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John Van Zee  
*University of South Carolina - Columbia, vanzee@engr.sc.edu*

Ralph E. White  
*University of South Carolina - Columbia, white@cec.sc.edu*

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Using Parameter Estimation Techniques with a Simple Model of a Diaphragm-Type Electrolyzer to Predict the Electrical Energy Cost for NaOH Production

John Van Zee*
Department of Chemical Engineering, University of South Carolina, Columbia, South Carolina 29208

R. E. White*
Department of Chemical Engineering, Texas A&M University, College Station, Texas 77843

ABSTRACT

Predictions of the electrical energy cost for NaOH production are determined as a function of the independent operating variables and diaphragm characterizing properties. The predictions are based on data from a statistically designed experiment, a simple model of a diaphragm-type electrolyzer, a simple model of the cell voltage losses, and parameter estimation techniques. The data were obtained over a sufficiently large range of operating conditions so that the resulting design equation may be industrially useful. The simple model of the diaphragm is based on the mass transport of the hydroxyl ion, a linear potential gradient, and is presented in terms of measurable diaphragm properties. These properties are the thickness of the diaphragm (t) and a resistivity ratio, \( \rho / \rho_0 \), where \( \rho \) is the resistivity of the diaphragm filled with electrolyte and \( \rho_0 \) is the resistivity of the electrolyte (this ratio may come to be known as the MaCullin number, \( N_{\text{M}} \)). It is shown that, according to the model of the cell, the caustic yield or current efficiency of the diaphragm cell depends on the product of \( N_{\text{M}} \) and \( t \) and not on each separately. The simple model of the cell voltage considers the diaphragm voltage drop, anode and cathode kinetics, and the bubble-filled brine-gap voltage drop. Parameter estimation techniques are used to determine the best values of the diffusion coefficient, average specific conductivity, exchange current densities, and transfer coefficients; these parameters and the simple models provide a design equation for the electrical energy cost of NaOH production using a diaphragm cell. The design equation is used to predict a minimum electrical-energy cost at a particular \( N_{\text{M}} \).

In a diaphragm-type chlorine/caustic cell (see Fig. 1), hydroxyl ions are produced at the cathode according to the electrochemical reaction

\[
\text{H}_2\text{O} + e^- \rightarrow \text{OH}^- + \frac{1}{2}\text{H}_2 \quad [1]
\]

The energy cost for the production of hydroxyl ions depends upon the diaphragm characteristics and the operating conditions of current density and percolation velocity. That is, to prevent the loss of OH\(^-\) ions due to migration and diffusion, cell electrolyte percolates through the diaphragm from the anolyte as shown in Fig. 1. This percolation rate must not be too large, however, because the concentration of OH\(^-\) in the catholyte decreases as the percolation rate increases, which leads to a larger steam requirement if the catholyte is to be concentrated to the typical 50% by weight solution. Increasing the current density increases the concentration of OH\(^-\) ions in the catholyte, but also increases the voltage drop through the diaphragm, which increases the electrical energy cost. Also, the diaphragm characteristics affect the diffusion and migration of hydroxyl ion and the voltage drop through the diaphragm. It is desirable, therefore, to have a simple model which is consistent with industrial production cells and which can be used to predict the concentration of OH\(^-\) ions in the catholyte and the diaphragm voltage drop as a function of the percolation velocity, current density, and diaphragm characterizing properties. It is also desirable to combine this simple diaphragm model with a simple model of the cell voltage losses which include the thermodynamics, kinetics, and ohmic losses so that predictions of the electrical energy cost for NaOH production can be made. (A more quantitative definition of electrical energy cost is given below in the “Energy Cost” section).

These predictions are highly dependent on the transport and kinetic parameters used in the model. Consequently, it is necessary to use a set of parameters which (i) is consistent with experimental data over a large range of operating conditions and (ii) has reasonably small confidence intervals for the parameters. Here, we use the theory of nonlinear least squares regression (1-4) to obtain a suitable set of parameters for a simple model. In this sense, we do not test various models to determine the most reasonable, but, rather, we assume that the simple model presented here is reasonable and then determine the parameters which give the “best fit” of the data. In the same sense, it is not the purpose of this paper to compare the model predictions with experimental data that were not used to obtain the parameters. [See Lee (5) for a general discussion of the use of parameter estimation in electrochemical reactor design.]

* Electrochemical Society Active Member.
Simple models of the diaphragm\(^1\) have been presented before (6-10), but none have included measurable diaphragm properties as independent variables, which is required for the determination of diaphragm-independent transport parameters by regression. Also, none of the previous works have shown the effects of these diaphragm properties and the operating conditions on the energy cost for the production of NaOH in a diaphragm-type electrolyzer. Consequently, the diaphragm characterizing properties used here will be discussed, and the previously published models will be reviewed. Then, a simple model of the diaphragm-type chlorine/caustic cell which considers OH\(^-\) ion only will be developed and discussed in terms of dimensionless groups. The model then will be compared in more detail to previously published models and then to experimental data using nonlinear regression to estimate the transport and kinetic parameters. Finally, predictions of the electrical energy cost per metric ton of NaOH will be discussed as a function of the independent diaphragm properties and operating conditions.

**Literature Review**

In a recently reported, factorially designed experiment (11), two quantities were used to characterize the diaphragm in a metal anode chlorine/NaOH electrolyzer. These two properties are the MacMullin number, \(N_M\), and the diaphragm thickness, \(t\). The MacMullin number is defined (12, 13) as follows

\[
N_M = \frac{\tau}{\varepsilon} = \frac{\rho}{\rho_s} \tag{2}
\]

where \(\rho/\rho_s\) is the ratio of the electrical resistivity of an electrolyte-saturated porous medium to the resistivity of the same thickness of electrolyte. An experimental procedure is available for measuring independently both the MacMullin number and the thickness of a diaphragm (11). It should be noted that \(N_M\) has also been referred to as the formation factor (14) and the labyrinth factor (15).

Of the simple models of the diaphragm that have been proposed (6-10), only Koh (9, 10) and Mukaibo (7) included diaphragm characterizing properties, but neither recognized that \(N_M\) can be measured directly from relatively simple experiments. Koh (9, 10) used a diaphragm characterizing parameter which was obtained from an assumed value for \(\varepsilon\) or the product \(\tau\) and a presumably measured value for \(\varepsilon\). Mukaibo (7) \(\text{[see also Hine (14, 16, 17)]}\) used the ratio of the diaphragm area to the area of the diaphragm pores, which is not measurable directly, and, hence, this ratio was an assumed quantity when the model was compared with experimental data (16). The often-used model of Stender et al. (6) does not include a parameter such as \(N_M\), but some recent modifications of this model (17, 18) have recognized the need to include diaphragm properties which are independent of the transport parameters; again, these recent modifications use assumed values for \(\varepsilon\) or \(\tau\), and therefore they cannot be used to determine the best values of the transport parameters for use with the model. Kubasov et al. (19) include the thickness of the diaphragm multiplied by a “sinuosity coefficient” as the characterizing parameter, but this coefficient was not reported as a measurable quantity.

In addition to the lack of measurable diaphragm properties, other differences exist between the previously published diaphragm models and the model presented here. For example, Gallone and Rubino (8) neglected the effect of ionic migration. Hine (14, 16, 17) does not show the difference between the solution conductivity and the effective solution conductivity in the diaphragm. Mukaibo (7) assumed that the ratio of the transference number to the concentration of hydroxyl ion is constant throughout the diaphragm.

Also, the model presented here differs from the previously reported models in the specification of the boundary condition at the catholyte/diaphragm interface. That is, the model of Stender et al. (6), for example, is developed with a physically unrealistic boundary condition, a fixed catholyte concentration. Consideration of Fig. 1 reveals that the concentration in the catholyte depends on the velocity and the current density as well as the diaphragm properties and therefore cannot be specified a priori as an independent, fixed quantity. Thus, Stender’s expression for the concentration profile of hydroxyl ion (Eq [13] in Ref. (6)) does not show the correct dependence on velocity and current density because it includes the concentration at the interface.

The previously reported simple diaphragm models (6-10) have not been used to analyze the combined effects of diaphragm properties and operating conditions on the energy cost for NaOH production. That is, although Koh (9, 10) showed the effect of his diaphragm effectiveness parameter on electrolyzer energy consumption, the interaction between current density, velocity, and diaphragm properties (e.g., \(N_M\) and \(t\)) was not discussed. The contribution of the diaphragm voltage drop to energy cost and the effect of diaphragm parameters on the voltage drop were not discussed by Koh or the authors of the other simple models. Hine (14) showed diaphragm IR data for a stagnant laboratory-scale diaphragm cell, but comparison of this data to model predictions was not reported. Also, the contributions of electrode kinetics to the energy consumption have not been reported previously but are included here. More complicated model (12) of chlorine/NaOH metal anode electrolyzer has shown the effect of the product of \(N_M\) and \(t\) on specific energy consumption; however, only the essence of the model was presented, and the details were avoided for proprietary reasons.

**Model**

The assumptions of the simple models are as follows.

1. Dilute solution theory (20) applies.
2. The hydroxyl ion is the only species of interest within the diaphragm, and all reactions of OH\(^-\) with other species (e.g., H\(^+\) and Cl\(^-\)) occur at the anolyte/diaphragm interface. (This assumption is reasonable because the concentrations of the other species in the diaphragm are relatively small, on the order of 2% of that of the OH\(^-\) ion.)
3. The spatial dimension in the direction parallel to the velocity (see Fig. 1) is the only important dimension for material balances.
4. The effective diffusion coefficient for hydroxyl ion in the porous diaphragm can be written in terms of the MacMullin number (12)

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\(^1\) Throughout this paper, the phrase “simple model of the diaphragm” is used to indicate a model with a linear potential gradient that can be solved by analytical integration of the governing differential equations.
\[ D_e = \frac{D_i}{N_m} \]  

5. The current density through the diaphragm is simply related to the potential gradient through the diaphragm by an effective average specific conductivity

\[ i = -\frac{\kappa_{\text{avg}}}{N_m} \frac{d\Phi}{dx} \]  

6. Water vapor loss from the catholyte is negligible, and the generated \( H_2 \) gas mixes the catholyte so that the hydroxyl ion concentration at the diaphragm/catholyte interface equals the hydroxyl ion concentration in the electrolyzer effluent.

7. The electrochemical kinetics at the anode and cathode can be approximated by a Tafel approximation

\[ \Delta V_{\text{kin},i} = \frac{RT}{\alpha_i \Phi} \ln \left( \frac{i}{i_{\text{th}}} \right) \]  

where \( i = 1 \) and 2 for cathode and anode, respectively.

8. The effect of temperature on \( \Delta U^e \) is negligible.

9. The Nernst concentration correction to the open-circuit or thermodynamic voltage of the electrolyzer is negligible.

10. The voltage drop between the anode and cathode can be approximated by an effective average specific conductivity

\[ \Delta V_{\text{anode}} = \frac{is}{(1 - \epsilon_i)^{1.5} \kappa_{\text{anode}}} \]  

where \((1 - \epsilon_i)^{1.5}\) is the Bruggeman correction for the effect of bubbles in the anolyte (21, 22) and \( \epsilon_i \) is assumed to be independent of current density.

With these assumptions, the steady-state material balance for hydroxyl ion in the porous diaphragm is

\[ \frac{dN_i}{dx} = 0 \]  

where the expression for the flux of hydroxyl ion in the porous diaphragm can be written (12) as

\[ N_i = \frac{D_i}{N_m} \frac{dC_i}{dx} + \frac{D_i}{N_m} \frac{Fi}{RT} C_i \frac{d\Phi}{dx} + vC_i \]  

The boundary conditions can be obtained from the second and sixth assumptions above and by recognizing that the anolyte and catholyte approximate completely mixed reactors. That is, for a typical anolyte pH of 2, the \( \Omega \) concentration is

\[ at \ x = 0, \ C_1 = 0 \]  

Since \( OH^- \) is produced at the diaphragm/catholyte interface, and since the flux in the catholyte chamber consists of only convection (i.e., \( vC_i \)), the material balance is

\[ at \ x = t, \ N_i(x = t) = \frac{i}{F} = vC_i(x = t) \]  


\[ N_i = -\frac{D_i}{N_m} \frac{dC_i}{dx} - \frac{D_i}{N_m} \frac{Fi}{RT} C_i \frac{d\Phi}{dx} + vC_i \]  

Substituting Eq. [11] into Eq. [7] yields the second-order differential equation which governs the concentration of hydroxyl ion throughout the diaphragm

\[ \frac{D_i}{N_m} \frac{dC_i}{dx^2} + \left( \frac{D_i}{N_m} \frac{Fi}{\kappa_{\text{avg}}RT} - v \right) \frac{dC_i}{dx} = 0 \]  

Integration of Eq. [12] subject to the boundary conditions (Eq. [9] and [10]) is readily accomplished [see Ref. (23), for example], and the result can be written as

\[ C_i(x) = \frac{i}{vF} \left\{ 1 - \exp \left( \frac{FiD_i}{RT\kappa_{\text{avg}}v} - \exp \left( A_i, t \right) \right) \right\} \]  

where

\[ A_i = \left( \frac{-FiN_m}{RT\kappa_{\text{avg}}} \right) \frac{vN_m}{D_i} \]  

Equation [13] is plotted in Fig. 12 and 13 of Ref. (23) and can be used to obtain an expression for the hydroxyl ion concentration in the effluent

\[ C_i(t) = \frac{i}{vF} \left\{ 1 - \exp \left( A_i, t \right) \right\} \]  

Equation [14] shows that the effluent concentration is a dependent variable when the velocity and current density are considered independent variables. An expression for the caustic yield, \( \eta \), can be obtained by using the following definition

\[ \eta = \frac{vC_i(t)F}{i} \]  

where by the sixth assumption above, \( C_i(\text{effluent}) = C_i(t) \).


\[ \eta = \left\{ 1 - \exp \left( A_i, t \right) \right\} \frac{FiD_i}{RT\kappa_{\text{avg}}v} \]  

Note that Eq. [14] and [16] show that \( C_i(t) \) and \( \eta \) depend on the product of \( N_m \) and \( t \) and not on either quantity separately. This should be expected, since \( N_m t \) is simply the effective thickness of the diaphragm. Also, it should be emphasized that \( \eta \) is a derived quantity, not a parameter.

That is, \( \eta \) is calculated according to Eq. [15] after the governing equation for \( C_i(x) \) (Eq. [12]) has been solved subject to the boundary conditions (Eq. [9] and [10]). Also, note that none of Eq. [7]-[12] contain \( \eta \) and that this is different from the formation of Caldwell et al. (12) and Stender et al. (6).

**Energy Cost**

The specific electrolyzer energy cost for NaOH, \( E_{c_e} \), can be formulated as the ratio of the energy consumption rate to the mass production rate of NaOH multiplied by the electrical energy cost, \( CE \)

\[ E_{c_e} = \frac{iV_T}{M C_i(t) \omega} \]  

In Eq. [17], the current density, \( i \), and the velocity, \( v \), are considered independent variables, while \( C_i(t) \) is deter-
DITHODIC AND ANODIC REACTIONS, THE VOLTAGE DROP IN THE ANO-
thermodynamic voltage required for the sum of the ca-
implemented by Eq. [14] as a dependent variable. Also, the sum
includes the kinetic voltage drops at each electrode, the ther-
modynamic voltage required for the sum of the cath-
odic and anodic reactions, the voltage drop in the ano-
tode drop. The diaphragm is typically deposited onto the cathode and, hence, any volt-
dage drop in the catholyte is negligible. Using the fifth
and seventh through tenth assumptions above gives
\[ V_\text{t} = \frac{iN_{\text{at}}}{\kappa_{\text{ave}}} + \frac{RT}{F} \left[ \left( \frac{1}{\alpha_1} + \frac{1}{\alpha_2} \right) \ln \left| \frac{\ln (i_{\text{at}})}{\alpha_1} - \frac{\ln (i_{\text{an}})}{\alpha_2} \right| + \Delta U' \right] \]
\[ + \frac{\Delta U''}{(1 - \phi)} \kappa_{\text{ave}} \]  \[ \text{[18]} \]

Other Dimensionless Groups
It is, perhaps, worth mentioning that dimensionless
groups other than the ones shown in Eq. [16] can be for-
mulated. For example, Eq. [16] can be rewritten as
\[ \eta = \frac{1 - \exp (P_e + \Delta \phi)}{-\Delta \phi - \exp (P_e + \Delta \phi)} \]  \[ \text{[19]} \]
where \( P_e \) is the Peclet number
\[ P_e = \frac{vN_{\text{at}}}{D_1} \]  \[ \text{[20]} \]
and \(-\Delta \phi\) is the dimensionless diaphragm IR drop
\[ -\Delta \phi = -\frac{F}{RT} \left[ \Phi (x = t) - \Phi (x = 0) \right] = \frac{FlN_{\text{at}}}{RTk_{\text{ave}}} \]  \[ \text{[21]} \]
The Peclet number is a measure of the effect of convec-
tion relative to diffusion and is used routinely by chem-
ical engineers. The dimensionless diaphragm IR drop, \(-\Delta \phi\), can be thought of as a measure of the importance of the effect of ionic migration.

These dimensionless groups can also be used to write in
dimensionless form an expression for the concentra-
tion distribution for \( \text{OH}^- \) ions
\[ \theta_i(x) = \frac{C_i(x)}{F_1} = \frac{N_a(1 - \exp \left[ (P_e + \Delta \phi)\theta_i \right])}{-\Delta \phi - \exp (P_e + \Delta \phi)} \]  \[ \text{[22]} \]
where \( F_1 \) is the concentration of the NaCl in the brine
feed (a constant) and \( N_a \) is the Hine number defined as
\[ N_a = \frac{r}{FF_1v} \]  \[ \text{[23]} \]
since Hine and Yasuda (24) were apparently the first to recog-
nize the significance of \( i/Fv \).

Comparison of Diaphragm Model to Existing Models
Expressions similar to those given above for \( C_i(x) \), \( C_i(t) \), and \( \eta \) have been presented by Stender et al. (8), Koh (9),
and Mukaiho (7) which with modifications or definitions of effective thickness can be shown to be consistent with the model presented here. The expressions presented by Stender et al. (8) for \( C_i(x) \) and \( \eta \) are not correct because they do not contain \( N_{\text{at}} \) or a similar quantity. Their equa-
tions are written in terms of \( \delta \) (defined to be the thick-
ness of the diaphragm), but their expression for \( \eta \) can be seen to be equivalent to Eq. [16] by defining \( \delta \) in terms of measurable diaphragm properties
\[ \delta = N_a t \]  \[ \text{[24]} \]
Thus, their \( \delta \) should be the effective thickness and not the
measured diaphragm thickness. Using Eq. [24], their di-

dimensionless parameter \( \Delta U' \) is shown to be equal to
\( A_{t} \) of Eq. [13], [14], and [16]. In addition, their equation
for \( C_i(x) \) is not complete because it depends on the concen-
tration of \( \text{OH}^- \) in the catholyte, which also depends
on other variables in their expression for \( C_{\text{oh}}(x) \). That is,
for example, both \( v \) and \( C_i(t) \) cannot be set while holding
\( i \) fixed because only two independent operating variables
exist for the isothermal case. This point is easily over-
looked when \( C_i(x) \) is made dimensionless by \( C_i(t) \) and
the resulting expression (i.e., divide Eq. [13] by Eq. [14]) is
graphed as a function of distance, \( x \), as is shown by Hine
et al. (14) in their Fig. 12. The resulting expression, and
hence Fig. 12 of Ref. (14), appears as a function of only
one dimensionless variable, \( \Delta U' \), which is misleading
because the dimensionless concentration profile is de-
scribed by three dimensionless groups (divide both sides
of Eq. [13] by \( F \), or see Eq. [22]). Furthermore, if \( C_i(t)F_1 \) is
held constant, then \( v/FV \) must be changed as \( A_{t} \) is
changed; this point is illustrated in Fig. 2, which shows
that \( C_i(t)/F_1 \) depends on both \( A_{t} \) and \( v/FV \). Two ex-
tceptions to this dependence occur as follows
\[ A_{t} < -20; \quad C_i(t) = \frac{RTk_{\text{ave}}}{FF_1} \]  \[ \text{[25]} \]
\[ A_{t} > 20; \quad C_i(t) = \frac{i}{FF_1} \]  \[ \text{[26]} \]

Also, when \( A_{t} = 0 \), Eq. [13], [14], and [16] become indeter-
determinate forms because the quantity \( F_1F/Vk_{\text{ave}} \)
equals 1.0. For these indeterminate forms, application of
H'ope's rule results in the following limit
\[ C_i(x) = \frac{1}{D_1F_1} \left( \frac{FF_1}{vF_1} \right) \]  \[ \text{[27]} \]
when
\[ A_{t} = 0 \]

Next, consider the equation for \( \eta \) presented by Koh (9).
His equation for \( \eta \) contains a length parameter, \( L_\tau \),
which can be shown to be equal to \( N_{\text{at}} \) by considering
Koh's definition of \( \eta \)
\[ EL_i = \frac{FL_\tau}{\eta} \]  \[ \text{[28]} \]
and the definitions of \( l \) (average pore length) and \( N_a \)
\[ l = rt \]  \[ \text{[29]} \]
\[ N_a = \frac{r}{\epsilon} \]  \[ \text{[30]} \]
where \( \tau \) is the tortuosity and \( \epsilon \) is the porosity of the dia-
aphragm.\(^2\) Substitution of Eq. [29] and [30] into Eq. [28]
shows that
\[ EL = N_a t \]  \[ \text{[31]} \]

However, even though Koh's equation for \( \eta \) does contain
an effective thickness parameter, he did not recognize
that it can be determined by measuring \( N_{\text{at}} \) and \( l \).
Instead, he used an assumed value for \( \eta \) and a presum-
ably measured value for \( \epsilon \) to obtain \( N_{\text{at}} \) (his EL). Unfortu-
nately, his \( N_{\text{at}} \) values are scaled for proprietary reasons, and his
equation for \( \eta \) is difficult to use because it contains a pa-
rameter (his \( A \)) which is incorrect as written.

Mukaiho's (6, 16) expression for \( \eta \) is also similar to Eq. [16];
however, his equation is based on a different ap-
proach. He defined a transference number for \( \text{OH}^- \) as
\[ n_{\text{i}} = \frac{t_{\text{i}}(x)}{C_i(x)} \]  \[ \text{[32]} \]
and assumed that \( n_{\text{i}} \) (not \( t_{\text{i}} \)) is constant throughout the di-
aphragm. He then defined the flux of \( \text{OH}^- \) through the
diaphragm to be
\[ F_{\text{di}} = -D_1 \frac{dC_i}{dx} - n_{\text{i}}C_i \frac{i}{vF} \]  \[ \text{[33]} \]
and integrated Eq. [7] with \( N_{\text{i}} \) given by Eq. [33] in a man-
ner.
\(^2\) Actually, Caldwell et al. (12) define \( N_{\text{at}} \) as \( N_{\text{at}} \), but it is imma-
terial whether \( \eta \) is squared or not, since it is not a quantity that
can be measured directly.
ner similar to that shown in Ref. (23). The equations he obtained for $C_i(t)$ and $n_i$ do have the correct dependence on $N_M$, since $N_M$ is related simply to his area ratio

$$N_M = A_D/A_a$$  \[34\]

as can be seen by defining (10) the porosity of the diaphragm as

$$e = A_D/t A_a$$  \[35\]

and using Eq. [29] and [30]

$$N_M = \frac{1}{e} = \frac{A_D/\Delta t}{A_a}$$  \[36\]

Even though Mukaibo presented equations that do have the correct dependence on $N_M$, he did not recognize that $N_M$ can be measured directly and he did not present an equation for $C_i(x)$. Also, his concept of a constant transfer number ($n_i$) is perhaps less appealing than the concept of a constant, average specific conductivity. This may be so because $\kappa_{avg}$ can be measured directly by assuming that $\kappa_{avg}$ is equal to the specific conductivity of an aqueous solution of NaCl and NaOH at their average concentrations over the range of effluent concentrations of interest (e.g., 2.5M of each), whereas $n_i$ cannot. However, it is interesting to note that an average value for $n_i$ can be obtained from $\kappa_{avg}$ if $D_i$ is known.

This can be seen by considering the definitions of $t_i$ and $\kappa$. That is, according to Newman (20), the transport number for species $j$ in an electrolyte solution is given by

$$t_i = \frac{z_i^2 u_i C_i}{\sum_j z_j u_j C_j}$$  \[37\]

and the specific conductivity is given by

$$\kappa = \frac{F \sum z_i u_i C_i}{\kappa}$$  \[38\]

Substitution of Eq. [38] into Eq. [37] written for OH$^-$ yields

$$U_i = \frac{D_i}{RT}$$  \[39\]

which, assuming that the Nernst-Einstein equation (20) is valid

$$n_i = \frac{t_i}{C_i} = \frac{F D_i}{RT}$$  \[40\]

Thus, once values for $D_i$ and $\kappa_{avg}$ are known, an average value for $n_i$ could be calculated according to Eq. [41].

**Parameter Estimation**

**Diaphragm model.**—The diaphragm model presented above is formulated in terms of two transport properties of the electrolyte solution within the diaphragm, $D_i$ and $\kappa_{avg}$. Both $D_i$ and $\kappa_{avg}$ are average quantities which depend on temperature and the average concentration within the diaphragm. Values for these average quantities are not available in the literature.

Their values can be estimated by nonlinear least squares (LS) regression of Eq. [14] or [16] against measured values of $C_i(t_i)$ or $n_i$, respectively. Note that $\eta$ is derived from a combination of dependent and independent variables. With this regression approach, the model is "fitted" to the data, and statistical theory (1-4) states that the estimates of $D_i$ and $\kappa_{avg}$ are the best values for the data in the sense that the estimates result in the minimum difference between the observed and predicted values of $\eta$. Then the model with these estimates can be used for interpolation. Confidence is gained in the model if the parameter estimates obtained by LS are physically realistic. If the parameter estimates are physically unrealistic, extrapolations beyond the experimental range could be made within the limits of the assumptions of the model. Also, if the number of data points is large, confidence intervals on the parameter estimates can be obtained in the same manner as in linear regression (3).

The estimation of $D_i$ and $\kappa_{avg}$ by LS requires experimental data in which both $N_M$ and $t$ are measured quantities. The factorially designed experiments of Ref. (1) provide data in which $N_M$ was varied from 3.3 to 7.5 and $t$ was varied from 0.17 to 0.33 cm. Also, the current density and velocity were measured precisely and cell temperature was controlled at 70$^\circ$ ± 0.5$^\circ$C. In addition, the brine feed concentration was set with either a high or low acid and a constant salt concentration. The diaphragm voltage drop and the concentration of OH$^-$ ion in the effluent were measured simultaneously as dependent variables. Note that $D_i$ and $\kappa_{avg}$ are independent of the diaphragm properties and, therefore, are free stream parameters rather than effective parameters of the particular diaphragm. Thus, by fixing the values of $N_M$ and $t$ and the independent operating variables, $i$ and $v$, the only parameters of the model which can account for an inadequate model are the values of $D_i$ and $\kappa_{avg}$.

It should be noted that the experimental cells of Ref. (11) consisted of laboratory cells which were designed by scaling down industrial-size electrolyzers so that geometric similarity was maintained. These cells contained a diaphragm which was placed in contact with a perforated steel cathode as shown in Fig. 1. The experimental cells were therefore consistent with the majority of industrial, metal anode cells which have the diaphragm vacuum deposited on the cathode.

Also, the model presented above was formulated to be consistent with the laboratory cells of Ref. (11). These cells were run for a period of 35 days. The replicate steady-state data were obtained over the entire period (26).

The predictions of the caustic yield and the diaphragm voltage drop are coupled through the average conductivity, $\kappa_{avg}$, and thus an appropriate LS objective function is

$$G(\bar{\theta}) = \sum_{i=1}^{n} \left( \eta_i^o - \eta_i^p \right)^2 + \sum_{k=1}^{m} \left( \Delta \Phi_k^o - \Delta \Phi_k^p \right)^2$$  \[42\]

where $\eta_i^o$ is predicted by Eq. [16] at the experimental conditions corresponding to the $i$th datum, $\Delta \Phi_k^o$ is predicted by integration of Eq. [4] at the experimental conditions corresponding to the $k$th datum, and $\eta_i^p$ and $\Delta \Phi_k^p$ correspond to the estimated variance of $\eta$ and $\Delta \Phi$, respectively.

The nonlinearity of Eq. [42] results from the nonlinear model equation for $\eta$, but it does not affect the theory behind LS regression (3, 4). The computations necessary to minimize this objective function become more complicated with a nonlinear function, but many computers have subroutine libraries which can perform the necessary calculations. In this work, minimization subroutines of the International Mathematical and Statistical Library (25) were used (26).

Each of the estimated variance ($\sigma_i^2$ and $\sigma_k^2$) in Eq. [42] correspond to the sum of the variance associated with the measurement error and the variance associated with the model error. This is, we assume (in accordance with the assumptions of LS theory) any difference between the observed and predicted values is a lumped error which is distributed randomly. $\sigma_i^2$ for each experimental value was estimated by dividing the minimum value of $G(\theta)$ when $\eta_i^p = \infty$ by the degrees of freedom [in this case, $N - 2$, since two parameters are adjusted to minimize $G(\theta)$]. Similarly, $\sigma_k^2$ was calculated by dividing the minimum value of $G(\theta)$ when $\Delta \Phi_k^p = \infty$ (by $(M - 1)$ only one parameter, $\kappa_{avg}$ is adjusted to minimize $G(\theta)$ when $\eta_i^p = \infty$).
Table I. Parameter estimates for diaphragm model

<table>
<thead>
<tr>
<th>Case</th>
<th>Parameter estimates with $\zeta_j^2 = \omega; N = 84$</th>
<th>$\zeta_j^2 = \omega; M = 64$</th>
<th>$\zeta_j^2 = \omega; \delta_j^2 = 1.118 \times 10^{-3}$ and $\delta_j^2 = 2.688 \times 10^{-3}$V</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Parameter Estimate ± interval Units t-statistic</td>
<td>Parameter Estimate ± interval Units t-statistic</td>
<td>Parameter Estimate ± interval Units t-statistic</td>
</tr>
<tr>
<td></td>
<td>$D_j$</td>
<td>$3.352 \times 10^{-3}$ ± $0.275 \times 10^{-3}$ cm/s</td>
<td>$0.422$ ± $0.060$ cm$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>$\kappa_{avg}$</td>
<td>$0.338$ ± $0.015$ cm$^{-1}$</td>
<td>$1.627 \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>$G(\delta)$</td>
<td>$0.326$ ± $0.015$ cm$^{-1}$</td>
<td>$2.688 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

The weighting of the dependent variables in the LS objective function in this fashion gives the "best values" of the parameters for Eq. [16] and [21] and the data (27). These estimated variances are shown in cases A and B of Table I. Note that $\delta_1$ is dimensionless, since $\eta$ is dimensionless, whereas $\delta_2$ has the dimensions of $\Delta \phi$. The parameter estimates for $D_j$ and $\kappa_{avg}$ shown for cases A and B can be compared with the parameters of case C, which were estimated with the objective function weighted as described above. That is, including the data on the voltage drop through the diaphragm lowers the estimates of $D_j$ and $\kappa_{avg}$ and narrows the confidence intervals. The narrow confidence intervals indicate a greater sensitivity of the case C objective function to changes in the parameter values.

Figures 3 and 4 compare the predicted and observed values of $\eta$ and $\Delta \phi$ at the estimates of case C in Table I. The slopes and intercepts shown on Fig. 3 and 4 indicate that the diaphragm model agrees well enough with the experimental data to be useful for approximate design purposes. The large dispersion of observed voltage drops for a given predicted voltage drop may be a result of the fifth assumption made above; that is, the potential drop is probably a nonlinear function of the operating variables. Figures 5 and 6 show that the residuals (i.e., the difference between the predicted and observed values) are independent of the dependent variables as required by LS regression theory (2, 3, 27). Similar plots of the residuals and effective thickness ($N_M t$), current density, and velocity indicate no correlation between these independent variables and residuals (26). Thus, it can be concluded that the model with the LS parameter estimates of case C in Table I can be used to predict both the caustic yield and the diaphragm voltage drop.

Also, if the diaphragm effective thickness, $N_M t$, was known to change with time (due to plugging of the diaphragm, for example), the model could be adapted for interpolation purposes by minimizing Eq. [42] by adjusting $N_M t$ with the values of $D_j$ and $\kappa_{avg}$ held constant at the specified values of case C. This adjusting of $N_M t$ was not necessary for the experimental data used here because both the values of $N_M$ and $t$ were not significantly different before and after the experiments (11).

Electrode kinetics.—Calculation of the cell voltage, $V_T$, by Eq. [18] requires knowledge of the kinetic parameters corresponding to the Tafel equations for the anode and

---

Fig. 3. Comparison of model predictions and experimental caustic yield data from Ref. (11) using the LS parameters of case C, Table I.

Fig. 4. Comparison of model predictions and experimental diaphragm voltage-drop data from Ref. (11) using LS parameters of case C, Table I.
cathode. The kinetic data obtained in Ref. (11) are proprietary, but for purposes of illustration, the data of Caldwell (28) can be used to estimate these kinetic parameters. That is, Caldwell reports hydrogen and chlorine overpotentials as functions of temperature and current density. By assuming that these overpotentials are independent of NaOH and NaCl concentrations, estimates of \( \alpha_1 \) and \( i_{0,1} \) can be obtained by LS for use in Eq. [18] and then in Eq. [17] for prediction of the specific energy cost.

Since the overpotential data for hydrogen on low-carbon steel in 2.5M NaOH/3.01M NaCl electrolyte are large negative numbers, the Butler-Volmer expression can be inverted to give an explicit expression for \( V_1 \), the dependent variable

\[
V_1 = \frac{RT_1}{\alpha_1} \ln (i_{0,1}) - \frac{RT_1}{\alpha_1} \ln i
\]  

[43]

Thus an appropriate objective function for this data is

\[
H_1(\alpha_1, i_{0,1}) = \sum_{i=1}^{n} (V_{1,i} - V_{1,(i)})^2
\]  

[44]

Equation [44] can be minimized easily with a hand calculator or statistical subroutines (25, 26). Unfortunately, the residuals of Eq. [44] exhibit a large correlation with temperature when all of the data (28) are used to estimate the parameters (26). Consequently, the parameter estimates (\( \alpha_1 \) and \( i_{0,1} \)) were determined using only the data (28) for 343 K (i.e., \( N = 5 \)) as shown in Table II. The confidence intervals on \( i_{0,1} \) and \( \alpha_1 \) are small, even though the number of data points is small. It should be noted that even though the determination of values for \( \alpha_1 \) and \( i_{0,1} \) is simple, the determination of their confidence intervals is complicated because the Tafel equation confidence intervals correspond to \( 1/\alpha \) and \( \ln (i_{0,1})/\alpha_1 \). The confidence intervals of Table II were determined from nonlinear regression routines (26). Figure 7 compares the predictions of Eq. [43] with the data of Caldwell (28). Residual plots (26) did not show a correlation of predicted overpotentials with current density.

The overpotential data for production of chlorine on RuO\(_2\)-TiO\(_2\) on titanium (28) should not be analyzed with a Tafel expression similar to Eq. [43] because the cathodic part of the Butler-Volmer expression is significant at small overpotentials. Instead, an implicit calculation should be performed to determine the dependent variable \( V_2 \). This calculation is performed by forming the function,

\[
f_{1,2} = 0 = i_{1,2} - i_{0,2} \left( \exp \left( \frac{\alpha_2 F}{RT_2} V_{2,i} \right) - \exp \left( \frac{(\alpha_2 - 2) FV_{2,i}}{RT_2} \right) \right)
\]  

[45]

Then for the given independent variables, \( i_{1,2} \) and \( T_1 \) and assumed values of \( \alpha_2 \) and \( i_{0,2} \), values of \( V_{2,i} \) can be determined (by Newton’s method, for example) such that \( f_{1,2} \) is

Table II. Kinetic parameter estimates

<p>| Case A. Hydrogen on low-carbon steel in 2.5M NaOH and 3.01M NaCl electrolyte at 343.15 K |</p>
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Estimate</th>
<th>±</th>
<th>95% Confidence Interval</th>
<th>Units</th>
<th>t-statistic</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha_1 )</td>
<td>0.5723</td>
<td>±</td>
<td>0.0153</td>
<td>none</td>
<td>119.0</td>
</tr>
<tr>
<td>( i_{0,1} )</td>
<td>4.065 \times 10^{-4}</td>
<td>±</td>
<td>4.90 \times 10^{-4}</td>
<td>A/cm²</td>
<td>28.5</td>
</tr>
</tbody>
</table>

<p>| Case B. Chlorine on RuO(_2)-TiO(_2) on titanium in 5.02M NaCl determined using Eq. [45] and [46] |</p>
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Estimate</th>
<th>±</th>
<th>95% Confidence Interval</th>
<th>Units</th>
<th>t-statistic</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha_2 )</td>
<td>1.809</td>
<td>±</td>
<td>0.592</td>
<td>none</td>
<td>6.3</td>
</tr>
<tr>
<td>( i_{0,2} )</td>
<td>3.710 \times 10^{-3}</td>
<td>±</td>
<td>3.607 \times 10^{-3}</td>
<td>A/cm²</td>
<td>2.5</td>
</tr>
</tbody>
</table>

* Based on data presented by Caldwell (28).

** See Ref. (26).
Fig. 7. Comparison of hydrogen overpotential predictions and data of Ref. (28), and comparison of chlorine overpotential data of Ref. (28) and predictions from Eq. [45] and LS parameters of case B, Table II, at 343.15 K.

approximately zero. The assumed values of $\alpha_2$ and $i_{0.2}$ can be adjusted to obtain a minimized objective function which can be defined

$$H_2(\alpha_2, i_{0.2}) = \sum_{i=1}^{n} (V_{2,\alpha} - V_{2,\alpha})^2$$

Nonlinear regression techniques (26) must be used to minimize Eq. [46]. It should be noted that Eq. [45] assumes that the apparent transfer coefficients sum to the number of electrons evolved in the overall oxidation of chloride to chlorine (two here).

The estimated parameters using this implicit formulation for the chlorine reaction are shown in case B of Table II. The confidence intervals for these parameters are large, which indicates the need for more data at larger current densities. Figure 7 compares the experimental and predicted values at these parameter estimates. Residual plots (26) did not indicate significant correlations of the residuals with either current density or temperature, and, therefore, all of the data reported by Caldwell (28) was used.

Electrical Energy Cost Predictions

The specific electrolyzer energy cost for NaOH production (i.e., Eq. [17]) can be predicted with confidence for the range of industrial conditions covered by the factorial experiment by using the parameter estimates of Tables I and II. An example of these energy cost predictions is shown in Fig. 8. The physical properties and parameters used for the calculations are shown in Table III. It should be noted that the only assumed value in Table III is the void fraction of bubbles in the anolyte; all other values correspond to either parameter estimates, physically measurable properties (i.e., diaphragm, electrolyte, or cell geometry properties), or operating conditions. Consideration of Fig. 8 shows that an $N_{\text{et}}$ can be selected which minimizes the specific electrical energy cost for NaOH production at a specified current density and caustic effluent concentration (or effluent velocity as shown in Fig. 9). However, it is important to note that this minimum occurs at a value of $N_{\text{et}}$ beyond that used in the experimental work and may, consequently, be invalid.

Conclusion

Development of a simple model of the diaphragm in terms of measurable diaphragm properties has provided a design equation which allows direct comparison of experimental data and theoretical predictions. This comparison, accomplished with parameter estimation techniques, shows that the models of the caustic yield and the voltage drop through the diaphragm are reasonable; changing the assumption of a linear potential gradient through the diaphragm may provide an improvement. The parameter estimates and the simple model provide a design equation which can be used to predict the minimum specific electrical energy required for NaOH production as a function of the effective thickness, $N_{\text{et}}$, the current density, and the caustic concentration in the effluent (or the effluent velocity).

Acknowledgments

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Table III. Physical parameters for minimum energy calculation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_1$</td>
<td>2.825 $\times 10^{-2}$ cm/s</td>
</tr>
<tr>
<td>$i_1$</td>
<td>0.200 A/cm$^2$</td>
</tr>
<tr>
<td>$i_{\text{b,2}}$</td>
<td>3.710 $\times 10^{-3}$ A/cm$^2$</td>
</tr>
<tr>
<td>$i_{\text{b,3}}$</td>
<td>4.085 $\times 10^{-4}$ A/cm$^2$</td>
</tr>
<tr>
<td>$s$</td>
<td>0.633 cm</td>
</tr>
<tr>
<td>$T$</td>
<td>343.15 K</td>
</tr>
<tr>
<td>$\alpha_0$</td>
<td>0.5723</td>
</tr>
<tr>
<td>$\alpha_1$</td>
<td>1.806</td>
</tr>
<tr>
<td>$\Delta U_{\text{f}}$</td>
<td>2.186V</td>
</tr>
<tr>
<td>$e_0$</td>
<td>0.6</td>
</tr>
<tr>
<td>$\kappa_{\text{neo}}$</td>
<td>0.491 $\Omega^{-1}$ cm$^{-1}$</td>
</tr>
<tr>
<td>$\kappa_{\text{ave}}$</td>
<td>0.338 $\Omega^{-1}$ cm$^{-1}$</td>
</tr>
</tbody>
</table>

*From Caldwell (28) for 5.13M NaCl at 70°C.*
### LIST OF SYMBOLS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_i$</td>
<td>area of pores within the diaphragm ($cm^2$)</td>
</tr>
<tr>
<td>$A_{de}$</td>
<td>area of diaphragm ($cm^2$)</td>
</tr>
<tr>
<td>$C'_p$, $C(x)$</td>
<td>position dependent concentration of $OH^{-}$ ion (mol/cm$^3$)</td>
</tr>
<tr>
<td>$C(0) = 0$, $C(t)$</td>
<td>concentration of $OH^{-}$ ion at diaphragm/catheode interface (mol/cm$^3$)</td>
</tr>
<tr>
<td>$C_{leak}$</td>
<td>concentration of $OH^{-}$ ion in catholyte (mol/cm$^3$)</td>
</tr>
<tr>
<td>$CE$</td>
<td>cost of electrical energy ($$/J)</td>
</tr>
<tr>
<td>$D_i$</td>
<td>free stream diffusion coefficient of $OH^{-}$ ion (cm$^2$/s)</td>
</tr>
<tr>
<td>$D_e$</td>
<td>effective diffusion coefficient of $OH^{-}$ ion (cm$^2$/s)</td>
</tr>
<tr>
<td>$EC_{el}$</td>
<td>specific electrical energy cost for NaOH production ($$/kg)</td>
</tr>
<tr>
<td>$EL$</td>
<td>length parameter (see Eq. [28]) (cm)</td>
</tr>
<tr>
<td>$F^*$</td>
<td>Faraday’s constant (96,487 C/mol)</td>
</tr>
<tr>
<td>$F_i$</td>
<td>feed concentration of NaCl (mol/cm$^3$)</td>
</tr>
<tr>
<td>$f_{i1}$</td>
<td>functional representation of Butler-Volmer equation equal to zero at 1th datum (see Eq. [45])</td>
</tr>
<tr>
<td>$G(\beta)$</td>
<td>least squares objective function with parameter vector $\beta$, see Eq. [42]</td>
</tr>
<tr>
<td>$H_1, H_2$</td>
<td>least squares objective function for hydrogen and chlorine electrode kinetics, respectively, see Eq. [44] and [46]</td>
</tr>
<tr>
<td>$i$</td>
<td>current density through the diaphragm (A/cm$^2$)</td>
</tr>
<tr>
<td>$i_{12}, i_{21}$</td>
<td>current density on anode corresponding to 1th and 2th datum (A/cm$^2$)</td>
</tr>
<tr>
<td>$i_{1s}, i_{2s}$</td>
<td>exchange current density of hydrogen and chlorine electrodes, respectively (A/cm$^2$)</td>
</tr>
<tr>
<td>$l$</td>
<td>average pore length, see Eq. [29] (cm)</td>
</tr>
<tr>
<td>$M$</td>
<td>number of data points for diaphragm voltage drop (A/cm$^2$)</td>
</tr>
<tr>
<td>$M_i$</td>
<td>molecular weight of NaOH (39.99 g/mol)</td>
</tr>
<tr>
<td>$N_i$</td>
<td>number of data points for caustic yield or hydrogen overpotential (A/cm$^2$)</td>
</tr>
<tr>
<td>$N_1$</td>
<td>Hine number, see Eq. [23], dimensionless</td>
</tr>
<tr>
<td>$n_t, n_1$</td>
<td>transference number of $OH^{-}$ ion (cm$^2$/mol)</td>
</tr>
<tr>
<td>$Pe$</td>
<td>Peclet number, see Eq. [20], dimensionless</td>
</tr>
<tr>
<td>$R$</td>
<td>dimensionless gas constant (8.3143 J/mol K)</td>
</tr>
<tr>
<td>$S$</td>
<td>distance between anode and diaphragm anolyte face (cm)</td>
</tr>
<tr>
<td>$t$</td>
<td>temperature (K)</td>
</tr>
<tr>
<td>$t_{1n}, t_i$</td>
<td>transport number of species $j$, $j = 1$ for $OH^{-}$ ion (cm$^2$/mol-s)</td>
</tr>
<tr>
<td>$u_{1n}, u_{i1}$</td>
<td>mobility of species $j$, $j = 1$ for $OH^{-}$ ion (cm$^2$/V-s)</td>
</tr>
<tr>
<td>$U$</td>
<td>relative velocity expression of Stender et al. (8) (cm/s)</td>
</tr>
<tr>
<td>$\Delta U^e$</td>
<td>open-circuit potential for chlorine/caustic cell (2.188V)</td>
</tr>
<tr>
<td>$V$</td>
<td>total cell voltage, see Eq. [18] (V)</td>
</tr>
<tr>
<td>$V_{1r}, V_{1s}$</td>
<td>hydrogen and chlorine overpotential, respectively (V)</td>
</tr>
<tr>
<td>$V_{1r}', V_{1s}'$</td>
<td>observed hydrogen and chlorine kinetic overpotential, respectively, at 1th datum (V)</td>
</tr>
<tr>
<td>$V_{1s}', V_{1s}''$</td>
<td>predicted hydrogen and chlorine kinetic overpotential, respectively, at independent variables corresponding to 1th datum (V)</td>
</tr>
<tr>
<td>$\nu$</td>
<td>percolation velocity through the pores (cm/s)</td>
</tr>
<tr>
<td>$x$</td>
<td>diaphragm dimensional coordinate (cm)</td>
</tr>
<tr>
<td>$\varepsilon_0, \varepsilon_1$</td>
<td>ionic charge for species $j$, $j = 1$ for $OH^{-}$ ion (cm)</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>apparent transfer coefficients for hydrogen and chlorine reactions, respectively (V)</td>
</tr>
<tr>
<td>$\delta$</td>
<td>porosity of diaphragm, dimensionless</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>void fraction of gas bubbles in anolyte, dimensionless</td>
</tr>
<tr>
<td>$\kappa_{equiv}$</td>
<td>average specific conductivity of electrolyte in the diaphragm (1 cm$^{-2}$ cm$^{-1}$)</td>
</tr>
<tr>
<td>$\phi(x)$</td>
<td>specific conductivity of anolyte (1 cm$^{-2}$ cm$^{-1}$)</td>
</tr>
<tr>
<td>$\Phi$</td>
<td>dimension voltage in diaphragm at position $x$ (V)</td>
</tr>
<tr>
<td>$\Delta\phi$</td>
<td>dimensionless voltage drop through the diaphragm (V)</td>
</tr>
<tr>
<td>$\Delta\phi$</td>
<td>dimensionless voltage drop through the diaphragm (V)</td>
</tr>
<tr>
<td>$\rho$</td>
<td>resistivity of diaphragm filled with electrolyte (ohm cm)</td>
</tr>
<tr>
<td>$\rho_0$</td>
<td>resistivity of electrolyte with an equivalent thickness of the diaphragm (ohm cm)</td>
</tr>
<tr>
<td>$\delta_i$</td>
<td>estimation variance of caustic yield, dimensionless</td>
</tr>
<tr>
<td>$\delta_i$</td>
<td>dimensionless estimated variance of diaphragm voltage drop (V$^2$)</td>
</tr>
<tr>
<td>$\tau$</td>
<td>tortuosity of diaphragm, dimensionless</td>
</tr>
<tr>
<td>$\theta_i(\zeta)$</td>
<td>dimensionless concentration of $OH^{-}$ ion at $i$ dimensional coordinate (z = x/t)</td>
</tr>
</tbody>
</table>

### REFERENCES

25. International Mathematical and Statistical Library subroutines ZXSSQ and ZXMIN, IMSL, Inc., Houston, TX.