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# Thermal effect on liquid-phase free convection at gas evolving electrodes

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**Abstract**—Recently, attention has been drawn to a disregarded mass transfer mechanism active at gas evolving electrodes in an industrially applied current density range: liquid-phase free convection in the liquid is controlled by gradients of concentrations and of temperature. But reliable data of the overtemperature of electrodes are not available. Literature data are contradictory. An analysis on the basis of heat and mass transfer equations evidences that overtemperature of the electrode surface in the usual range of current density is smaller than 1 K. Thermal effects on the extent of liquid-phase free convection are negligible. Concentration gradients resulting from the electrode reactions are predominant.

## 1. INTRODUCTION

IN ELECTROCHEMICAL processes, the effect of free convection mass transfer has been recognized for a long time, but only for those cases where gases are not evolved at the electrode. A typical example of industrial relevance is the cathodic copper deposition from acidic solutions of copper sulfate, provided the current density is not too large [1]. A gas, in this case hydrogen, would only be evolved at large values of the current density as the result of a competing side reaction [2].

Conditions are different if the solution is pure sulfuric acid. Hydrogen formation is then the only cathodic reaction in the whole operational range of the current density. From extraordinarily small values of below 0.1 A $m^{-2}$ [3] up to the critical current density (signalizing the transition from nucleate gas evolution to the formation of a gas film [4] and corresponding to the critical heat flux density in boiling) of about 200 kA $m^{-2}$ [5] gas bubbles are formed at the electrode. These are the conditions prevailing at many industrially important electrochemical processes, e.g. in chlorine production, in water decomposition, and in alumina electrolysis.

It is known that the microconvective action of growing and detaching bubbles enhances mass transfer considerably [1, 6]. This fact has given rise to considering this bubble-induced microconvection the only mass transfer mechanism, at least in the absence of forced flow. If the electrolyte liquid is pumped through the interelectrode gap or if the liquid–gas dispersion moves past the electrode owing to buoyancy forces in self-circulation systems, a second mass transfer mechanism superimposes and may be the controlling one [7, 8]. In both mechanisms, the temperature within the boundary layer only affects the substance properties. Small variations exert little effect on mass transfer, and that is probably the reason why the question of the electrode temperature has not attracted much scientific interest.

Recently, it has been shown that in the lower range of the current density a mechanism is effective which had hitherto been disregarded at gas evolving electrodes, i.e. free convection in the liquid phase [9]. As usual, this mechanism is controlled by gradients of temperature and of concentration in the liquid. It is the same liquid-phase free convection mentioned initially but now being active in a fluid system composed of a liquid–gas dispersion. The mechanism must not be confused with the two-phase free convection resulting from the buoyancy of the dispersion, a mechanism which has been discussed earlier [10].

In this context, the old open question of the overtemperature of electrodes deserves immediate interest. Usually, whenever values of the temperature of the electrode surface are required, they are simply assumed to be equal to the electrolyte bulk temperature. In few cases where the question of the overtemperature of electrodes was raised, the answers are contradictory. Breiter and Guggenberger [11] stated an overtemperature of the electrolyte in the vicinity of the electrode at elevated current densities, but quantitative information was not given. Ibl and Venczel [12] found a considerable overtemperature of a hydrogen evolving laboratory electrode at a current density near 20 kA $m^{-2}$ and estimated a value of roughly 2–4 K. Janssen and Hoogland [13] pointed out the possibility of a considerable heating of the diffusion layer at high current densities. In lack of reliable mass transfer coefficients Müller [14] calculated the overtemperature of a coated titanium anode (at 10 kA $m^{-2}$) and obtained about 200 K. Thanos [15] calculated a temperature difference of 5 K (at 6 kA $m^{-2}$). An experimental investigation was carried out by Lewis *et al.* [16]. They concluded from results with a platinum wire electrode which was used as a resistance thermometer that up to current densities of 5 kA $m^{-2}$

## NOMENCLATURE

| | |
|---|---|
| $A$ | electrode surface area [$m^2$] |
| $c$ | concentration [$mol\ m^{-3}$] |
| $d$ | bubble break-off diameter [m] |
| $D$ | diffusion coefficient [$m^2 s^{-1}$] |
| $F$ | Faraday constant, 96 487 A s $mol^{-1}$ |
| $f_G$ | gas evolution efficiency [–] |
| $g$ | acceleration of gravity [$m\ s^{-2}$] |
| $I$ | current [A] |
| $k$ | mass transfer coefficient [$m\ s^{-1}$] |
| $K$ | numerical constant, equation (2) |
| $K_m$ | migration factor [–] |
| $L$ | characteristic length in free convection [m] |
| $M$ | molar mass [$kg\ mol^{-1}$] |
| $n$ | charge number [–] |
| $N^{\blacksquare}$ | flux [$mol\ s^{-1}$] |
| $p$ | pressure [$kg\ m^{-1} s^{-2}$] |
| $Q^{\blacksquare}$ | Joule heat flux [W] |
| $R$ | universal gas constant, 8.3143 $kg\ m^2 s^{-2} mol^{-1} K^{-1}$ |
| $T$ | temperature [°C, K] |
| $U$ | electrode potential [V]. |

Greek symbols

| | |
|---|---|
| $\alpha$ | overall expansion coefficient [$m^3 mol^{-1}$] |
| $\alpha_i$ | expansion coefficient due to concentration, equation (12) [$m^3 mol^{-1}$] |
| $\beta$ | thermal expansion coefficient, equation (3) [$K^{-1}$] |
| $\varepsilon_i$ | current efficiency [–] |
| $\theta_\delta$ | effective shielding number [–] |
| $\theta_s$ | apparent shielding number [–] |
| $\lambda$ | thermal conductivity [$W\ m^{-1} K^{-1}$] |
| $\nu$ | stoichiometric number |
| $\nu_L$ | kinematic viscosity [$m^2 s^{-1}$] |
| $\rho$ | density [$kg\ m^{-3}$]. |

Dimensionless parameters

| | |
|---|---|
| $Ga$ | Galilei number, equation (4) |
| $Gr$ | Grashof number, equation (3) |
| $Nu$ | Nusselt number, equation (17) |
| $Pr$ | Prandtl number |
| $Re_G$ | Reynolds number of gas evolution, equation (8) |
| $Sc$ | Schmidt number, equation (5) |
| $Sh$ | Sherwood number, equation (6). |

Subscripts

| | |
|---|---|
| A | transferred ion ($H^+$) |
| B | dissolved gas ($H_2$) |
| c | critical |
| C | electrolyte ($H_2SO_4$) |
| D | solvent (water) |
| $i$ | substance, $i$ = A, B, C, D |
| s | single-phase |
| sat | saturation |
| w | electrode surface |
| $\infty$ | liquid bulk. |

the overtemperature raised by less than 3 K in acidic solutions and by 4 K in alkaline solutions. From careful experiments using thermoelements Krenz [17] obtained overtemperatures of less than 1 K for current densities up to 12 kA $m^{-2}$.

When comparing the mass transfer equation derived for liquid-phase free convection [9] with experimental data it was assumed that at gas evolving electrodes temperature gradients are negligible compared to concentration gradients [18]. Satisfactory agreement between theory and experiment could indeed be stated. It is the object of the present paper to verify the assumption by a quantitative investigation of the problem in order to get reliable ideas not only of the surface overtemperature but also of its effect on liquid-phase free convection.

## 2. DESIGN EQUATION FOR LIQUID-PHASE FREE CONVECTION AT GAS EVOLVING ELECTRODES

At electrodes, mass transfer of the reactant $A$ to the electrode surface is superimposed by mass transfer of the product $B$ from the surface. The flux density $N^{\blacksquare}_{iw}/A$ of any of these substances $i$ generated or consumed at the electrode is linked with the nominal electric current density $I/A$ by Faraday's law

$$\frac{N^{\blacksquare}_{iw}}{A} = k_i(c_{iw} - c_{i\infty}) = \frac{I/A\varepsilon_i}{(n/\nu_i)F}, \tag{1}$$

where $(n/\nu_i)$ is given by the reaction equation: the current efficiency $\varepsilon_i$ includes all possible losses of the substance $i$ due to competing electrode reactions and chemical reactions with the electrode or the liquid, and any absorption by or diffusion through the electrode [19, 20]. In many cases $\varepsilon_i = 1$ is a useful approximation.

In a single-phase fluid, free convective mass transfer is usually described by equations of the type

$$Sh_{si} \equiv \frac{k_{si}L}{D_i} = K_i(Gr\,Sc_i)^m \tag{2}$$

where $L$ denotes a characteristic length. The dimensionless groups are the Grashof number

$$Gr \equiv Ga\frac{\rho_\infty - \rho_w}{\rho_\infty} \tag{3}$$

with the Galilei number

$$Ga \equiv \frac{gL^3}{\nu_L^2} \tag{4}$$

and the Schmidt number

$$Sc_i \equiv \frac{\nu_L}{D_i}. \tag{5}$$

At gas evolving electrodes where the fluid phase is composed of a dispersion of liquid and gas bubbles, equation (1) must be extended for several reasons [9].

$$Sh_i \equiv \frac{k_i L}{D_i} = K_i (Gr\, Sc_i)^m (K_m)_i \frac{1-\theta_\delta}{1-2/3(f_G)_i} \tag{6}$$

where $\theta_\delta$ takes account of the fact that the electrode surface is partly covered by adhering bubbles and only a fraction is available for the mass flux in the electrode boundary layer [21]. $(f_G)_i$ has been introduced [2, 21] to account for the desorption of dissolved gas into adhering bubbles when transferred from the electrode surface to liquid bulk [22]. The migration factor $(K_m)_i$ considers the transport of electrically charged substances in the electric field [23a].

The density difference in equation (3) can be set proportional to the concentration difference of an arbitrarily selected transferred species, preferably the dissolved gas *B*,

$$\frac{\rho_\infty - \rho_w}{\rho_\infty} \equiv \alpha (c_{Bw} - c_{B\infty}) \tag{7}$$

where $\alpha$ represents an overall expansion coefficient which takes account of the combined effect of temperature and concentration gradients of reactant(s) and product(s) and which will be discussed below. Applying equations (1) and (6) to the substance *B* with the introduction of a Reynolds number of gas evolution [21]

$$Re_G \equiv \frac{(I/A)\varepsilon_B M_G d}{(n/\nu) F \rho_G \nu_L} \tag{8}$$

allows us to eliminate the concentration difference in equation (7) and to obtain a Grashof number

$$Gr = \left\{ Ga\, Re_G \frac{L \alpha \rho_G}{d M_G} Sc_B^{1-m} \frac{[1-2/3(f_G)_B]}{K_B(1-\theta_\delta)} \right\}^{1/(1+m)}. \tag{9}$$

Combining equations (6) and (9) and introducing the equation of state of the ideal gases yields an equation for liquid-phase free convection mass transfer of a substance *i* at gas evolving electrodes [9]:

$$Sh_i = K_i (K_m)_i \frac{(1-\theta_\delta)^{1/(1+m)}}{1-2/3(f_G)_i} \left[ Ga\, Re_G \frac{L}{d} \frac{\alpha p}{RT} \times Sc_i^{1+m} Sc_B^{1-m} \frac{[1-2/3(f_G)_B]}{K_B} \right]^{m/(1+m)}. \tag{10}$$

Particular attention is due to the expansion coefficient $\alpha$.

## 3. OVERALL EXPANSION COEFFICIENT

The density difference in equation (7) is affected by the temperature difference between liquid bulk and the electrode–electrolyte interface in addition to the corresponding concentration differences of all substances *i*.

$$\frac{\rho_\infty - \rho_w}{\rho_\infty} = -\sum \alpha_i (c_{i\infty} - c_w) - \beta (T_\infty - T_w) \tag{11}$$

where $\alpha_i$ represents the isothermal (and isobaric) expansion coefficient of the liquid at varying concentration of the solutes *i*

$$\alpha_i \equiv \rho \left( \frac{\partial(1/\rho)}{\partial c_i} \right)_{T,p} \tag{12}$$

and $\beta$ the thermal expansion coefficient at constant concentration (and pressure)

$$\beta \equiv \rho \left( \frac{\partial(1/\rho)}{\partial T} \right)_{c,p}. \tag{13}$$

As a typical example, the cathodic formation of hydrogen from sulfuric acid may be considered. The depletion of hydrogen ions (substance A) at the electrode–electrolyte interface caused by the reaction at the electrode corresponds to the enrichment of dissolved hydrogen (substance B). Owing to electroneutrality, the sulfuric acid (C) is diluted at the interface. The overall expansion coefficient comprises the concentration differences of B and C in addition to the temperature difference across the boundary layer. Equation (11) is written explicitly

$$\frac{\rho_\infty - \rho_w}{\rho_\infty} = \alpha_B (c_{Bw} - c_{B\infty}) + \alpha_C (c_{Cw} - c_{C\infty}) + \beta (T_w - T_\infty). \tag{14}$$

From comparison with equation (7) follows an expression of the overall expansion coefficient $\alpha$

$$\alpha = \alpha_B \left[ 1 + \frac{\alpha_C (c_{Cw} - c_{C\infty})}{\alpha_B (c_{Bw} - c_{B\infty})} \left( 1 + \frac{\beta (T_w - T_\infty)}{\alpha_C (c_{Cw} - c_{C\infty})} \right) \right]. \tag{15}$$

Three problems arise from equation (15) for practical application. The effect of the temperature contained in the last term has to be investigated. It must further be elucidated in which way the concentration differences are interrelated. Finally, reliable values of the expansion coefficients $\alpha_B$ and $\alpha_C$ have to be given.

### 3.1. *Thermal effect on* $\alpha$

The thermal effect on heat and mass transfer is mainly represented by the last term of equation (15). Whereas the expansion coefficients $\alpha_B$, $\alpha_C$, and $\beta$ are substance properties, the differences of temperature and of concentration depend on the operating conditions and are interrelated. The mass transfer equation (6) in application to the ionic reactant A with $(f_G)_A = 0$ is

$$Sh_A \equiv \frac{N^{\blacksquare}_{Aw} L}{A(c_{Aw} - c_{A\infty}) D_A} = K_A (Gr\, Sc_A)^m (K_m)_A (1 - \theta_\delta). \qquad (16)$$

With the corresponding heat transfer equation

$$Nu \equiv \frac{Q^{\blacksquare} L}{A(T_w - T_\infty)\lambda} = K_T (Gr\, Pr)^m (1 - \theta_\delta) \qquad (17)$$

results

$$\frac{T_w - T_\infty}{c_{Cw} - c_{C\infty}} = \frac{Q^{\blacksquare} D_A (K_M)_A}{N^{\blacksquare}_{Aw} \lambda} \left(\frac{Sc_A}{Pr}\right)^m \frac{K_A (c_{Aw} - c_{A\infty})}{K_T (c_{Cw} - c_{C\infty})} \qquad (18)$$

where the ratio of the concentration differences

$$\frac{c_{Aw} - c_{A\infty}}{c_{Cw} - c_{C\infty}} = 2 \qquad (19)$$

follows from the dissociation reaction

$$H_2SO_4 \rightarrow 2H^+ + SO_4^{2-} \qquad (20)$$

provided the fraction of dissociated acid does not vary noticeably across the boundary layer. Faraday's law allows us to introduce the current density $I/A$

$$\frac{N^{\blacksquare}_{Aw}}{A} = \frac{(I/A)\varepsilon_A}{(n/\nu_A)F} \qquad (21)$$

where $(n/\nu_A) = -1$ as seen from the charge transfer reaction

$$2H^+ + 2e^- \rightarrow H_2. \qquad (22)$$

Combining equations (18) and (21) under consideration of equation (19) results in

$$\frac{T_w - T_\infty}{c_{Cw} - c_{C\infty}} = -\frac{2F(Q^{\blacksquare}/A) D_A (K_m)_A}{(I/A)\lambda} \left(\frac{Sc_A}{Pr}\right)^m \frac{K_A}{K_T}. \qquad (23)$$

The boundary layer in free convection at gas evolving electrodes turned out to be laminar [9]. Hence, the exponent is $m = 0.25$, and the numerical values $K_A$ and $K_T$ may be calculated from [24]

$$K_i = [5(1 + Sc_i^{-0.5} + 0.5\, Sc_i^{-1})]^{-0.25} \qquad (24)$$

with $i = A$ and

$$K_T = [5(1 + Pr^{-0.5} + 0.5\, Pr^{-1})]^{-0.25}. \qquad (25)$$

Furthermore, supposing that heat is predominantly evolved at the electrode–electrolyte interface as a consequence of the overpotential $\Delta U$ (including amounts dissipated at or near the interface), i.e.

$$\frac{Q^{\blacksquare}}{A} = \frac{I}{A} \Delta U \qquad (26)$$

the last term in equation (15) results in

$$\frac{\beta(T_w - T_\infty)}{\alpha_C (c_{Cw} - c_{C\infty})} = -\frac{2\beta F \Delta U D_A (K_m)_A}{\alpha_C \lambda} \left(\frac{Sc_A}{Pr}\right)^m \frac{K_A}{K_T}. \qquad (27)$$

Table 1. Calculation data for evolution of hydrogen from 0.5 M sulfuric acid at 25°C

| | |
|---|---|
| $T$ | 25°C |
| $c_{C\infty}$ | 500 mol m$^{-3}$ |
| $c_{Bsat}$ | 0.72 mol m$^{-3}$ |
| $\rho$ | 1030 kg m$^{-3}$ |
| $\eta$ | $1.0 \times 10^{-3}$ kg m$^{-1}$ s$^{-1}$ |
| $\lambda$ | 0.50 W m$^{-1}$ K$^{-1}$ |
| $D_A$ | $1.8 \times 10^{-9}$ m$^2$ s$^{-1}$ |
| $D_B$ | $3.7 \times 10^{-9}$ m$^2$ s$^{-1}$ |
| $Sc_A$ | 540 |
| $Sc_B$ | 260 |
| $Pr$ | 9.3 |
| $\alpha_B$ | $+13 \times 10^{-6}$ m$^3$ mol$^{-1}$ |
| $\alpha_C$ | $-62 \times 10^{-6}$ m$^3$ mol$^{-1}$ |
| $\beta$ | $0.25 \times 10^{-3}$ K$^{-1}$ |
| $(K_m)_A$ | 1.5 |

Assuming an overpotential $\Delta U = 0.4$ V typical of platinum electrodes at a current density $I/A = 1000$ A m$^{-2}$ [23b] and inserting the data compiled in Table 1 yields

$$\frac{\beta(T_w - T_\infty)}{\alpha_C (c_{Cw} - c_{C\infty})} = 0.005 \ll 1. \qquad (28)$$

It is seen that the ratio is much smaller than unity. The result may be generalized since the physical properties in equation (27) do not vary considerably, at least in aqueous electrolyte solutions. The example shows typically that thermal effects on the overall expansion coefficient $\alpha$ are negligibly small even in cases of considerably larger values of the overpotential. Of course, this finding cannot be valid for electrodes operated as heating or cooling surfaces as used industrially where equation (26) does not hold. In all other cases, the expression of the overall expansion coefficient $\alpha$, equation (15), may be simplified without noticeable loss of accuracy:

$$\alpha = \alpha_B \left[1 + \frac{\alpha_C (c_{Cw} - c_{C\infty})}{\alpha_B (c_{Bw} - c_{B\infty})}\right]. \qquad (29)$$

### 3.2. *Elimination of the concentration from* $\alpha$

The concentration differences of the substances B and C in equation (29) are interrelated, as already pointed out earlier [25]. For the mass transfer of the dissolved gas B follows from equation (6) with $(K_m)_B = 0$ but under consideration of the desorption in the electrode bubble layer adjacent to the electrode, $(f_G)_B > 0$,

$$Sh_B \equiv \frac{N^{\blacksquare}_{Bw} L}{A(c_{Bw} - c_{B\infty}) D_B} = K_B (Gr\, Sc_B)^m \frac{1 - \theta_\delta}{1 - 2/3(f_G)_B}. \qquad (30)$$

With the ratio of the concentration differences of both transferred species from equation (1)

$$\frac{c_{\mathrm{Aw}}-c_{\mathrm{A}\infty}}{c_{\mathrm{Bw}}-c_{\mathrm{B}\infty}}=\frac{N^{\blacksquare}_{\mathrm{Aw}}k_{\mathrm{B}}}{N^{\blacksquare}_{\mathrm{Bw}}k_{\mathrm{A}}} \tag{31}$$

follows with equations (16) and (30)

$$\frac{c_{\mathrm{Cw}}-c_{\mathrm{C}\infty}}{c_{\mathrm{Bw}}-c_{\mathrm{B}\infty}}=\frac{(c_{\mathrm{Cw}}-c_{\mathrm{C}\infty})N^{\blacksquare}_{\mathrm{Aw}}}{(c_{\mathrm{Aw}}-c_{\mathrm{B}\infty})N^{\blacksquare}_{\mathrm{Bw}}} \times\left(\frac{D_{\mathrm{A}}}{D_{\mathrm{B}}}\right)^{m-1}\frac{1}{(K_{\mathrm{m}})_{\mathrm{A}}[1-2/3(f_{\mathrm{G}})_{\mathrm{B}}]}\frac{K_{\mathrm{B}}}{K_{\mathrm{A}}}. \tag{32}$$

With large Schmidt numbers as typical of electrolyte solutions, equation (24) gives $K_{\mathrm{B}}/K_{\mathrm{A}} = 1$, resulting in an overall expansion coefficient

$$\alpha=\alpha_{\mathrm{B}}+\alpha_{\mathrm{C}}\frac{(c_{\mathrm{Cw}}-c_{\mathrm{C}\infty})N^{\blacksquare}_{\mathrm{Aw}}}{(c_{\mathrm{Aw}}-c_{\mathrm{B}\infty})N^{\blacksquare}_{\mathrm{Bw}}} \times\left(\frac{D_{\mathrm{B}}}{D_{\mathrm{A}}}\right)^{1-m}\frac{1}{(K_{\mathrm{m}})_{\mathrm{A}}[1-2/3(f_{\mathrm{G}})_{\mathrm{B}}]}. \tag{33}$$

The ratio of the fluxes of the reactant and the product follows from the reaction equation, in the present example from equation (22),

$$\frac{N^{\blacksquare}_{\mathrm{Aw}}}{N^{\blacksquare}_{\mathrm{Bw}}}=-2. \tag{34}$$

The ratio of the concentration differences is given by equation (19), and for laminar free convection, $m = 0.25$, the expansion coefficient results with equations (19) and (34) in

$$\alpha=\alpha_{\mathrm{B}}-\alpha_{\mathrm{C}}\left(\frac{D_{\mathrm{B}}}{D_{\mathrm{A}}}\right)^{0.75}\frac{1}{(K_{\mathrm{m}})_{\mathrm{A}}[1-2/3(f_{\mathrm{G}})_{\mathrm{B}}]}. \tag{35}$$

It is seen that $\alpha$ consists of constant values except for the gas evolution efficiency, $(f_{\mathrm{G}})_{\mathrm{B}}$, which depends on the current density and may be estimated from [27]

$$(f_{\mathrm{G}})_{\mathrm{B}}=1-(1-\theta_{\mathrm{s}})^{2.5} \tag{36}$$

where $\theta_{\mathrm{s}}$ denotes the fraction of the electrode surface shielded by adhering bubbles in orthogonal projection [26] and can approximately be associated with $\theta_{\delta}$. For mean current densities $\theta_{\mathrm{s}}$ is calculated from [27]

$$\theta_{\mathrm{s}}=0.8\left[\frac{(I/A)}{(I/A)_{\mathrm{c}}}\right]^{0.25} \tag{37}$$

where $(I/A)_{\mathrm{c}}$ denotes the critical current density characteristic of the onset of a bubble film [4], $(I/A)_{\mathrm{c}} \approx 200\ \mathrm{kA\ m^{-2}}$ [5]. Values of $(f_{\mathrm{G}})_{\mathrm{B}}$ increases as the current density is increased; in the lower current density range where free convection prevails, $\alpha$ behaves approximately as a constant value.

### 3.3. *Individual expansion coefficients*

For the sulfuric acid (C) the expansion coefficient $\alpha_{\mathrm{C}}$ due to varying concentration can easily be calculated from available density data [28]. A problem arises for the product B, a gas dissolved in aqueous electrolyte solutions. Data of $\alpha_{\mathrm{B}}$ cannot be found in comprehensive data compilations, such as Landolt-Börnstein [28]. However, recently a prediction method has been derived permitting a satisfactorily reliable estimate of the required $\alpha_{\mathrm{B}}$ data for all gases in water and electrolyte solutions [29]. The method only requires the molar masses of the solute B (dissolved gas) and of the components of the electrolyte solution, C ($H_2SO_4$) and D (water), in addition to the critical data of the pure dissolved gas and of pure water:

$$\alpha_{\mathrm{B}}=\frac{1}{\rho_{\infty}}\left\{M_{\mathrm{D}}\frac{1+x_{\mathrm{C}}M_{\mathrm{C}}/(x_{\mathrm{D}}M_{\mathrm{D}})}{1+x_{\mathrm{C}}/x_{\mathrm{D}}} -M_{\mathrm{B}}\left[1-\frac{\rho_{\mathrm{Dc}}}{\rho_{\mathrm{Bc}}}\left(1-\frac{T_{\mathrm{Dc}}/p_{\mathrm{Dc}}}{T_{\mathrm{Bc}}/p_{\mathrm{Bc}}}\right)\right]\right\}. \tag{38}$$

The prediction equation (38) has been found to correlate experimentally obtained data with satisfactory accuracy [29].

## 4. THE RANGE OF SINGLE-PHASE FREE CONVECTION

With the aid of equations (33) and (37) the mass transfer coefficient for single-phase free convection can be calculated from equation (10). It must be noted that the characteristic length $L$ is not given by the overall dimensions of the electrode but by the mean distance between the adhering bubbles protruding from the concentration boundary layer. From a geometrical consideration it follows

$$\frac{L}{d}=\frac{0.7}{\theta_{\mathrm{s}}^{0.5}}-0.5 \tag{39}$$

valid for electrodes the dimensions of which are larger than $L$, i.e. practically all electrodes, because the mean bubble break-off diameter $d$ is much smaller at electrodes than in nucleate boiling. It has been found to depend on the shielding number $\theta_{\mathrm{s}}$ [30] and may be estimated from

$$d=\left[50^2+\left(\frac{10}{\theta_{\mathrm{s}}}\right)^2\right]^{0.5}\ \mu\mathrm{m}. \tag{40}$$

Results are shown in Fig. 1 using data compiled in Table 1 for hydrogen evolution from sulfuric acid at a platinum electrode. These are the conditions applied by Shibata [31] in experiment, the results of which are also shown in Fig. 1.

Two ranges are clearly discernible characterizing different mass transfer mechanisms. It is seen that up to a current density of about $1000\ \mathrm{A\ m^{-2}}$, the agreement between the measured data points and the calculated line is satisfactory. Under the present conditions this is the upper limit of liquid-phase free convection. With larger values of the current density, bubble-induced microconvection prevails. In this upper range the experimental data were shown to be

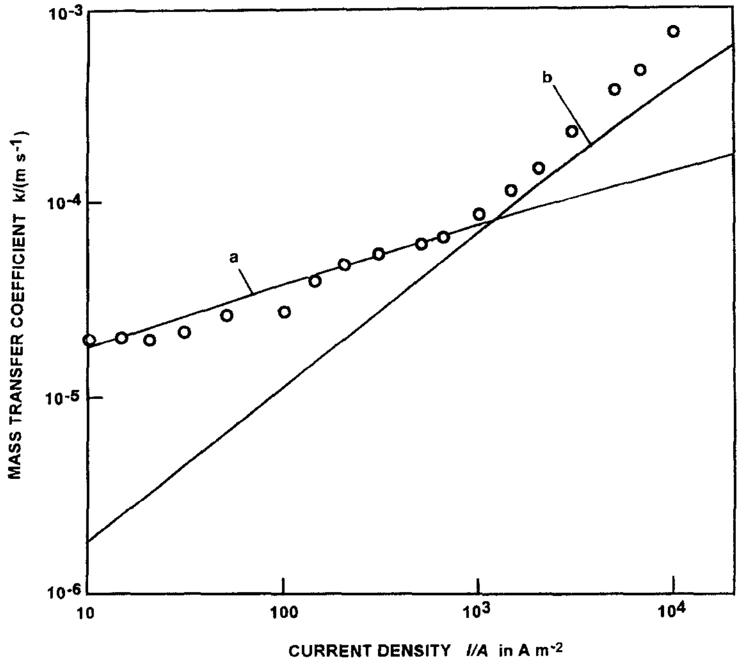

FIG. 1. Experimental data of the mass transfer coefficient in comparison with mass transfer equations. Hydrogen evolution from sulfuric acid at 25°C at a platinum cathode. ○—Shibata [31], corrected for interfacial dilution of sulfuric acid [33]. a—Liquid-phase free convection, equation (10); b—bubble-induced microconvection, equation (41).

satisfactorily correlated by the mass transfer equation [9, 32]

$$Sh_i \equiv \frac{k_i d}{D_i}$$

$$= 1.89\frac{[Re_{\mathrm{G}}(f_{\mathrm{G}})_{\mathrm{B}}]^{0.5}Sc_i^{0.487}[\theta_{\mathrm{s}}^{0.5}(1-\theta_{\mathrm{s}}^{0.5})]^{0.5}}{1-2/3(f_{\mathrm{G}})_i}(K_{\mathrm{m}})_i. \tag{41}$$

The agreement additionally supports the above finding that temperature effects in single-phase free convection are negligible confirming an assumption made earlier [18].

## 5. ESTIMATE OF THE OVERTEMPERATURE

An estimate of the overtemperature of the electrode surface is easily possible by combination of equations (17) and (30) resulting in

$$\frac{T_{\mathrm{w}}-T_{\infty}}{c_{\mathrm{Bw}}-c_{\mathrm{B}\infty}} = \frac{Q^{\blacksquare}D_{\mathrm{B}}}{N^{\blacksquare}_{\mathrm{Bw}}\lambda}\left(\frac{Sc_{\mathrm{B}}}{Pr}\right)^{0.25}\frac{K_{\mathrm{B}}}{K_{\mathrm{T}}[1-2/3(f_{\mathrm{G}})_{\mathrm{B}}]}. \tag{42}$$

Consideration of equations (1) and (26) gives

$$\frac{T_{\mathrm{w}}-T_{\infty}}{c_{\mathrm{Bw}}-c_{\mathrm{B}\infty}} = \frac{\Delta U(n/\nu_{\mathrm{B}})FD_{\mathrm{B}}}{\varepsilon_{\mathrm{B}}\lambda}\left(\frac{Sc_{\mathrm{B}}}{Pr}\right)^{0.25}\frac{K_{\mathrm{B}}}{K_{\mathrm{T}}[1-2/3(f_{\mathrm{G}})_{\mathrm{B}}]}. \tag{43}$$

Inserting a supersaturation $c_{\mathrm{Bw}}-c_{\mathrm{B}\infty} = 59$ mol m$^{-3}$ at a current density of 1000 A m$^{-2}$ as obtained experimentally by Shibata [31] and corrected by Vogt [33], together again with $\Delta U = 0.4$ V and $K_{\mathrm{B}}/K_{\mathrm{T}} = 1.07$ and with the properties of Table 1 yields an overtemperature

$$T_{\mathrm{w}}-T_{\infty} = 0.1 \text{ K}.$$

This value, although amazingly small, reflects the correct order of magnitude. From experiment, Krenz [17] obtained an overtemperature of 0.15 K at a platinated platinum electrode in a different electrolyte liquid but at the same temperature and current density. One must conclude that much larger values of the overtemperature as reported in the older literature and based on rough estimates are not compatible with reality. The agreement with the experimental value obtained by Krenz also supports the finding of the superiority of the concentration gradients on thermal effects.

## 6. CONCLUSIONS

1. In absence of forced flow, mass and heat transfer at gas evolving electrodes up to mean current densities of about 1000 A m$^{-2}$ are controlled by liquid-phase free convection, although gas evolution is active in the whole range of current densities. It is not compatible with reality to use equations representative of bubble-induced heat and mass transfer in the total current density range as has usually been done.

2. In free convective mass transfer at gas evolving electrodes, temperature gradients are of a subordinate, probably always negligible effect compared

to the effect of concentration differences caused by reactants as well as by the produced dissolved gas.

3. A heat transfer calculation evidences that overtemperatures of electrode surfaces are much smaller than assumed in the older literature.

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