}^1 i_r dy_r dy_r). \quad (51)$$

Introducing Eqs (12), (29)–(32), (50) and (51) into (1) and using the correction F_3 , Eq. (44), we obtain the following expression for the local current density in a flow electrolyzer with a diaphragm and with current leads at the bottom:

$$i_r = [K_1 - K_4(1 - y_r - \int_{y_r}^1 \int_{y_r}^1 i_r dy_r dy_r)] \cdot \{F_2K_2 + F_3[1 + 1.5K_3(1 - \int_0^{y_r} i_r dy_r)]\}^{-1}. \quad (52)$$

By numerical solution of Eq. (46), where i_r is expressed from (52), we obtain the K_1 value from which the terminal voltage of the electrolyzer can be calculated.

Assuming that $F_{1A} \approx F_{1K}$, $F_2 \approx F_3 \approx 1$ and $i_r \approx 1$, the first integral in Eq. (52) can be set approximately equal to $0.5y_r^2 - y_r - 0.5$ and Eq. (52) is simplified to

$$i_r = [K_1 - 0.5K_4(1 - y_r^2)]/[1 + K_2 + 1.5K_3(1 - y_r)]. \quad (53)$$

On introducing this result into Eq. (46) we obtain after integration the following relation for the criterion K_1 for an electrolyzer with current lead at the bottom:

$$K_1 = 0.5K_4 - 0.5K_4K_5 - (0.25K_4 + 0.5K_4K_5 + 1.5K_3) \cdot \{\ln [(1 + K_2)/1.5K_3K_5]\}^{-1}, \quad (54)$$

where K_5 is defined by Eq. (49).

Equations Valid for Both Models P and Q

We define a function φ so that $\varphi = 1$ for an electrolyzer with current lead at the top and $\varphi = 0$ for that with current lead at the bottom. Then it is possible to join Eq. (47) with (59) and Eq. (48) with (54) to obtain expressions valid for both models P and Q:

$$i_r = K_1 - 0.5K_4[1 + \varphi(2y_r - 1) - y_r^2]/[1 + K_2 + 1.5K_3(1 - y_r)], \quad (55)$$

$$K_1 = K_4K_5 + 0.5K_4(1 - \varphi) - 0.5K_4K_5 + \\ + [(\varphi - 0.25)K_4 - 0.5K_4K_5 - 1.5K_3]/\ln [(1 + K_2)/1.5K_3K_5]. \quad (56)$$

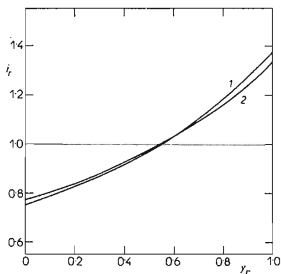


FIG. 3

Dependence of Relative Local Current Density on Electrode Height for a Single Cell of a Bipolar Diaphragm Electrolyzer

1 Numerical solution; 2 analytical solution.

Bipolar Diaphragm Electrolyzer

By arranging the individual cells shown in Fig. 1 in series and placing the current leads only to the first and last electrodes in the series we obtain a bipolar electrolyzer. If the electric currents flowing through other circuits (*e.g.* electrolyte inlet channels) are neglected, the calculation of voltage and current densities in a single cell can be performed. If also the electrode resistances are neglected then Eqs (47) and (48) can be used in the calculation ($K_4 = 0$). If the electrode resistances are taken into account, then the voltage loss in the electrodes is given by

$$U_A = i_p i_r \rho_A S_A, \quad U_K = i_p i_r \rho_K S_K. \quad (57), (58)$$

TABLE I
Analytical Solution for Monopolar Electrolyzer

y_r	i_r	e_A	$-e_K$	U_A	U_K	U_{MA}	U_{MK}	U_D
Current lead at the top; terminal voltage 2.917 V								
0.0	1.606	1.430	0.1349	0.0000	0.0000	0.4274	0.4435	0.4820
0.1	1.444	1.425	0.1309	0.1003	0.1003	0.3575	0.3706	0.4331
0.2	1.291	1.420	0.1271	0.1901	0.1901	0.2961	0.3065	0.3875
0.3	1.152	1.416	0.1236	0.2693	0.2693	0.2429	0.2510	0.3455
0.4	1.026	1.412	0.1204	0.3380	0.3380	0.1975	0.2037	0.2078
0.5	0.916	1.409	0.1177	0.3961	0.3961	0.1596	0.1642	0.2750
0.6	0.826	1.406	0.1154	0.4436	0.4436	0.1287	0.1321	0.2480
0.7	0.759	1.404	0.1137	0.4806	0.4806	0.1043	0.1066	0.2278
0.8	0.718	1.403	0.1127	0.5070	0.5070	0.0855	0.0869	0.2156
0.9	0.710	1.402	0.1125	0.5228	0.5228	0.0715	0.0722	0.2132
1.0	0.741	1.403	0.1133	0.5281	0.5281	0.0610	0.0610	0.2226
Current lead at the bottom; terminal voltage 2.821 V								
0.0	0.3230	1.390	0.1028	0.5281	0.5281	0.0859	0.0892	0.0969
0.1	0.3495	1.391	0.1035	0.5228	0.5228	0.0866	0.0897	0.1049
0.2	0.4041	1.393	0.1049	0.5070	0.5070	0.0927	0.0959	0.1212
0.3	0.4909	1.396	0.1070	0.4806	0.4806	0.1035	0.1070	0.1473
0.4	0.6148	1.399	0.1101	0.4436	0.4436	0.1184	0.1221	0.1845
0.5	0.7817	1.404	0.1143	0.3961	0.3961	0.1361	0.1400	0.2345
0.6	0.9989	1.411	0.1197	0.3380	0.3380	0.1556	0.1596	0.2997
0.7	1.275	1.419	0.1266	0.2693	0.2693	0.1752	0.1790	0.3826
0.8	1.622	1.430	0.1353	0.1901	0.1901	0.1930	0.1963	0.4868
0.9	2.054	1.443	0.1461	0.1003	0.1003	0.2066	0.2087	0.6164
1.0	2.590	1.459	0.1595	0.0000	0.0000	0.2129	0.2129	0.7770

Introducing the criterion

$$K_6 = (\varrho_A S_A + \varrho_K S_K) / R_D \quad (59)$$

we obtain the expression for the local current density

$$i_r = K_1 / \{K_2 F_2 + K_6 + F_3 [1 + 1.5K_3 (1 - \int_0^{y_r} i_r dy_r)]\}, \quad (60)$$

by which Eq. (45) is replaced. If $i_r \approx 1$, then $F_2 \approx F_3 \approx 1$ and the integral in Eq. (60) is approximately equal to y_r , so that Eq. (60) simplifies to

$$i_r = K_1 / (1 + K_2 + K_6 + 1.5K_3 - 1.5K_3 y_r). \quad (61)$$

After introducing this result into Eq. (46) the integration can be performed analytically and the criterion K_1 can be expressed as function of K_2 , K_3 and K_6 :

$$K_1 = 1.5K_3 / \ln[(1 + K_2 + K_6 + 1.5K_3) / (1 + K_2 + K_6)]. \quad (62)$$

An analytical solution of Eq. (60) is possible for $F_{1A} = F_{1K} = F_2 = F_3 = 1$ yielding the following expressions for i_r and K_1 :

$$i_r = K_1 [(K_1 + 0.75K_3)^2 - 3K_1 K_3 y_r]^{-1/2} \quad (63)$$

$$K_1 = 1 + K_2 + 0.75K_3 + K_6. \quad (64)$$

Calculation of the Distribution of Voltage and Local Current Densities in an Electrolyzer for Production of Chlorine from Waste Hydrochloric Acid

From the derived equations, we calculated the terminal voltage and the distribution of voltage and current densities for a monopolar diaphragm electrolyzer with current leads at the top and at the bottom, and for a bipolar electrolyzer using the technological data published by Gallone and Messner¹³. These authors studied a bipolar electrolyzer of the type de Nora 260 D - 50 C for chlorine production from waste hydrochloric acid. Our calculations were performed on a type NCR 4100 digital computer. To judge the applicability of the simplifications used in the solution of Eqs (45) and (46), we chose two alternatives for calculating the terminal voltage and the distribution of voltage and current densities along the height of the electrolyzer. First, numerical integration of Eq. (46) with (45), (52) or (60) by the Runge-Kutta-Merson method with the use of all corrections defined by Eqs (26), (37) and (44), and numerical solution of the integrals in calculating all parameters.

Second, solution of Eq. (56) or (61) obtained by analytical integration with the use of the mentioned simplifications in calculating all desired values. The necessary data are given in the List of symbols and the results are presented in Tables I and II.

Further calculations were performed for one cell of a so-called „ideal” bipolar electrolyzer of the above-mentioned type. The term “ideal” denotes an electrolyzer whose all cells are loaded with the total current I_T so that the currents in other circuits are zero. The corresponding results are presented in Table III.

The results illustrate clearly the influence of the construction of the electrolyzer. In the monopolar arrangement (Table I), the voltage losses in such large graphite electrodes are intolerably high. It follows from a graphical representation of the

TABLE II
Numerical Solution for Monopolar Electrolyzer

J_r	i_r	ε_A	$-\varepsilon_K$	U_A	U_K	U_{MA}	U_{MK}	U_D
Current lead at the top; terminal voltage 2.825 V								
0.0	1.443	1.422	0.1289	0.0000	0.0000	0.4121	0.4290	0.4328
0.1	1.327	1.420	0.1268	0.0982	0.0982	0.3355	0.3487	0.3981
0.2	1.217	1.417	0.1247	0.1823	0.1823	0.2717	0.2819	0.3651
0.3	1.115	1.414	0.1225	0.2536	0.2536	0.2194	0.2271	0.3346
0.4	1.023	1.412	0.1203	0.3130	0.3130	0.1772	0.1828	0.3070
0.5	0.943	1.409	0.1183	0.3616	0.3616	0.1436	0.1477	0.2830
0.6	0.877	1.407	0.1165	0.4002	0.4002	0.1175	0.1203	0.2633
0.7	0.8283	1.405	0.1151	0.4295	0.4295	0.0977	0.0995	0.2485
0.8	0.7984	1.404	0.1141	0.4500	0.4500	0.0830	0.0841	0.2395
0.9	0.7905	1.404	0.1139	0.4621	0.4621	0.0727	0.0731	0.2372
1.0	0.8064	1.405	0.1144	0.4658	0.4658	0.0663	0.0663	0.2419
Current lead at the bottom; terminal voltage 2.722 V								
0.0	0.496	1.390	0.1022	0.3987	0.3987	0.4445	0.4801	0.1489
0.1	0.523	1.391	0.1036	0.3923	0.3923	0.4327	0.4667	0.1569
0.2	0.563	1.394	0.1054	0.3810	0.3810	0.4262	0.4591	0.1689
0.3	0.618	1.396	0.1078	0.3645	0.3645	0.4238	0.4558	0.1856
0.4	0.695	1.400	0.1107	0.3419	0.3419	0.4237	0.4549	0.2086
0.5	0.799	1.404	0.1142	0.3124	0.3124	0.4235	0.4234	0.2399
0.6	0.942	1.409	0.1183	0.2748	0.2748	0.4192	0.4472	0.2826
0.7	1.139	1.415	0.1230	0.2274	0.2274	0.4049	0.4295	0.3419
0.8	1.421	1.422	0.1286	0.1681	0.1681	0.3714	0.3905	0.4265
0.9	1.838	1.430	0.1350	0.0938	0.0938	0.3068	0.3173	0.5514
1.0	2.459	1.438	0.1423	0.0000	0.0000	0.2021	0.2021	0.7378

dependence of the local current density on the electrode height that the current density in the upper part of the electrolyzer is about twice as large as that in the lower part. This fact would have an undesirable consequence in an unequal corrosion of the graphite electrodes. The analytical solution of Eq. (46) with the above-mentioned simplifying assumptions gives a terminal voltage higher by up to 100 mV and a more unequal distribution of local current densities than the numerical solution (Figs 2 and 3).

The voltage distribution in a bipolar electrolyzer (Table III) corresponds approximately to a single cell of the type de Nora 260 D - 50 C electrolyzer. The distribution of local current densities (Fig. 3) has an inverse character as compared with the

TABLE III
Solution for Bipolar Electrolyzer

y_r	i_r	ε_A	$-\varepsilon_K$	U_A	U_K	U_{MA}	U_{MK}	U_D
Analytical solution; terminal voltage 2.167 V								
0.0	0.770	1.404	0.1140	0.0001	0.0001	0.2050	0.2128	0.2312
0.1	0.804	1.405	0.1149	0.0001	0.0001	0.1992	0.2065	0.2414
0.2	0.841	1.406	0.1158	0.0002	0.0002	0.1929	0.1997	0.2524
0.3	0.881	1.407	0.1168	0.0002	0.0002	0.1860	0.1922	0.2646
0.4	0.926	1.409	0.1179	0.0002	0.0002	0.1784	0.1839	0.2780
0.5	0.975	1.410	0.1192	0.0002	0.0002	0.1699	0.1748	0.2928
0.6	1.031	1.412	0.1205	0.0002	0.0002	0.1605	0.1647	0.3093
0.7	1.092	1.414	0.1221	0.0002	0.0002	0.1500	0.1533	0.3277
0.8	1.162	1.416	0.1238	0.0002	0.0002	0.1382	0.1405	0.3485
0.9	1.240	1.418	0.1258	0.0002	0.0002	0.1247	0.1260	0.3721
1.0	1.330	1.421	0.1280	0.0002	0.0002	0.1093	0.1093	0.3991
Numerical solution; terminal voltage 2.183 V								
0.0	0.756	1.403	0.1128	0.0001	0.0001	0.2160	0.2249	0.2268
0.1	0.788	1.404	0.1138	0.0001	0.0001	0.2101	0.2185	0.2367
0.2	0.825	1.405	0.1150	0.0001	0.0001	0.2036	0.2115	0.2447
0.3	0.866	1.407	0.1162	0.0002	0.0002	0.1963	0.2037	0.2600
0.4	0.913	1.408	0.1175	0.0002	0.0002	0.1881	0.1949	0.2741
0.5	0.967	1.410	0.1189	0.0002	0.0002	0.1789	0.1849	0.2902
0.6	1.029	1.412	0.1205	0.0002	0.0002	0.1683	0.1734	0.3088
0.7	1.101	1.414	0.1222	0.0002	0.0002	0.1562	0.1602	0.3303
0.8	1.183	1.416	0.1240	0.0002	0.0002	0.1425	0.1452	0.3550
0.9	1.275	1.418	0.1258	0.0002	0.0002	0.1274	0.1287	0.3824
1.0	1.367	1.421	0.1276	0.0002	0.0002	0.1123	0.1123	0.4100

monopolar arrangement, *i.e.* the maximum current density is in the lower part of the electrolyzer where the volume concentration of the gaseous phase in the electrolyte is least. The analytical solution of Eq. (60) is accurate enough since the difference in the terminal voltages calculated by numerical and analytical integrations is only 10 mV.

A survey of terminal voltages of the electrolyzer for various positions of current leads, other conditions being equal, is given in Table IV. From this the advantage of the bipolar electrolyzer is obvious.

TABLE IV
Terminal Voltages for Various Cases

Electrolyzer type	Current lead	Solution	U , V
monopolar	at the top	analytical	2.917
monopolar	at the bottom	analytical	2.821
monopolar	at the top	numerical	2.825
monopolar	at the bottom	numerical	2.722
bipolar	—	analytical	2.167
bipolar	—	numerical	2.183
De Nora ¹³ , bip.	measured value		2.450
De Nora ¹³ , bip.	without voltage drop in graphite electrode junctions		2.200

From the comparison of the voltage loss in graphite electrodes for a bipolar electrolyzer with published data¹³ we find that the latter include voltage losses in junctions of the graphite electrodes. The voltage losses in junctions represent a substantial increment to the terminal voltage of the electrolyzer, their value being *e.g.* about 250 mV at a current density of 0.2 A/cm². We therefore assume that the terminal voltage of industrial bipolar electrolyzers for the decomposition of hydrochloric acid can be further lowered if graphite electrode junctions of low resistance are used.

APPENDIX

Derivation of the correction F_3 : After Meredith and Tobias¹¹, the specific resistance of the heterogeneous anolyte-gas mixture can be expressed as

$$\varrho_{MA} = \varrho_{EA}(4 + \alpha_A)(4 - \alpha_A)/8(2 - \alpha_A)(1 - \alpha_A). \quad (A1)$$

Eq. (A1) gives analogously to (18) the dependence of ϱ_{MA} on α_A and ϱ_{EA} . If this expression is introduced into (16), and an analogous expression into (17), equations are obtained for the calculation of voltage losses in the anolyte and catholyte, analogous to (29) and (30):

$$U_{MA} = i\varrho_{EA}d_A(4 + \alpha_A)(4 - \alpha_A)/8(2 - \alpha_A)(1 - \alpha_A), \quad (A2)$$

$$U_{MK} = i\varrho_{EK}d_K(4 + \alpha_K)(4 - \alpha_K)/8(2 - \alpha_K)(1 - \alpha_K). \quad (A3)$$

The total voltage loss in the anolyte, catholyte and diaphragm is given by the sum of Eqs (A2), (A3) and (12):

$$U_D + U_{MA} + U_{MK} = i[d_D\varrho_D r_D + \varrho_{EA}d_A(4 + \alpha_A)(4 - \alpha_A)/8(2 - \alpha_A)(1 - \alpha_A) + \varrho_{EK}d_K(4 + \alpha_K)(4 - \alpha_K)/8(2 - \alpha_K)(1 - \alpha_K)]. \quad (A4)$$

To make the equation for voltage loss in the diaphragm, anolyte and catholyte, obtained as the sum of Eqs (12), (29) and (30), formally identical with (A4), we introduce the correction F_3 defined as follows:

$$U_D + U_{MA} + U_{MK} = F_3 i R_D [1 + 1.5 K_3 (1 - \int_0^{y_r} i_r d_r)]. \quad (A5)$$

On comparing the right-hand sides of Eqs (A4) and (A5) we obtain after rearrangement Eq. (44).

LIST OF SYMBOLS

a_A, a_K	constants of Tafel equation [V] (1.46; 0.16)
a'_A, a'_K	constants defined by Eqs (33) and (34) [V]
a_j	activity of j -th ion
$a_{j,EA}, a_{j,EK}$	value of a_j in anolyte or catholyte
b_A, b_K	constants of Tafel equation [V] (0.0304; 0.025)
b'_A, b'_K	constants defined by Eqs (35) and (36) [$\Omega \text{ cm}^2$]
d_A, d_K	distance between diaphragm and anode or cathode [cm] (both 0.6)
d_D	thickness of diaphragm [cm] (0.2)
d_{GA}, d_{GK}	mean diameter of gas bubbles in anolyte or catholyte [cm] (both 0.02)
F	Faraday constant
$F_1 - F_3$	corrections defined by Eqs (26), (37), (44)
g	acceleration of gravity [cm/s^2]
i	local current density [A/cm^2]
i_p	mean current density [A/cm^2] (0.2)
i_r	relative current density
I_T	total current flowing through electrolyzer [A]
$K_1 - K_6$	criteria defined by Eqs (39)–(42), (49) and (59)

K_{3A}, K_{3K}	criteria defined by Eqs (28)–(30)
L	height of electrode [cm] (162.5)
n_A, n_K	number of electrons in anodic or cathodic process (both 2)
P_D	atmospheric pressure [atm] (1)
P_s	water vapour tension above electrolyte at $T^\circ\text{K}$ [atm] (0.323)
r_D	ratio of specific resistance of diaphragm soaked with electrolyte to specific resistance of electrolyte (10.95)
R	gas constant [$\text{cm}^3\text{atm/mol grad}$]
R_D	quantity defined by Eq. (43)
Re_{GA}, Re_{GK}	Reynolds number of bubbles in anolyte or catholyte
s_A, s_K	specific gravity of anolyte and catholyte [g/cm^3] (both 1.1)
S_A, S_K	thickness of anode or cathode [cm] (both 3 for monopolar and both 1.5 for bipolar)
t_j	Hittorf transference number of j -th ion
T	absolute temperature [$^\circ\text{K}$] (353)
U	voltage on electrolyzer terminals [V]
U_A, U_K, U_D	voltage losses in anode, cathode and diaphragm [V]
U_{MA}, U_{MK}	voltage losses in anolyte and catholyte in presence of gaseous phase [V]
U_{dif}	diffusion potential in diaphragm [V]
v_{EA}, v_{EK}	linear velocity of flow of anolyte or catholyte [cm/s]
v_{GA}, v_{GK}	linear velocity of gas flow in anode or cathode space [cm/s]
v_{RA}, v_{RK}	velocity of average gas bubbles in quiet anolyte or catholyte caused by buoyancy [cm/s]
V_{EA}, V_{EK}	volume rate of flow of anolyte or catholyte [cm^3/s] (both 720)
V_{GA}, V_{GK}	volume rate of flow of gas in anode or cathode space [cm^3/s]
w	electrode width [cm] (160)
x	distance from origin parallel to x -axis (cm)
x_l	distance of diaphragm from origin parallel to x -axis [cm]
y	distance from origin parallel to y -axis [cm]
y_r	relative distance equal to y/L
z	distance from origin parallel to z -axis [cm]
z_j	charge of j -th ion
α_A, α_K	volume fraction of gas in anode or cathode space
$\alpha_{A,max}, \alpha_{K,max}$	volume fraction of gas in anode or cathode space at $y_r = 0$
$\varepsilon_A, \varepsilon_K$	potential of anode or cathode [V]
η_A, η_K	current efficiency for anode or cathode gas formation (0.95; 1)
ν_{EA}, ν_{EK}	viscosity of anolyte or catholyte [cm^2/s] (both 0.0045)
ϱ_A, ϱ_K	specific resistance of anode or cathode [$\Omega\text{ cm}$] (both 0.0006)
$\varrho_{EA}, \varrho_{EK}$	specific resistance of anolyte or catholyte [$\Omega\text{ cm}$] (both 0.685)
$\varrho_{MA}, \varrho_{MK}$	specific resistance of gas-anolyte or gas-catholyte mixture [$\Omega\text{ cm}$]
ϱ	specific resistance of diaphragm defined by Eq. (11)
ϱ_D	mean specific resistance of diaphragm defined by Eq. (13)
φ	unit function; $\varphi = 1$ for current leads at the top, $\varphi = 0$ for current leads at the bottom of electrolyzer
χ	relative length defined by Eq. (10)

Values given in parentheses were used as input data in numerical calculations.

REFERENCES

1. McMullin R. B.: *Electrochem. Technol.* 1, 5 (1963).
2. Genin L. S., Krongauz E. L.: *Chim. promyšlennost* 2, 116 (1961).
3. Tobias Ch. W.: *J. Electrochem. Soc.* 106, 833 (1959).
4. Tobias Ch. W., Wijsman E.: *J. Electrochem. Soc.* 101, 459 (1953).
5. Eisenberg M.: *Advances in Electrochemistry and Electrochemical Engineering*, Vol. 2, p. 235. Interscience, New York 1962.
6. Roušar I., Regner A., Cezner V.: *This Journal* 31, 4193 (1966).
7. Roušar I., Cezner V.: *This Journal* 32, 1137 (1967).
8. Roušar I., Cezner V., Hostomský J.: *This Journal* 33, 808 (1968).
9. Roušar I.: *Thesis*. Institute of Chemical Technology, Prague 1968.
10. Regner A.: *Technická elektrochemie*, Part 1, p. 145. Academia, Prague 1967.
11. Meredith R. E., Tobias C. W.: *Advances in Electrochemistry and Electrochemical Engineering*, Vol. 2, p. 15. Interscience, New York 1962.
12. Zuber N.: *Chem. Eng. Sci.* 19, 897 (1964).
13. Gallone P., Messner G.: *Electrochem. Technol.* 3, 321 (1965).

Translated by K. Míčka.