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Mechanisms of mass transfer of dissolved gas from a gas-evolving electrode and their effect on mass transfer coefficient and concentration overpotential*

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Dissolved gases in the boundary layer of gas-evolving electrodes, in contrast to all other substances generated or consumed at electrodes, undergo two superimposed mass transfer mechanisms. Their interaction results in an increase of the effective mass transfer coefficient of dissolved gas. A correction factor to the coefficient calculated from available mass transfer equations is proposed. The effect on the concentration overpotential is discussed.

Nomenclature

a	distance, Fig. 2 (m)
A	electrode area (m^2)
A'	liquid cross-sectional area (m^2)
c	concentration of dissolved gas ($mol\,m^{-3}$)
C	correction factor, Equation 5
C_l	quotient, Equation 32
d	bubble diameter (m)
D	diffusion coefficient ($m^2\,s^{-1}$)
f_G	efficiency of gas evolution, Equation 2
F	Faraday constant, $F = 96\,487\,A\,s\,mol^{-1}$
Fo'	Fourier number, Equation 16
j	current density ($A\,m^{-2}$)
k	mass transfer coefficient at electrode ($m\,s^{-1}$)
k_b	mass transfer coefficient at bubble–liquid interface ($m\,s^{-1}$)
n/v	charge number of production of dissolved gas
N	flux density of dissolved gas ($mol\,m^{-2}\,s^{-1}$)
$N^{\square}$	flux of dissolved gas ($mol\,s^{-1}$)
p	pressure ($kg\,m^{-1}\,s^{-2}$)
r	radius, Fig. 2 (m)
R	bubble radius (m)
R_b	radius of detaching bubble (m)
R_m	gas constant, $R_m = 8.314\,kg\,m^2\,s^{-2}\,mol^{-1}\,K^{-1}$
t	time (s)
t_b	residence time (s)
T	temperature (K)
u	perimeter (m)
y	distance from electrode surface (m)
z	number of free bubbles
z_b	number of adhering bubbles
γ	interfacial tension ($kg\,s^{-2}$)
δ_c	bubble layer thickness (m)
δ_N	Nernst diffusion layer thickness (m)
ε	gas volume fraction
θ_s	shielding factor
ν_L	kinematic viscosity of liquid ($m^2\,s^{-1}$)
ϱ	density ($kg\,m^{-3}$)

Subscripts

b	bubble–liquid interface
e	electrode–liquid interface
G	gas
L	liquid
s	saturation
o	bulk

1. Introduction

For estimation of the rate of mass transfer to or from gas-evolving electrodes several design equations are available [1, 2], and these equations have proved useful in applied electrochemistry. However, it has obviously not been noted that these equations only apply to those substances the flux of which does not vary with distance through the electrode boundary layer.

This condition is well fulfilled for indicator ions as used in mass transfer experiments. The available mass transfer equations are also useful for many substances in industrial electrochemistry, if homogeneous reactions do not occur. But the condition of constant flux in the boundary layer is not fulfilled for an important case, namely the transport of dissolved gas formed at the electrode to the liquid bulk.

Mass transfer equations are also used to calculate the concentration of dissolved gas in an electrolyte immediately adjacent to the electrode [3–5]. Although this procedure is common practice it cannot be considered satisfactory. As shown below, it can lead to substantial inaccuracy. The problem is particularly important in the estimation of the concentration overpotential of gas-evolving electrodes, a problem which

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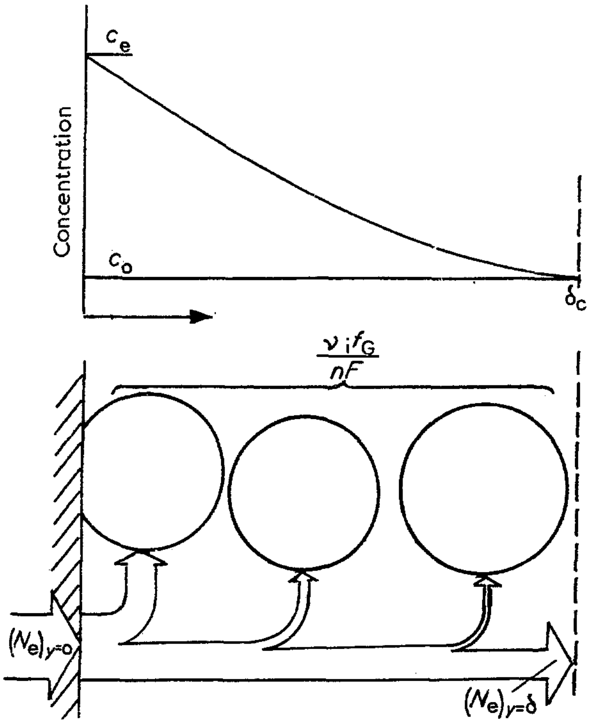

Fig. 1. Desorption in the concentration boundary layer of a gas-evolving electrode.

has attracted increasing interest mainly in connexion with the development of electrodes, the overpotentials of which are virtually controlled by concentration overpotential alone [6-8].

It is the object of the present paper to analyse how the available mass transfer equations should be modified to make them equally applicable to dissolved gases and, with respect to the concentration overpotential, how the concentration of dissolved gas immediately at the electrode is affected.

2. The two competing mass transfer mechanisms

It is a characteristic of dissolved gas that two mass transfer mechanisms are active in the concentration boundary layer adjacent to the electrode. One controls the flux of dissolved gas from the electrode to the liquid bulk, the other controls the flux from the supersaturated liquid to the liquid–gas interface of bubbles present in the concentration boundary layer of the electrode. This desorption means that the flux, $N_e^{\square}$, of dissolved gas from the electrode to the liquid bulk varies with the distance from the electrode surface (Fig. 1). At a distance y it is

$$N_e = \frac{N_e^{\square}}{A} = \frac{j}{(n/\nu)F} - \frac{1}{A}\int_0^y \mathrm{d}N_b^{\square} \tag{1}$$

where $N_b^{\square}$ denotes the flux to the gas–liquid interface where the dissolved gas is transferred to the gaseous phase. The (partial) current density j is that generating dissolved gas. We introduce a value f_G determining the fraction of dissolved gas which is desorbed within the total concentration boundary layer of the electrode.

$$f_G = \frac{(n/\nu)F}{jA}\int_0^{\delta_c} \mathrm{d}N_b^{\square} \tag{2}$$

This important quantity, the efficiency of gas evolution, $0 \leqslant f_G \leqslant 1$, is known to increase as the bubble population density on the electrode increases – commonly linked with an increase of the current density. Values of f_G were calculated [3, 20] and measured [18, 19, 26] but at present a general, reliable correlation is not available. Nevertheless, f_G can here be used to express the flux density N_e; immediately at the electrode, $y = 0$, it equals the total amount of dissolved gas generated

$$(N_e)_{y=0} = \frac{j}{(n/\nu)F} \tag{3a}$$

At the inner edge of the boundary layer, $y = \delta_c$, it is lowered to

$$(N_e)_{y=\delta_c} = \frac{j}{(n/\nu)F}(1 - f_G) \tag{3b}$$

For all substances which do not react and/or are not desorbed in the electrode boundary layer, the flux is constant at all distances within the boundary layer and equals that leaving (or reaching) the electrode surface. Mass transfer at electrodes can, therefore, be described by the common form

$$(N_e)_{y=0} = (N_e)_{y=\delta_c} = \frac{j}{(n/\nu)F} = k(c_e - c_0) \tag{4}$$

However, for a dissolved gas an extension of Equation 4 is required taking account of the flux variation:

$$\frac{j}{(n/\nu)F} = Ck(c_e - c_0) \tag{5}$$

C is a new correction factor to the mass transfer coefficient k as calculated from available mass transfer equations, e.g. [27]

$$\begin{aligned} Sh &= \frac{kd}{D} = 0.93 Re^{0.5} Sc^{0.487} \\ &= 0.93\left(\frac{jf_G R_m T d}{(n/\nu)Fp\nu_L}\right)^{0.5}\left(\frac{\nu_L}{D}\right)^{0.487} \end{aligned} \tag{6}$$

Equations 3a and 3b show the limits of the correction factor:

$$1 \leqslant C \leqslant (1 - f_G)^{-1} \tag{7}$$

3. Desorption in the electrode boundary layer

The flux $\mathrm{d}N_b^{\square}$ desorbed in the boundary layer adjacent to the electrode can generally be written

$$\mathrm{d}N_b^{\square} = k_b\,\mathrm{d}A_b\,(c - c_b) \tag{8}$$

where the mass transfer coefficient, k_b, refers to the gas–liquid interface of bubbles in the electrode boundary layer. c_b is the interfacial concentration of dissolved gas. Due to the curvature of the interface, c_b is larger than the saturation concentration, c_s, at a planar interface [1]

$$\frac{c_b}{c_s} = 1 + \frac{2\gamma}{Rp}\frac{\varrho_L}{\varrho_L - \varrho_G} \tag{9}$$

However, introducing realistic values of the bubble radius, R, shows that the difference of these concentrations is small, $(c_b - c_s)/c_s \ll 1$, and commonly it is not detrimental to assume that the interfacial concentration equals the saturation concentration.

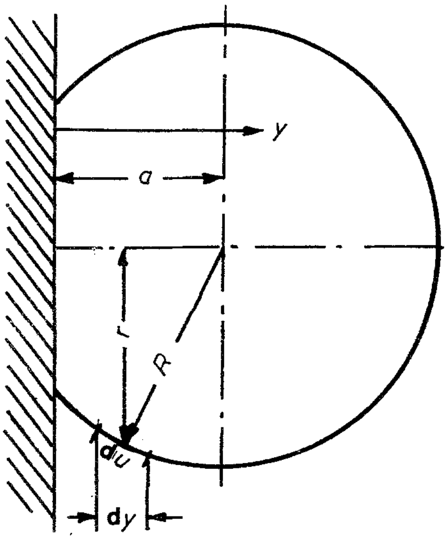

Fig. 2. Geometry of an adhering bubble.

The concentration of dissolved gas remote from the gas–liquid interface (but inside the electrode boundary layer) is controlled by mass transfer from the electrode to the liquid bulk and varies with the distance from the electrode. In this paper we will refer to the Nernst diffusion layer starting from an assumed concentration profile

$$c = c_e - (c_e - c_0)\frac{y}{\delta_N} \tag{10}$$

where c_e denotes the concentration at the electrode, $y = 0$, and c_0 the bulk concentration at $y = \delta_N$. It must be kept in mind that the concentration field around each bubble near the electrode is superimposed on the field in the electrode boundary layer as already discussed earlier [9, 10]. Using the Nernst diffusion layer involves the possibility of equating its thickness with the (not explicitly defined) boundary layer thickness of the electrode,

$$\delta_c = \delta_N \tag{11}$$

and Equation 2 takes the form

$$f_G = \frac{(n/v)F}{jA}\int_0^{\delta_N} dN_b^{\square} \tag{12}$$

A special problem is the active mass transfer area A_b in Equation 8 which will be treated differently for two cases: the Nernst diffusion layer thickness is either smaller or larger than the mean diameter of bubbles adhering to the electrode. In the first case, the area of bubbles before detachment from the electrode will be effective. In the second case, the mass transfer area will be furnished predominantly by freely moving bubbles in the bubble layer of the electrode.

3.1. *Small concentration boundary layer thickness*

The first case is characterized by the condition that the Nernst diffusion layer thickness is smaller than the mean height of adhering bubbles (Fig. 2).

$$\delta_N/(a + R) < 1 \tag{13}$$

It is assumed that the flux of dissolved gas to the bubble is essentially parallel to the electrode surface. Assuming the bubble to have spherical form, a geometrical consideration yields

$$dA_b = 2\pi r\, du = 2\pi R\, dy \tag{14}$$

The bubble radius depends on time. During the residence time, t_b, of one bubble, the amount of desorbed gas referred to the electrode area A/z_b appertaining to one adhering bubble is

$$\frac{d^2 N_b}{dt dy} = \frac{k_b}{t_b}\frac{2\pi R(t)}{A/z_b}[c(y) - c_b] \tag{15}$$

where z_b denotes the number of simultaneously adhering bubbles to a (sufficiently large) electrode surface area A. Except for the very short initial period of bubble growth, the growth law can be expressed through the constant Fourier number for mass transport condition [1, 11]

$$Fo' = \frac{Dt}{R^2} = \frac{Dt_b}{R_b^2} \tag{16}$$

where R_b is the radius of the detaching bubble. The flux of desorbed gas is thus

$$\frac{dN_b^{\square}}{dy} = k_b \frac{4}{3}\frac{\pi R_b (c_e - c_b)}{A/z_b}\left(1 - \frac{c_e - c_0}{c_e - c_b}\frac{y}{\delta_N}\right) \tag{17}$$

3.2. *Large concentration boundary layer thickness*

In the opposite case,

$$\delta_N/(a + R) > 1 \tag{18}$$

mass transfer of dissolved gas to the adhering bubbles becomes less important as compared with the mass transfer to freely moving bubbles in the concentration boundary layer adjacent to the electrodes. The mass transfer area, i.e. the gas–liquid interfacial area, depends on the bubble distribution inside the gas bubble layer. In general, this layer thickness, δ_b, need not coincide with the Nernst diffusion layer thickness but may extend over it, $\delta_b/\delta_N \geqslant 1$. The active mass transfer area can be estimated by use of a volume fraction, ε, of gas bubbles in the bubble layer,

$$\varepsilon = \frac{(\pi/6)d^3}{\Delta y A/z} \tag{19}$$

By definition, $\Delta yA/z$ is the average volume containing one bubble, if a number z of such cubes covers the total electrode area A (Fig. 3). With the bubble–liquid interfacial area of one bubble,

$$\Delta A_b/z = \pi d^2 \tag{20}$$

one obtains on transition to the differential form

$$\frac{dA_b}{A dy} = \frac{6\varepsilon}{d} \tag{21}$$

An assumption is necessary for the profile of the void fraction, ε, within the bubble layer of thickness δ_b. Experimental investigation shows that the void fraction varies non-linearly with the distance [12], and a non-linear profile is also taken into account in

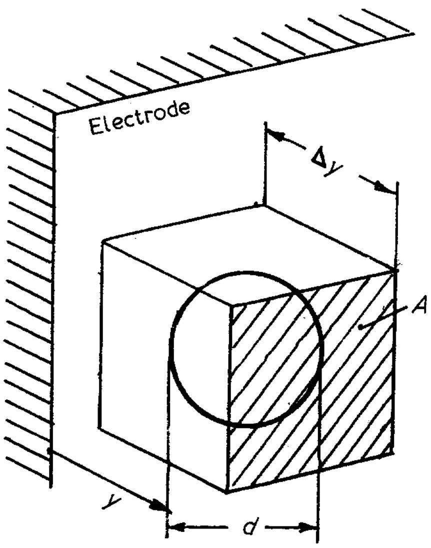

Fig. 3. Geometry of a free bubble near the electrode.

theoretical investigations [13–15]. But here a linear profile will be assumed not least with respect to the linear concentration profile used. We set

$$\varepsilon = \varepsilon_e(1 - y/\delta_b) \qquad (22)$$

for the range $0 \leqslant y/\delta_b \leqslant 1$.

Inserting Equations 10, 21 and 22 into 8 one obtains the flux of desorbed gas

$$\frac{dN_b^\square}{dy} = k_b \frac{6\varepsilon_e A}{d}(c_e - c_0)\left(1 - \frac{c_e - c_0}{c_e - c_b}\frac{y}{\delta_N}\right) \times \left(1 - \frac{y}{\delta_b}\right) \qquad (23)$$

4. Mass transfer from the electrode to the bulk

Using the Nernst diffusion layer allows application of Fick's first law to the transport of dissolved gas from the electrode to the liquid bulk:

$$\frac{N_e^\square}{A'} = -D\frac{dc}{dy} \qquad (24)$$

where A' represents the area available for mass transfer to the bulk. This is the area not blocked by bubbles. In case I of adhering bubbles,

$$A' \approx (1 - \theta_s)A \qquad (25)$$

yields

$$\frac{N_e^\square}{A} = -D(1 - \theta_s)\frac{dc}{dy} \qquad (26)$$

θ_s denotes the shielding factor, i.e. the fraction of the electrode area shadowed by adhering bubbles in orthogonal projection. In case II, the area A' not blocked by freely moving bubbles depends on the void fraction ε and varies with the distance from the electrode, Equation 22. By analogy to the effective conductivity of a dispersion of gas bubbles in electrolyte, as given by Maxwell [16] and Rayleigh [17], the are A' may be approximated by

$$A' = (1 - 1.5\varepsilon)A \qquad (27)$$

Equation 27 with Equation 22 leads to

$$\frac{N_e^\square}{A} = -D\left[1 - 1.5\varepsilon_e\left(1 - \frac{y}{\delta_b}\right)\right]\frac{dc}{dy} \qquad (29)$$

On the other hand, the flux density can be expressed by combining Equations 1 and 12:

$$\frac{N_e^\square}{A} = \frac{j}{(n/\nu)F}\left[1 - f_G\frac{\int_0^y dN_b^\square}{\int_0^{\delta_N} dN_b^\square}\right] \qquad (30)$$

Inserting Equation 17 yields after integration with k_b = constant for case I

$$\frac{N_e^\square}{A} = N_e = \frac{j}{(n/\nu)F}\left[1 - f_G\frac{y}{\delta_N}\frac{2 - C_1\, y/\delta_N}{2 - C_1}\right] \qquad (31)$$

with the abbreviation

$$C_1 \equiv \frac{c_e - c_0}{c_e - c_b} \qquad (32)$$

For case II one obtains from Equation 30 with Equation 23

$$\frac{N_e^\square}{A} = N_e = \frac{j}{(n/\nu)F} \times \left[1 - f_G\frac{y}{\delta_N}\frac{2 - \frac{y}{\delta_b} - C_1\frac{y}{\delta_N}\left(1 - \frac{2}{3}\frac{y}{\delta_b}\right)}{2 - \frac{\delta_N}{\delta_b} - C_1\left(1 - \frac{2}{3}\frac{\delta_N}{\delta_b}\right)}\right] \qquad (33)$$

Combination of Equations 26 and 31 for case I and of 29 and 33 for case II presents a basis for determining the concentration profiles within the Nernst diffusion layer.

5. Modified mass transfer coefficient

Equation 5 is a generalized mass transfer equation,

$$(N_e)_{y=0} = \frac{j}{(n/\nu)F} = (Ck)(c_e - c_0)$$

where (Ck) represents a modified mass transfer coefficient suitable for all transported substances including dissolved gases. To obtain expressions of the correction factor C, three different conditions will be studied.

5.1. *The Nernst diffusion layer is smaller than the diameter of adhering bubbles*

This condition refers to case I and is related to large current densities with correspondingly large mass transfer coefficients. Combination of Equations 26 and 31 yields, after integration with the boundary condition

$$c = c_0 \quad \text{at} \quad y = \delta_N$$

a modified concentration profile

$$\frac{D}{\delta_N}(1-\theta_s)\frac{(n/\nu)F}{j}(c-c_0) = 1 - \frac{y}{\delta_N} - f_G\frac{1-\frac{C_1}{3}-\left(\frac{y}{\delta_N}\right)^2\left(1-\frac{C_1}{3}\frac{y}{\delta_N}\right)}{2-C_1} \tag{34}$$

For the special condition

$$c = c_e \quad \text{at} \quad y = 0$$

Equation 34 reduces to

$$\frac{D}{\delta_N}(1-\theta_s)\frac{(n/\nu)F}{j}(c_e-c_0) = 1 - \frac{1-\frac{C_1}{3}}{2-C_1}f_G \tag{35}$$

The special mass transfer equation of a non-desorbed substance is Equation 4; Equation 35 must coincide with Equation 4 for $f_G = 0$. The mass transfer coefficient is therefore

$$k = \frac{D}{\delta_N}(1-\theta_s) \tag{36}$$

The general mass transfer Equation 5 here extended for the first time to substances desorbed in the boundary layer, is thus

$$\frac{(n/\nu)F}{j}k(c_e-c_0) = 1 - \frac{1-C_1/3}{2-C_1}f_G \tag{37}$$

A calculation of the bulk concentration of electrolytes in a cell with gas-evolving electrodes yields values of c_0 which can be substantially larger than the saturation concentration c_s [19]. However, experimental investigations of the gas concentration, c_e, at the electrode–electrolyte interface show that, except for very low current densities, c_e is always much larger than c_s [5, 17–19]. One must conclude that $c_e/c_s \gg c_0/c_s > 1$ for the range of current density of interest. The ratio, C_1 of the concentration differences is only slightly smaller than unity:

$$C_1 \equiv \frac{c_e - c_0}{c_e - c_b} \approx 1 \tag{38}$$

With this simplification the modifed mass transfer coefficient (Ck) thus reduces to

$$(Ck) = \frac{k}{1-\frac{2}{3}f_G} \tag{39}$$

where k is the value calculated from available mass transfer equations, e.g. from Equation 6. It is further confirmed that the desired multiplier

$$C = (1-\tfrac{2}{3}f_G)^{-1} \tag{40}$$

is situated within the limits given by the inequality 7.

5.2. *The Nernst diffusion layer thickness is much smaller than the thickness of the bubble layer but larger than the bubble diameter*

The condition $\delta_N \ll \delta_b$ means that the concentration, c_0, is attained at a distance, y, far lower than the thickness of the bubble layer at the electrode. This case becomes the more important the larger the current density, linked not only with larger mass transfer coefficients, but also with larger values of f_G. One must, therefore, expect small values of δ_N together with large values of δ_b. However, the thickness δ_b is not only controlled by the current density but also by hydrodynamics [14].

Combination of Equation 29 and 33 with $y/\delta_b \leq \delta_N/\delta_b \ll 1$ and under consideration of Equation 38 gives the simple form

$$-D(1-1.5\varepsilon_e)\frac{(n/\nu)F}{j}\frac{\mathrm{d}c}{\mathrm{d}y} = 1 - 2f_G\frac{y}{\delta_N}\left(1-\frac{y}{2\delta_N}\right) \tag{41}$$

Integration with the boundary condition

$$c = c_0 \quad \text{at} \quad y = \delta_N$$

yields

$$\frac{D}{\delta_N}(1-1.5\varepsilon_e)\frac{(n/\nu)F}{j}(c-c_0) = 1 - \frac{y}{\delta_N} - f_G\left[\frac{2}{3}-\left(\frac{y}{\delta_N}\right)^2\left(1-\frac{y}{3\delta_N}\right)\right] \tag{42}$$

Using the same procedure as in the previous section, one obtains with the condition

$$c = c_e \quad \text{at} \quad y = 0$$

$$\frac{D}{\delta_N}(1-1.5\varepsilon_e)\frac{(n/\nu)F}{j}(c_e-c_0) = 1 - \tfrac{2}{3}f_G \tag{43}$$

Irrespective of the fact that the mass transfer coefficient is now

$$k = \frac{D}{\delta_N}(1-1.5\varepsilon_e) \tag{44}$$

one finds the same correction factor to the mass transfer coefficient:

$$C = (1-\tfrac{2}{3}f_G)^{-1} \tag{45}$$

5.3. *The Nernst diffusion layer thickness equals the thickness of the bubble layer*

For the limiting condition $\delta_N/\delta_b = 1$, the concentration of disolved gas varies throughout the whole bubble layer and attains the bulk concentration c_0 at $y = \delta_b$. Combination of Equations 29, 33 and 38 with the condition $\delta_N/\delta_b = 1$ results in

$$-D\left[1-1.5\varepsilon_e\left(1-\frac{y}{\delta_N}\right)\right]\frac{(n/\nu)F}{j}\frac{\mathrm{d}c}{\mathrm{d}y} = 1 - 3f_G\frac{y}{\delta_N}\left[1-\frac{y}{\delta_N}+\frac{1}{3}\left(\frac{y}{\delta_N}\right)^2\right] \tag{46}$$

For the sake of simplicity, we use an approximation

$$\left[1-1.5\varepsilon_e\left(1-\frac{y}{\delta_n}\right)\right]^{-1} \approx 1 + 2\left[1.5\varepsilon_e\left(1-\frac{y}{\delta_N}\right)\right] \tag{47}$$

The inaccuracy of Equation 47 up to $\varepsilon_e < 0.4$ is smaller than 12% and appears acceptable for the present purpose. Integration of Equation 46 with 47 with consideration again of the boundary condition

$$c = c_0 \quad \text{at} \quad y = \delta_N$$

yields a concentration profile

$$\frac{D}{\delta_N}\frac{(n/v)F}{j}(c - c_0) = -\frac{\ln\left[1 - 1.5\varepsilon_e\left(1 - \frac{y}{\delta_N}\right)\right]}{1.5\varepsilon_e}$$
$$+ 3f_G\left\{\left(\frac{y}{\delta_N}\right)^2\left[(\tfrac{1}{2} + \tfrac{3}{2}\varepsilon_e) - (\tfrac{1}{3} + 2\varepsilon_e)\frac{y}{\delta_N}\right.\right.$$
$$\left.\left. + (\tfrac{1}{12} + \varepsilon_e)\left(\frac{y}{\delta_N}\right)^2 - \frac{\varepsilon_e}{5}\left(\frac{y}{\delta_N}\right)^3\right] - (\tfrac{1}{4} + 0.3\varepsilon_e)\right\} \tag{48}$$

The special form of Equation 48 for the conditions $f_G = 0$ and $c = c_e$ at $y = 0$ must coincide with Equation 4 and yields the expression

$$k = -\frac{D}{\delta_N}\frac{1.5\varepsilon_e}{\ln(1 - 1.5\varepsilon_e)} \tag{49}$$

for the mass transfer coefficient, Equation 6. Correspondingly, one obtains from Equation 48 together with Equation 49 a correction factor

$$C = \left[1 + \frac{9}{8}\frac{f_G\varepsilon_e(1 + 1.2\varepsilon_e)}{\ln(1 - 1.5\varepsilon_e)}\right]^{-1} \tag{50}$$

For the condition $\varepsilon_e \to 0$, the correction factor C approaches

$$C = (1 - 0.75f_G)^{-1} \tag{51}$$

In the range $\varepsilon_e < 0.4$ Equation 51 is an approximation of Equation 50 with a deviation of less than 4%.

6. Discussion

The effect of f_G on the correction factor C is shown in Fig. 4. All the three conditions studied yield exactly or nearly the same effect on the mass transfer coefficient. The result for desorption into adhering bubbles, Equation 40, agrees with the result for desorption into freely moving bubbles under the special condition of a small Nernst diffusion layer thickness as compared to the bubble layer thickness, Equation 45. If the thicknesses of both layers coincide, the factor C takes a more complex form, Equation 50, slightly depending on the gas void fraction ε_e. A further approximation yields Equation 51 which differs only slightly from the previous results. What is common to all these results is the finding that the mass transfer coefficient of dissolved gas differs from that of non-desorbed substances.

As a by-product, the analysis yields concentration profiles of dissolved gas within the Nernst diffusion layer (Fig. 5). One only needs to combine Equations 34 and 36, 42 and 44, or 48 and 49 for the three conditions under discussion. Although the numerical factor in Equations 40, 45 and 51 is loaded with some uncertainty, Fig. 5 shows that the concentration of the electrolyte immediately contacting the electrode is strongly affected by the gas yield, f_G. In predicting the concentration overpotential of gas-evolving electrodes it must be taken into account that increasing gas yield substantially lowers the wall concentration. The effect is particularly large at large current densities of nucleate gas evolution with correspondingly large f_G values [3, 18, 19]. As seen from Equation 40, if $f_G = 0.75$ the effective mass transfer coefficient is twice the uncorrected one. It is thus generally inadmissible to use an uncorrected mass transfer coefficient as

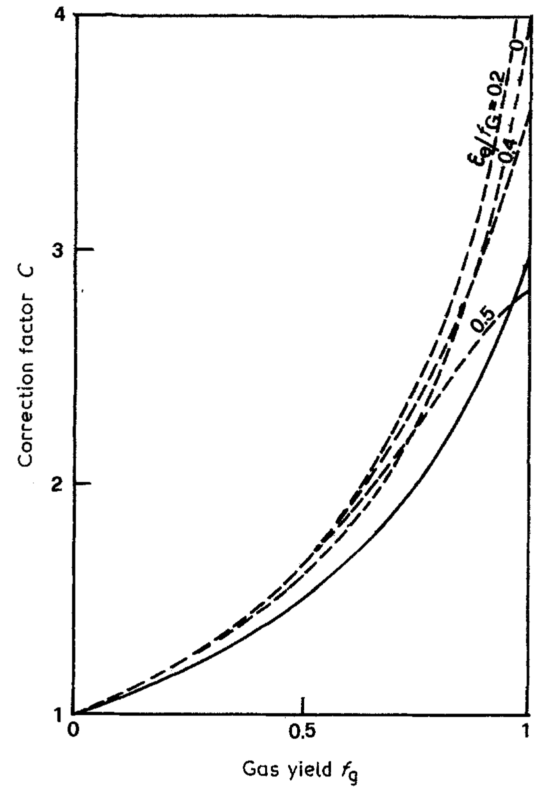

Fig. 4. Correction factor vs gas yield f_G. (——) Equations 40 and 45; (- - -) Equation 50.

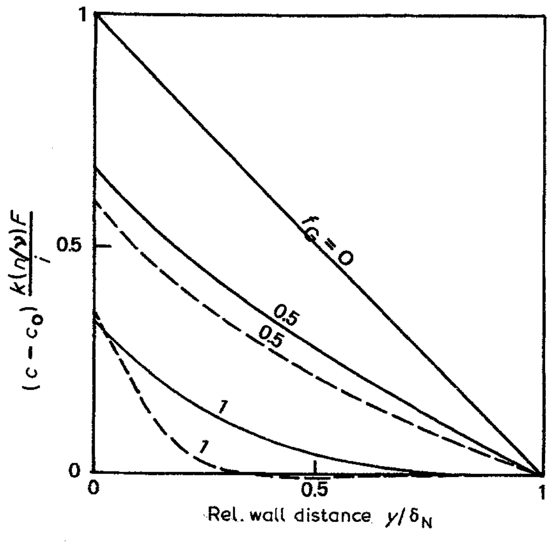

Fig. 5. Relative concentration profile in the Nernst diffusion layer. (——) Equations 34 and 36, $C_1 = 1$; (- - -) Equations 48 and 49.

calculated from available mass transfer equations if the concentration of dissolved gas has to be estimated.

The three conditions discussed are of further use in elucidating the meaning of the quantity f_G which has been introduced as an efficiency of gas evolution understood as the desorbed fraction of the total amount of dissolved gas generated [3, 20]. In case I, as discussed in Section 4, f_G represents the fraction passing over the bubble–liquid interface of gas bubbles adhering to a gas-evolving electrode. In contrast, in case II f_G includes the amount desorbed into freely moving bubbles contained in the bubble layer adjacent to the electrode. The f_G values differ, the second being larger than the first. And further, due to the fact that the bulk concentration, c_0, is larger than the gas–liquid interfacial concentration c_b [21–25], desorption continues (to a smaller extent) within the bubble layer remote from the electrode. It is not surprising that the values f_G obtained experimentally [18, 19] are larger than those calculated for adhering bubbles [3]. A more precise definition of the particular meaning of f_G thus becomes inevitable.

7. Conclusions

(1) Mass transfer of a dissolved gas from a gas-evolving electrode is distinguished from mass transfer of other substances in that the transport from the electrode–liquid interface to the bulk of liquid is supplemented by a second mass transfer of dissolved gas from the liquid to the gas–liquid interface of bubbles contained in the boundary layer adjacent to the electrode. Consequently, the flux of transferred dissolved gas varies with the distance from the electrode surface.

(2) Calculating the mass transfer coefficient for the transport of dissolved gas from a gas-evolving electrode requires a treatment different from that for other species. The mass transfer coefficient, k, as calculated from available mass transfer equations, e.g. Equation 6, must be modified to fit the particular mass transfer conditions.

(3) The present analysis gives an effective mass transfer coefficient (Ck), where the correction factor is

$$C = (1 - \tfrac{2}{3} f_G)^{-1} \geqslant 1$$

to be used in the generalized mass transfer Equation 6 for desorbed, as well as for non-desorbed, substances. For substances the flux of which is not affected by desorption or homogeneous chemical reactions on the way to or from the electrode a correction is not necessary. The condition $f_G = 0$ is that for which available mass transfer equations have been derived.

(4) The particular mass transfer mechanisms of dissolved gas effect a decrease of the electrode–electrolyte concentration of dissolved gas as compared to other substances. The correction factor, C, is an important quantity in estimating the concentration overpotential of gas-evolving electrodes.

References

[1] H. Vogt, in 'Comprehensive Treatise of Electrochemistry' (edited by E. Yeager, J. O'M. Bockris, B. E. Conway and S. Sarangapani), Plenum, New York (1983) Vol. 6, pp. 445–489.
[2] H. Vogt, in 'Ullmann's Encyclopedia of Industrial Chemistry', VCH, Weinheim (1987) Vol. A9, p. 195.
[3] H. Vogt, *Electrochim. Acta* **29** (1984) 167.
[4] L. J. J. Janssen, C. W. M. P. Sillen, E. Barendrecht and S. J. D. van Stralen, *Electrochim. Acta* **29** (1984) 633.
[5] L. J. J. Janssen and E. B. Barendrecht, *Electrochim. Acta* **30** (1985) 683.
[6] M. Ya. Bune, L. E. Chuvaeva and V. V. Losev, *Elektrokhim.* **23** (1987) 1249.
[7] M. Ya. Bune, L. E. Chuvaeva and V. V. Losev, *Elektrokhim.* **23** (1987) 1579.
[8] M. D. Spasojević, N. V. Krstajić and M. M. Jakšić, *J. Molec. Catal.* **40** (1987) 311.
[9] H. Vogt, *Electrochim. Acta* **25** (1980) 527.
[10] H. Vogt, *Chem-Ing.-Techn.* **52** (1980) 418.
[11] N. P. Brandon and G. H. Kelsall, *J. Appl. Electrochem.* **15** (1985) 475.
[12] H. Bergemann, K. Hertwig and I. Roušar, *Chem. Technik (Leipzig)* **39** (1987) 51.
[13] B. E. Bongenaar-Schlenter, Diss. Techn. Hogeschool Eindhoven (1984).
[14] H. Vogt, *Physicochem. Hydrodyn.* **8** (1987) 373.
[15] L. J. J. Janssen, *J. Appl. Electrochem.* **17** (1987) 1177.
[16] J. C. Maxwell, 'A Treatise on Electricity and Magnetism', 3rd edn, Clarendon Press, Oxford (1892) p. 440.
[17] Lord Rayleigh, *Phil. Mag.* **34** (1892) 481.
[18] L. Müller, M. Krenz and R. Landsberg, *J. Electroanal. Chem.* **180** (1984) 453.
[19] L. J. J. Janssen and E. Barendrecht, *Electrochim. Acta* **30** (1985) 683.
[20] H. Vogt, *Electrochim. Acta* **29** (1984) 175.
[21] V. A. Panov and Zh. A. Kravchenko, *Electrokhim.* **10** (1974) 1427; *Sov. Electrochem.* **10** (1974) 1366.
[22] I. V. Kadija, *J. Electrochem. Soc.* **127** (1980) 509.
[23] I. V. Kadija, *J. Electrochem. Soc.* **131** (1984) 601.
[24] H. Vogt, *Electrochim. Acta* **30** (1985) 265.
[25] B. Krause and H. Vogt, *J. Appl. Electrochem.* **15** (1985) 509.
[26] J. M. Chin Kwie Joe, L. J. J. Janssen, S. J. D. van Stralen, J. H. G. Verbunt and W. M. Sluyter, *Electrochim. Acta* **33** (1988) 769.
[27] K. Stephan and H. Vogt, *Electrochim. Acta* **24** (1979) 11.