

THEORETICAL EQUATIONS FOR THE DECOMPOSITION RATE IN A HORIZONTAL AMALGAM DECOMPOSER*

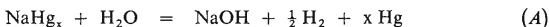
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Theoretical equations for the rate of decomposition of the sodium amalgam in a horizontal decomposer were derived. The calculation is based on the solution of the Laplace equation for the electric potential in the electrolyte in a short-circuited amalgam-hydrogen cell representing an element of the decomposer. The obtained equations enable to calculate the decomposition rate as a function of the temperature, concentrations of the amalgam and soda lye, rate of flow of the amalgam, Tafel constants for cathodic hydrogen evolution, the contact resistance between the anode and cathode of the decomposition cell, and the dimensions of the latter.

The decomposition of the sodium amalgam with water



is one of the fundamental reactions in the production of chlorine and soda lye by the amalgam method. The decomposition proceeds in horizontal troughs or in towers with a graphite bed¹. Our aim was to derive theoretical equations for the kinetics of amalgam decomposition in a horizontal decomposer. The basic ideas about the elementary decomposition process can be applied also to the amalgam decomposition in tower decomposers².

A horizontal amalgam decomposer is normally constructed as a rectangular trough with a slight slope (Fig. 1). On its bottom there are grids assembled from graphite plates whose side walls form with the bottom of the trough narrow rectangular channels for a countercurrent flow of the amalgam and electrolyte. The decomposer functions as a short-circuited galvanic cell with an amalgam anode and graphite cathode. The positive electric current flows from the amalgam through the electrolyte into the graphite and returns through the amalgam-graphite interface into the amalgam. The current distribution on the cell electrodes is unequal; the local current densities are such that along every closed line of current the electromotive force of the cell is compensated by the sum of the anodic and cathodic overvoltage and the ohmic potential drop.

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In the available literature^{3,4} the current distribution in a horizontal decomposer was calculated by solving the Laplace equation for the electric potential in the electrolyte of a decomposer element. Hine and coworkers³ assume that both the anode and the cathode of a decomposer cell operate at their reversible potentials, *i.e.*, they neglect the polarization of the electrodes. The derived relations give a rough picture of the current distribution in the decomposer, however they lead to unrealistic (infinite) total decomposition currents so that they cannot be used to calculate the decomposition rate. Allgulin⁴ took the polarization of the graphite cathode into consideration, however he neglected (in contrast to the present work) the polarization of the amalgam anode, the increase of the specific resistance of the electrolyte by the presence of hydrogen bubbles and the contact resistance between the amalgam and the graphite.

THEORETICAL

Model Decomposer

We shall derive relations for the decomposition rate in a model horizontal decomposer with a usual arrangement of the graphite grid (Fig. 1). We define the decomposition rate as the absolute value of the electric current, I , entering the graphite per unit length of the three-phase boundary amalgam-graphite-electrolyte. Owing to changing concentration and temperature along the decomposer, the decomposition rate varies accordingly. To calculate the local decomposition rate, we shall consider one channel of the decomposer of width $2a$ and differential length dz (Figs 1 and 2). Because of obvious symmetry, we shall further consider only one half of the channel (see sections AA' and BB') of width a , length dz , and height of the electrolyte level b , and we shall denote it as the decomposer element. The local decomposition rate in this element will be denoted as $|I|$ (the cathodic current, I , is considered negative). In deriving equations for $|I|$, we make the following assumptions:

- 1) Constant temperature and concentration of NaOH in the element.

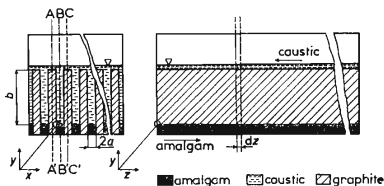


FIG. 1

Scheme of Transversal and Longitudinal Cross Section of Horizontal Decomposer

Sections AA' and BB' delimit one channel of the decomposer of half width a ; dz denotes length of decomposer element, b height of the graphite electrode wetted by the soda lye.

2) An effective mean value of the specific resistance ϱ_M of the mixture of the electrolyte and hydrogen bubbles in the element can be used in calculating the decomposition rate. This mean value depends on the decomposition rate, the geometry of the element, and the rate of the amalgam flow.

3) The overvoltage for the evolution of hydrogen on graphite obeys the Tafel equation, which we can write in the form

$$\eta_{x=0} = a_K - b'_K \ln \left| \left(\frac{1}{\varrho_M} \right) \left(\frac{\partial \eta}{\partial x} \right)_{x=0} \right|. \quad (1)$$

(In contrast to the electrode overvoltage $\eta_{x=0}$, the total overvoltage η is defined as the sum of $\eta_{x=0}$ and the ohmic voltage drop along the current line joining a given point in the electrolyte with the graphite surface.) Since the natural rather than decadic logarithm is used, the coefficient b'_K is distinguished by a prime.

4) The ohmic voltage drops in the graphite and in the amalgam are negligible since the corresponding specific resistances are at least by three orders of magnitude smaller than that of the concentrated hydroxide; the contact resistance on the amalgam-graphite interface, however, can be significant.

5) The concentration of sodium in the amalgam at the amalgam-electrolyte interface in the element is constant and generally different from that in the bulk. (Owing to an unequal distribution of the anodic current density, the surface concentration of the amalgam changes in reality along the x axis. The resulting gradient of the interfacial tension causes a surface streaming of the amalgam⁵⁻⁷ which we cannot express quantitatively, but which obviously suppresses the concentration differences at the amalgam surface; this is in support of the mentioned assumption).

6) The amalgam level in the decomposer element is everywhere horizontal and is at right angle with the graphite channel walls. The effects of the meniscus at the channel wall and of an eventual oscillatory motion of the amalgam surface are neglected.

7) The electric potential gradient along the z axis is negligible against the potential gradients along the x and y axes.

8) The evolution of hydrogen on the amalgam surface is owing to a high hydrogen overvoltage negligible against that on the graphite.

Surface Concentration of Sodium in the Amalgam

The overvoltage on the amalgam anode in the decomposer element is given by an insufficiently rapid transport of sodium from the bulk to the amalgam-electrolyte interface^{8,9}. In deriving a relation between the anodic current density and the

concentration at the interface, we define in the common way the thickness of the boundary layer: the convective transport of sodium from the bulk of the amalgam to the interface is equivalent to a diffusion-controlled flux through a stagnant amalgam layer of thickness δ . The stationary diffusion of sodium along the y axis is given as¹⁰

$$i_A = -D_{Na} F_{C_{Na}} \partial \ln a_{Na} / \partial y, \quad (2)$$

where the activity of sodium, a_{Na} , depends on the absolute temperature, T , and on the molar fraction of sodium, X_{Na} , according to¹¹

$$\ln(a_{Na}/X_{Na}) = -21887/T^{1.16} + BX_{Na} + CX_{Na}^2, \quad (3)$$

with $B = 493.4T^{0.46}$ and $C = 33.8 - 0.062T$. The volume concentration of sodium, c_{Na} , can be expressed by the mole fraction X_{Na} ; the density of the amalgam, s_{am} , is given by¹²

$$1/s_{am} = 1/s_{Hg} + k_1 N_{Na}, \quad (4)$$

where N_{Na} denotes concentration of sodium in weight percent and $k_1 = 5.6321 \cdot 10^{-3} + 4.5662 \cdot 10^{-6}(t - 20)$. Eq. (2) then takes the form

$$(i_A M_{Hg} / D_{Na} F_{S_{Hg}}) dy = -[(1 + BX_{Na} + 2CX_{Na}^2)/(1 - k_2 X_{Na})] dX_{Na}, \quad (5)$$

where

$$k_2 = 1 - (M_{Na}/M_{Hg})(1 + 100k_1 s_{Hg}) \quad (6)$$

depends only on the temperature.

Eq. (5) can be integrated from $y = 0$ to $y = -\delta$ (the negative sign is due to the orientation of the y axis); the amalgam concentration in the diffusion layer changes from $X_{Na,s}$ at the interface to $X_{Na,b}$ in the bulk. We use the approximate expression $\ln(1+x) \approx x - x^2/2$ for $x \ll 1$ and neglect k_2 against B (for example, at 80°C is $B = 33.2$ and $k_2 = 0.021$). Thus, we obtain

$$i_A = (D_{Na} F_{S_{Hg}} / M_{Hg} \delta) (1 + \frac{1}{2} B (X_{Na,b} + X_{Na,s})) (X_{Na,b} - X_{Na,s}). \quad (7)$$

In view of the turbulent flow of the amalgam in the decomposer we assume that the thickness of the diffusion layer δ is given by

$$a/\delta = k_A (q/\nu)^{0.8} \equiv k_A \text{Re}^{0.8}, \quad (8)$$

where k_A is an empirical constant, Re denotes Reynolds number for the amalgam flow and ν kinematic viscosity of the amalgam; its rate of flow (in $\text{cm}^3/\text{cm s}$) refers

to a unit width of the decomposer channel. By combining Eqs (7) and (8) and substituting the mean value of $|I|/a$ for the anodic current density i_A (compare the 5th assumption) we obtain the resulting equation for the molar fraction of sodium at the amalgam-electrolyte interface:

$$X_{\text{Na},s} = -1/B + B^{-1}[1 - 2B(|I| M_{\text{Hg}}/D_{\text{Na}} F k_{\text{A}} S_{\text{Hg}} \text{Re}^{0.8} - X_{\text{Na},b} - BX_{\text{Na},b}^2/2)]^{1/2}. \quad (9)$$

The values of the diffusion coefficient¹⁴ D_{Na} are $7.4 \cdot 10^{-6} \text{ cm}^2/\text{s}$ at 9.6°C and $8.6 \cdot 10^{-6} \text{ cm}^2/\text{s}$ at 25°C , whence with the aid of the Stokes-Einstein equation the values of D_{Na} at $70-90^\circ\text{C}$ were estimated and the product $D_{\text{Na}} S_{\text{Hg}}$ expressed by the empirical equation

$$D_{\text{Na}} S_{\text{Hg}} = 1.575 \cdot 10^{-4} + 8.5 \cdot 10^{-7}(t - 80). \quad (10)$$

Specific Resistance of the Bubble-Electrolyte Mixture

If we denote the volume fraction of hydrogen in the hydrogen emulsion as f_B , the specific resistance of the emulsion is given by the Bruggeman equation¹⁶

$$\varrho_M = \varrho_E(1 - f_B)^{-1.5}. \quad (11)$$

No data are available concerning the relative volume of hydrogen under the conditions corresponding to the amalgam decomposition in a horizontal decomposer. Therefore, we propose the following empirical equation for the calculation of f_B in the decomposer element:

$$f_B = (k_B |I|/a \text{Re}) / (1 + k_B |I|/a \text{Re}), \quad (12)$$

where k_B is a constant. The physical meaning of this equation is as follows: At low decomposition rates, the volume fraction of hydrogen is proportional to the mean current density $|I|/a$ (we assume a constant upward velocity of the hydrogen bubbles); at high decomposition rates, the value of f_B approaches 1. The dependence on the Reynolds number Re is elucidated in the following way: A major portion of the electric current flowing between the amalgam and graphite in the decomposer element passes through the electrolyte close to the amalgam-electrolyte-graphite boundary. The decomposition rate hence depends on the specific resistance of the electrolyte near to the mentioned three-phase boundary. With increasing rate of flow of the amalgam, the rate of the turbulent flow of the electrolyte caused by the flowing amalgam increases, the hydrogen bubbles are more effectively dissipated over the whole volume of the decomposer, and the effective mean value of ϱ_M considered in the calculation decreases.

On introducing Eq. (12) into (11) we obtain

$$\varrho_M = \varrho_E(1 + k_B|I|/a \operatorname{Re})^{1.5}. \quad (13)$$

Current Density Distribution and Decomposition Rate

The current I entering the graphite per unit length of the three-phase boundary is given by

$$I = (1/\varrho_M) \int_0^b (\partial\eta/\partial x)_{x=0} dy. \quad (14)$$

The local current density on the graphite, $(1/\varrho_M)(\partial\eta/\partial x)_{x=0}$, is determined by the electrode overvoltage, $\eta_{x=0}$. The distribution of the overvoltage η in the decomposer element is with respect to the assumptions 2) and 7) given by the two-dimensional Laplace equation

$$\partial^2\eta/\partial x^2 + \partial^2\eta/\partial y^2 = 0. \quad (15)$$

The boundary conditions are: a) On the graphite surface, the overvoltage $\eta_{x=0}$ is given by the Tafel equation (1). b) The overvoltage on the amalgam surface can be determined from the voltage balance for a closed current line in the decomposer element:

$$-\eta_{y=0} = E - (RT/F) \ln(a_{Na,b}/a_{Na,s}) - |I| \varrho_{AG}, \quad (16)$$

where E is the electromotive force of the decomposer element at the given temperature, bulk concentrations of soda lye and amalgam, and ϱ_{AG} is the contact resistance between amalgam and graphite per unit length of the three-phase boundary. The absolute value of $\eta_{y=0}$ is hence equal to the electromotive force of the decomposer element minus the overvoltage on the amalgam and minus the ohmic voltage drop on the amalgam-graphite contact resistance.

c) No current passes through the planes $x = a$ and $y = b$ (Fig. 2), hence

$$x = a : \partial\eta/\partial x = 0; \quad y = b : \partial\eta/\partial y = 0. \quad (17), (18)$$

We introduce the following dimensionless parameters:

$$X = x/a, \quad Y = y/a, \quad \phi = (\eta - \eta_{x=0})/b'_K. \quad (19)-(21)$$

Eqs (1), (15)–(18) then take the form

$$\partial^2\phi/\partial X^2 + \partial^2\phi/\partial Y^2 = 0, \quad X = 0 : \partial\phi/\partial X = -Z \exp(-\phi), \quad (22), (23)$$

$$Y = 0 : \phi = 0, \quad X = 1 : \partial\phi/\partial X = 0, \quad Y = Y_R : \partial\phi/\partial Y = 0, \quad (24)-(26)$$

where

$$Y_R = b/a, \quad Z = (i_0 q_M a / b'_K) \exp(-\eta_{y=0} / b'_K) \quad (27), (28)$$

are dimensionless parameters and i_0 is the exchange current density for the evolution of hydrogen on graphite; $\ln i_0 = a_K / b'_K$. Eq. (14) for the decomposition rate $|I|$, which is the main goal of the calculation, is transformed as

$$F_1 = - \int_0^{Y_R} (\partial\phi/\partial X)_{X=0} dY, \quad (29)$$

where the symbol F_1 stands for $|I| q_M / b'_K$. An analytical solution of the Laplace equation (22) is made impossible by the exponential boundary condition (23). In solving the system of equations (22)–(26) we therefore used a numerical method based on an approximation of the boundary condition (23) by a polynomial dependence of $(\partial\phi/\partial X)_{X=0}$ on Y . The mentioned system can then be solved analytically by the method of separation of variables; the constants of the polynomial dependence can be determined numerically so that in chosen points on the Y axis the original boundary condition (23) is fulfilled with a chosen accuracy. (This calculation method, which was used for $0.1 \leq Z \leq 200$, is a combination of the separation of variables and finite differences methods.) For $Z > 200$, the dependence of F_1 on Z and Y_R was derived from the data of ref.⁴ which contains calculated decomposition rates for various combinations of E and q_E ; the parameter Y_R was equal to 5 or 10. Since in the mentioned work the polarization of the amalgam anode,

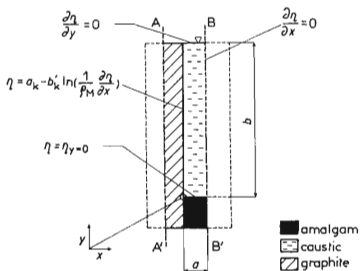


FIG. 2

Decomposer Element and Boundary Conditions for Eq. (15)
Sections AA' and BB' correspond to the sections in Fig. 1.

the presence of the gaseous phase in the electrolyte, and the voltage loss on the contact resistance were not considered, the equalities $\eta_{y=0} = -E$ and $q_E = q_M$ were obeyed; the Laplace equation for the electric potential was solved there numerically by the method of finite differences.

RESULTS AND DISCUSSION

The numerical results are summarized in Table I. According to Eqs (22)–(26) and (29), the dimensionless decomposition rate F_1 depends only on Z and Y_R ; with a given geometry of the decomposer channel ($Y_R = \text{const.}$), F_1 is a function of a single parameter, Z . For further calculations¹³, the dependence of F_1 on Z for $Y_R = 10$ was approximated by the empirical relationship

$$\log F_1 = 0.12146 + 0.48297 \log Z - 0.048577 \log^2 Z + 2.1154 \cdot 10^{-3} \log^3 Z \quad (0.1 \leq Z \leq 1.5 \cdot 10^5) \quad (30)$$

with a maximum error of $\pm 2\%$ with respect to F_1 . From Table I it follows that for $Z \geq 70$ (and $Y_R \geq 5$) F_1 does not depend any more on Y_R (the ratio of the height of the graphite wetted by the soda lye to the half-width of the gap between the plates of the graphite grid). With increasing value of Z namely the current distribution

TABLE I
Dependence of F_1 on Z and Y_R

Z	F_1			Z	F_1 ($Y_R \geq 5$)
	$Y_R = 5$	$Y_R = 10$	$Y_R = 20$		
0.1	0.312	0.388	0.424	200	10.0
0.2	0.497	0.576	0.609	400	12.2
0.4	0.759	0.834	0.862	700	14.2
0.7	1.04	1.11	1.13	1 000	15.5
1	1.25	1.32	1.34	2 000	18.3
2	1.77	1.82	1.84	4 000	21.4
4	2.43	2.48	2.49	7 000	24.0
7	3.09	3.13	3.15	10 000	25.8
10	3.58	3.61	3.62	20 000	29.4
20	4.68	4.70	4.70	40 000	33.2
40	6.03	6.05	6.05	70 000	36.5
70	7.34	7.34	7.34	100 000	38.6
100	8.20	8.20	8.20	200 000	42.8

for the evolution of hydrogen becomes more unequal, the current densities at the upper border of the graphite plates becoming negligible against the current densities at the three-phase boundary. An eventual increase of the height of graphite wetted by the soda lye (larger Y_R) then does not result in a higher decomposition rate $|I|$ (or its dimensionless form F_1). Therefore also Eq. (30) holds for any $Y_R \geq 5$ as long as $Z \geq 70$ (with common decomposer types, Y_R is always larger than 5 and also the condition $Z \geq 70$ is almost always fulfilled).

In the calculation of the decomposition rate, the input parameters are the temperature, the concentrations of the soda lye and the amalgam, Tafel constants for the cathodic evolution of hydrogen, the rate of the amalgam flow, the geometric parameters of the grid a and b , the constants k_A and k_B in Eqs (9) and (13), and the contact resistance between the amalgam and the graphite. Since the anodic overvoltage on the amalgam and the specific resistance of the bubble-electrolyte emulsion depend on the decomposition rate, the calculation must be carried out iteratively as follows:

1) For a given temperature and given concentrations of the amalgam (in the bulk) and soda lye we calculate the electromotive force of the amalgam-hydrogen cell¹⁷, the activity of sodium in the bulk of the amalgam from Eq. (3), the kinematic viscosity of the amalgam^{12,19} and the specific resistance of the soda lye¹⁸.

2) We choose a first approximation of the decomposition rate $|I|$ and thus the mean current density $i_A = |I|/a$ on the amalgam surface. From Eqs (3), (9), and (16) follow the surface concentration of the amalgam $X_{Na,s}$, and the overvoltage $\eta_{y=0}$.

3) From Eqs (13) and (28) we calculate ρ_M and Z . From Eq. (30) or Table I we obtain the value of F_1 , which gives the decomposition rate $|I|$. If there is no satisfactory agreement between the chosen and calculated value of $|I|$, we repeat the calculation with a new approximation of $|I|$ starting from the step 2). After 7–10 iterations by the regula falsi method the value of $|I|$ could be determined to 6 valid digits.

As an example, the dependences of the decomposition rate on some technically important parameters were calculated in the described way. The constants $k_A = 0.579$, $k_B = 8.85 \cdot 10^3 \text{ cm}^2/\text{A}$ were taken from ref.¹³. In Fig. 3 is shown the dependence of the decomposition rate on the amalgam concentration. At low concentrations, the decomposition of the amalgam proceeds as a reaction of the first order with respect to sodium since the anodic current in the decomposer is equal to the corresponding limiting current and the rate-controlling step in the decomposition is the transport of sodium from the bulk of the amalgam to its surface. At a higher concentration of sodium, the simultaneous rate-controlling steps are the evolution of hydrogen on graphite and the passage of electric current through the electrolyte. The influence of the amalgam concentration is then manifested only indirectly through the electromotive force of the decomposition cell and the kinematic viscosity of the amalgam. Under these conditions, the exponent n in the empirical equation $|I| = \text{const. } N_{Na}^n$ (the formal reaction order with respect to sodium) is considerably diminished.

In Fig. 4 is shown the dependence of the decomposition rate on the rate of amalgam flow. At low concentrations of sodium, accelerating the rate of flow leads to an increase of the anodic limiting current (*i.e.*, an increase of the decomposition rate). At higher concentrations of sodium the rate of flow of the amalgam influences the decomposition rate so that at a higher rate of flow the soda lye in the decomposer element is stirred more intensively and the mean specific resistance of the bubble-

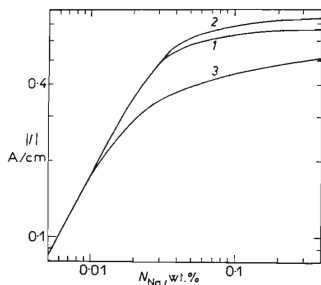


FIG. 3

Dependence of Decomposition Rate on Concentration of Na in Amalgam

$t = 80^{\circ}\text{C}$, $q = 35 \text{ cm}^3/\text{cm s}$, $a = 0.25 \text{ cm}$, $b = 2.5 \text{ cm}$, Tafel constants for graphite Elektrokohle Lichtenberg¹⁵, $\varrho_{AG} = 0.02 \Omega \cdot \text{cm}$. 1 10 weight %; 2 20 weight %; 3 40 weight % NaOH.

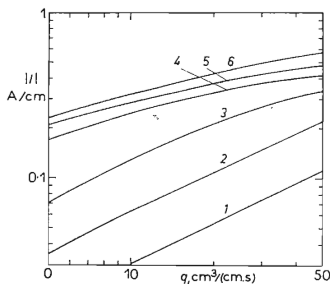


FIG. 4

Dependence of Decomposition Rate on Rate of Flow of Amalgam

40 weight % NaOH; the parameter values are the same as in Fig. 3. Concentration of Na (weight %): 1 0.005; 2 0.01; 3 0.02; 4 0.05; 5 0.1; 6 0.5.

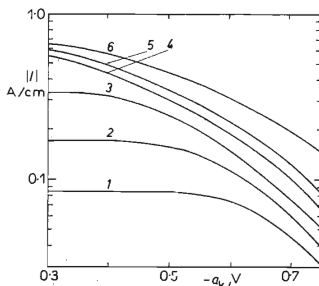


FIG. 5

Dependence of Decomposition Rate on Tafel Constant a_k

40 weight % NaOH; the parameter values are the same as in Fig. 3, curve numbers correspond to Fig. 4.

-electrolyte emulsion decreases. The decomposition rate then approaches gradually the value corresponding to the case where the specific resistance ρ_M is equal to the specific resistance ρ_E of the electrolyte without the gas phase.

The influence of the Tafel constant a_K on the decomposition rate is shown in Fig. 5. With decreasing absolute value of a_K the decomposition rate increases significantly unless the anodic limiting current is reached. For example, when a_K decreases by 250 mV, which is possible if a mixture of titanium carbide with nickel¹⁵ is substituted for the graphite, the decomposition rate at average amalgam concentrations (about 0.1 weight % Na) increases approximately by a factor of 2.

The derived theoretical relations will be used in our further work¹³ to correlate results of the measurement of the decomposition rate in a horizontal amalgam decomposer.

LIST OF SYMBOLS

a	half width of the decomposer channel, cm
a_K	constant of Tafel equation (1)
a_{Na}	activity of sodium in the amalgam
$a_{Na,b}$	and $a_{Na,s}$ values of a_{Na} in the bulk and at the surface of the amalgam
B	constant in Eq. (3) equal to $493.4/T^{0.46}$
b	height of the graphite electrode immersed in the soda lye, cm
b'_K	constant of Tafel equation (1)
C	constant in Eq. (3) equal to $33.8 - 0.062T$
c_{Na}	concentration of sodium in the amalgam, mol/cm ³
D_{Na}	diffusion coefficient of sodium in the amalgam, cm ² /s
E	electromotive force of the amalgam-hydrogen cell, V
F	Faraday's constant, 96487 C/mol
F_1	dimensionless decomposition rate equal to $ I \rho_M / b'_K$
f_B	volume fraction of hydrogen in the emulsion
I	current per unit length of the amalgam-graphite-electrolyte three-phase boundary A/cm; $ I $ gives the decomposition rate
i_A	current density for ionization of sodium on the amalgam, A/cm ²
k_A	constant in Eq. (8)
k_B	constant in Eq. (12), cm ² /A
k_1	and k_2 constants defined with Eqs (4) and (5)
M_{Na}	and M_{Hg} masses of 1 mol Na and Hg, g/mol
N_{Na}	concentration of sodium in amalgam, weight %
n	exponent in the relation $ I = \text{const. } N_{Na}^n$
q	rate of amalgam flow per unit width of decomposer channel, cm ³ /cm s
Re	Reynolds number for amalgam flow in decomposer element equal to q/ν
R	gas constant, $8.3143 \text{ J K}^{-1} \text{ mol}^{-1}$
s_{am}	and s_{Hg} densities of amalgam and mercury, g/cm ³
T	absolute temperature, K
t	Celsius temperature, °C
X_{Na}	mole fraction of sodium in amalgam
$X_{Na,b}$	and $X_{Na,s}$ values of X_{Na} in the bulk and at the surface of amalgam

X, Y	dimensionless coordinates
Y_R	dimensionless height of graphite electrode immersed in the soda lye
x, y, z	coordinates, cm
Z	dimensionless parameter defined by Eq. (28)
δ	thickness of diffusion layer for transport of sodium, cm
η	total overvoltage for cathodic hydrogen evolution, V (sum of electrode overvoltage and ohmic voltage drop in electrolyte)
ν	kinematic viscosity of amalgam, cm^2/s
ρ_{AG}	contact resistance between amalgam and graphite referred to unit length of the three-phase boundary, $\Omega \text{ cm}$
ρ_E	specific resistance of soda lye, $\Omega \text{ cm}$
ρ_M	specific resistance of hydrogen-soda lye emulsion, $\Omega \text{ cm}$
Φ	dimensionless overvoltage defined with Eq. (21)

REFERENCES

- Hund H.: Chem.-Ing.-Tech. 39, 702 (1967).
- Roušar I., Rajasekaran S., Cezner V.: J. Electrochem. Soc. 121, 336 (1974).
- Hine F., Yoshizawa S.: J. Electrochem. Soc. (Overseas Ed.) 27, E-63 (1959).
- Allgulin T.: Thesis. Royal Institute of Technology, Stockholm 1970.
- Good R. J., Givens W. G.: J. Phys. Chem. 68, 418 (1964).
- Indira K. S., Doss K. S. G.: Electrochim. Acta 12, 741 (1967).
- Paseka I., Balej J., Vondrák J., Regner A.: This Journal 31, 3859 (1966).
- Esin O., Loshkarev M., Sofiiskii K.: Zh. Fiz. Khim. 10, 132 (1937).
- Yeager E. in the book: *Fuel Cells* (W. Mitchell, jr, Ed.), p. 299. Academic Press, New York 1963.
- Dvořák J., Koryta J., Boháčková V.: *Elektrochemie*, p. 96. Academia, Prague 1966.
- Iverson M. L., Recht H. L.: J. Chem. Eng. Data 12, 262 (1967).
- Balej J., Paseka I., Vondrák J.: This Journal 28, 528 (1963).
- Hostomský J., Roušar I., Cezner V.: This Journal, in press.
- Spravochnik Khimika*, Vol. III, p. 922. Gos. Nauchno-Tech. Izd. Khim. Lit., Moscow 1962.
- Roušar I., Hostomský J., Rajasekaran S., Cezner V.: This Journal 39, 1 (1974).
- Meredith R. E., Tobias C. W.: Advan. Electrochem. Electrochem. Eng. 2, 15 (1962).
- Hostomský J., Roušar I., Cezner V.: This Journal 40, 483 (1975).
- MacMullin R. B. in the book: *Chlorine* (J. S. Sconce, Ed.), p. 177. Amer. Chem. Soc. Monograph No 154, New York 1962.
- Balej J., Paseka I., Vondrák J.: This Journal 28, 2242 (1963).

Translated by K. Micka.