

SHORT COMMUNICATION

Interfacial supersaturation at gas evolving electrodes

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Nomenclature

- c* concentration (mol m⁻³)
- D* diffusion coefficient (m s⁻²)
- F* Faraday constant (*F* = 96 487 A s mol⁻¹)
- f_G* gas evolution efficiency (-)
- j* nominal current density, (A m⁻²)
- k* mass transfer coefficient (m s⁻¹)
- K* numerical value (Equation 4)
- K_M* migration factor (-)
- n* charge number (-)
- R* universal gas constant (*R* = 8.3143 J mol⁻¹ K⁻¹)
- T* temperature (K)
- z* charge number (-)
- η_d* diffusion overpotential (V)
- θ_s* shielding number (-)
- ν* stoichiometric number (-)

Subscripts

- A transferred, reacting ion
- B dissolved gas
- C complementary ion to A, non-reacting
- e electrode
- s single-phase mass transfer
- sat saturation
- ∞ liquid bulk

1. Introduction

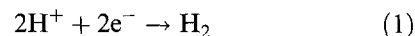
Numerous experimental investigations deal with supersaturation of dissolved gas at the electrode-liquid interface of gas evolving electrodes. The results are of great interest since they essentially contribute to elucidate the detailed events at all electrodes evolving gases. Shibata [1, 2] investigated the evolution of hydrogen from sulphuric acid at ambient temperature and found that the maximum concentration of dissolved hydrogen amounted to up to 177 times the saturation concentration, depending on the material and state of the electrode surface. At an oxygen evolving electrode a supersaturation ratio of 70 was found [3]. Losev and co-workers [4, 5] studied chlorine evolution from brine at 87° C, finding the interfacial concentration of dissolved chlorine to be 35 times the saturation concentration at the maximum current density investigated.

Both workers measured the diffusion overpotential as a function of the current density and calculated the supersaturation values from the Nernst equation. In both cases, it was tacitly assumed that the effect of the dilution of the electrolyte at the electrode-electrolyte

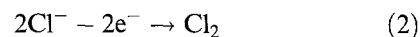
interface was negligible compared with the enrichment of dissolved gas. This view has been adopted without question in later investigations using Shibata's data [6-8] and appears plausible since the relative dilution of the reactants is doubtless much smaller than the enrichment of the products. However, with the aid of mass transfer equations it is possible to take account of the effect of the dilution of sulfuric acid in hydrogen evolution and of sodium chloride in chlorine evolution, respectively, at the interface on the diffusion overpotential in addition to the enrichment of dissolved gas. It can easily be shown that the dilution of the reactants must not be neglected at large values of the current density. The recalculated results presented below diverge substantially from those published in the original papers.

2. Theoretical

For the reactions of cathodic hydrogen formation



and of anodic chlorine formation



the Nernst equation taking account both of the species *A* transferred to the surface (hydrogen or chlorine ions) and of *B* transferred from the electrode surface (dissolved hydrogen or chlorine) reads

$$|\eta_d| = \frac{RT}{2F} \ln \left[\frac{c_{\text{Be}}}{c_{\text{B}\infty}} \left(\frac{c_{\text{Ae}}}{c_{\text{A}\infty}} \right)^{-2} \right] \\ = \frac{RT}{2F} \ln \left\{ \frac{c_{\text{Be}}}{c_{\text{B}\infty}} \left[1 + K \left(\frac{c_{\text{Be}}}{c_{\text{B}\infty}} - 1 \right) \right]^{-2} \right\} \quad (3)$$

where the abbreviation

$$K \equiv \frac{c_{\text{B}\infty}}{c_{\text{A}\infty}} \left(\frac{c_{\text{Ae}} - c_{\text{A}\infty}}{c_{\text{Be}} - c_{\text{B}\infty}} \right) \quad (4)$$

contains the concentration differences representative of mass transfer.

Generally, mass transfer of a species *i* to or from electrodes is defined by

$$\frac{\nu_i j}{nF} = k_i (c_{ie} - c_{i\infty}) \quad (5)$$

The mass transfer coefficient *k_i* is not simply the single-phase mass transfer coefficient, *k_{is}*, to be calculated from available mass transfer equations, but must be adapted to the particular conditions of gas evolving electrode by [9]

$$k_i = k_{is} K_{Mi} \frac{1 - \theta_s}{1 - 2f_{Gi}/3} \quad (6)$$

Table 1. Calculation data

	Evolution of	
	hydrogen [2] 0.5 M H ₂ SO ₄	chlorine [4] 4.3 M NaCl, PH 1.6
T/°C	25	87
c _{A∞} /mol m ⁻³	1000	4300
c _{Bsat} /mol m ⁻³	0.72	12
D _A /m ² s ⁻¹	1.8 × 10 ⁻⁹	3.8 × 10 ⁻⁹
D _B /m ² s ⁻¹	3.7 × 10 ⁻⁹	3.4 × 10 ⁻⁹
K _M	1.5	1.9

where K_M is a factor taking account of the effect of migration on overall mass transfer, e.g. $K_M = 1 - z_A/z_C$ in a single electrolyte; θ_s accounts for the fact that at gas evolving electrodes only the fraction $(1 - \theta_s)$ of the electrode surface is available for mass transfer in the concentration boundary layer. Finally, f_G considers that, owing to desorption of dissolved gas into bubbles adhering to the electrode surface, the rate of dissolved gas transferred to the liquid bulk varies across the boundary layer [10], whereas Equation 5 is based on a constant value.

For the present reactions application of Equation 6 to mass transfer of the reactant (species A) with $f_{GA} = 0$ gives

$$k_A = k_{As} K_M (1 - \theta_s) \quad (7)$$

and correspondingly for the product (species B) with $K_{MB} = 0$

$$k_B = k_{Bs} \frac{1 - \theta_s}{1 - 2f_G/3} \quad (8)$$

From equations 5, 7 and 8 the ratio of the concentration differences of both transferred species is

$$\frac{c_{Ae} - c_{A\infty}}{c_{Be} - c_{B\infty}} = \frac{\nu_A k_{Bs}}{\nu_B k_{As}} \frac{1}{K_M (1 - 2f_G/3)} \quad (9)$$

From available mass transfer equations

$$\frac{k_{Bs}}{k_{As}} = \left(\frac{D_B}{D_A} \right)^{1-m}$$

where $m = 0.5$ for bubble-induced mass transfer [11, 12] and $m = 0.25$ for natural convection single-phase mass transfer [13]. Combining Equations 9 and 10 and with $\nu_A/\nu_B = -2$, Equation 4 takes the form

$$K = - \frac{c_{B\infty}}{c_{A\infty}} \frac{2}{K_M (1 - 2f_G/3)} \left(\frac{D_B}{D_A} \right)^{1-m} \quad (11)$$

3. Evaluation of experimental data

From the measured values of the diffusion overpotential [2, 4, 5] the supersaturation ratio $c_{Be}/c_{B\infty}$ of dissolved gas was calculated for both reactions from Equations 3 and 11 assuming saturation of dissolved gas in the liquid bulk, $c_{B\infty} = c_{Bsat}$. Physical proper-

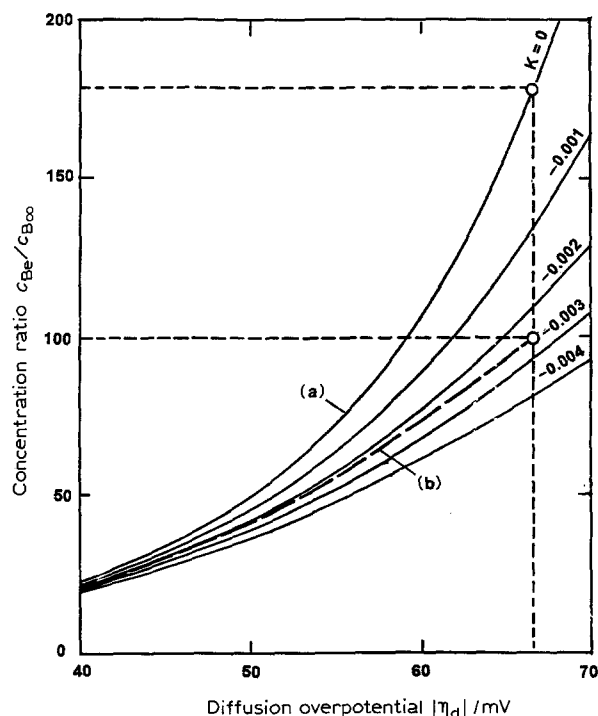


Fig. 1. Effect of the correction factor K on the relative supersaturation of dissolved gas $c_{Be}/c_{B\infty}$, Equation 10. Hydrogen evolution from 0.5 M sulphuric acid [2]. (a) Neglecting interfacial H₂SO₄ dilution, $K = 0$; (b) corrected operating line with consideration of H₂SO₄ dilution. The data points represent $j = 10^4$ A m⁻².

ties data used are compiled in Table 1. The gas evolution efficiency f_G was estimated from [8]

$$f_G = 1 - (1 - \theta_s)^{2.5} \quad (12)$$

where θ_s strictly denotes the fraction of the electrode surface shielded by adhering bubbles in orthogonal projection [14] and was calculated from [8]

$$\theta_s = 0.8 \left(\frac{j}{j_c} \right)^{0.25} \quad (13)$$

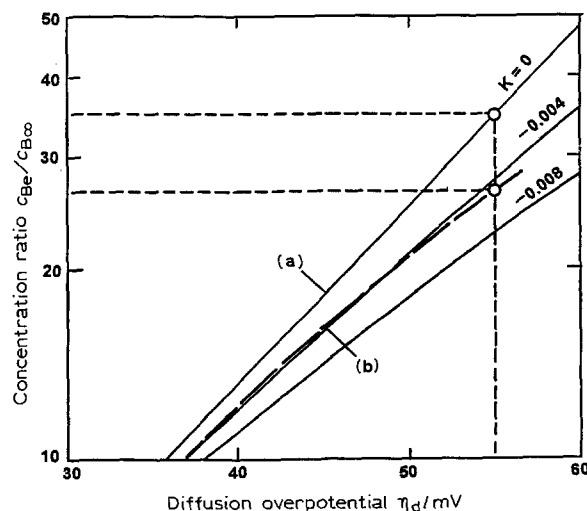


Fig. 2. Effect of the correction factor K on the relative supersaturation of dissolved gas $c_{Be}/c_{B\infty}$, Equation 10. Chlorine evolution from 4.3 M NaCl [4, 5]. (a) Neglecting interfacial brine dilution; (b) corrected operating line. The data points represent $j = 5000$ A m⁻².

where j_c denotes the critical current density characteristic of the onset of a bubble film [15], $j_c \approx 200\,000 \text{ A m}^{-2}$ [16].

Results for hydrogen evolution are shown in Fig. 1. For comparison, the supersaturation calculated neglecting the effect of dilution of the reactant at the electrode surface, $K = 0$, is shown as line *a*. The operational line *b* increasingly diverges from line *a* as the current density increases. It is seen that a considerable inaccuracy is involved if the variation of the sulphuric acid concentration is disregarded. At the maximum diffusion overpotential obtained by Shibata at $j = 10^4 \text{ A m}^{-2}$, the supersaturation with hydrogen is only 56% of the value read from line *a*. The corrected supersaturation ratio is $c_e/c_\infty = 100$ instead of the original value $c_e/c_\infty = 177$ [2].

A corresponding result follows for chlorine evolution, for which the corrected supersaturation value $c_e/c_\infty = 27$ is 23% lower than that reported [4], Fig. 2. A correction is seen to be the more necessary the larger the supersaturation.

4. Conclusion

At gas-evolving electrodes, the interfacial concentration of dissolved gas attains large values compared to the saturation concentration, but the calculations

indicate that the maximum values are considerably smaller than stated previously. True supersaturations are even smaller since the liquid bulk is always supersaturated to some extent [14, 17], where the calculations presented here assume zero supersaturation.

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