Short Communications

Mass Transfer by Laminar Free Convection at Vertical Electrodes

GÖSTA WRANGLÉN

Division of Applied Electrochemistry, Royal
Institute of Technology, Stockholm 70,
Sweden

The following notation is used:

x	= distance along electrode surface from lower edge of cathode or upper edge of anode
y	= distance from electrode surface
h	= electrode height
$\delta_{d0.99}$	= thickness of diffusion boundary layer or electrode film, defined so that $ c - c_e = 0.99 \Delta c$
δ_h	= thickness of hydrodynamic boundary layer
δ_N	= thickness of the Nernst diffusion layer or effective film thickness
$\delta_{=}$	= distance from electrode at which diffusion = convection
u	= vertical flow velocity in boundary layer
c, c_b, c_e and c_s	= concentrations in diffusion layer, of bulk electrolyte, on electrode surface and at saturation, respectively
Δc	= $ c_e - c_b $
ϱ	= density in diffusion layer
α	= $\frac{\delta \ln \varrho}{\delta c}$ = specific densification coefficient
ν	= kinematic viscosity
D	= diffusion coefficient
g	= acceleration of gravity
i	= current density
j	= $\frac{i(1-t)}{zF}$ = diffusion current density
t	= transference number of reacting ion

z	= valency of electrode reaction
F	= Faraday's constant
i_{lim}	= local limiting current density
Nu_x	= $jx/D\Delta c$ and Nu_{av} local and average Nusselt numbers, respectively
Sc	= $\frac{\nu}{D}$ = Schmidt number
Gr_x	= local Grashof number

In earlier work on mass transfer under free convection conditions, in which the analogy with heat transfer was used, δ_d and δ_h have usually been assumed identical^{1,2}. While this is often justified in heat transfer, available numerical solutions of the boundary layer equations^{3,4} show that with high Schmidt numbers ($Sc \simeq 1\,000$), as in mass transfer in liquids, δ_h is 10–15 times larger than δ_d . Generally⁵, $\delta_h/\delta_d \simeq Sc^{1/3}$. Furthermore, u_{max} is reached at a distance of about $2/3 \delta_d$ from the electrode.

As to boundary conditions, two important cases have to be distinguished, viz. I) constant concentration or potential on the electrode surface, and II) constant concentration gradient or current density on the electrode surface. Case I is probably realized only under limiting current conditions⁶.

Considering the numerical solutions referred to^{3,4}, the following approximations are applied for the concentration profile in the boundary layer

$$|c - c_b| = \Delta c \left(1 - \frac{y}{\delta_d}\right)^2 \quad (\text{case I})$$

$$|c - c_b| = \frac{j\delta_d}{2D} \left(1 - \frac{y}{\delta_d}\right)^2 \quad (\text{case II})$$

and for the velocity profile in both cases

$$u = 3.375 u_{max} \frac{y}{\delta_d} \left(1 - \frac{y}{2\delta_d}\right)^2 \text{ for } 0 \leq y \leq \frac{2}{3} \delta_d$$

and

$$u = 0.07 u_{max} Sc^{-1/3} \left(1.5 Sc^{1/3} - \frac{y}{\delta_d}\right) \text{ for } \frac{2}{3} \delta_d \leq y \leq 1.5 Sc^{1/3} \delta_d$$

With these expressions, the boundary layer equations can be integrated according to von Kármán to give approximate analytical solutions. The numerical coefficients are then obtained by comparison with the numerical solutions of the analogous heat transfer problems, corresponding to case I (3) and case II (4). The following results are obtained. They refer to cathodic deposition and anodic dissolution of metals. Details of the calculations will be published elsewhere.

Case I (limiting current density)

$$i_{\text{lim}} = 0.499 \frac{zF}{1-t} D \Delta c \left(\frac{g \alpha \Delta c}{D v x} \right)^{1/4}$$

$$\delta_{d0.99} = 3.54 \left(\frac{D v x}{g \alpha \Delta c} \right)^{1/4}$$

$$\delta_N = 0.57 \delta_{d0.99}, \quad \delta_- = 0.55 \delta_{d0.99}$$

$$u_{\text{max}} = 1.0 \left(\frac{D g \alpha \Delta c x}{v} \right)^{1/2}$$

$$Nu_x = 0.499 (ScGr_x)^{1/4}$$

$$Nu_{\text{av}} = \frac{4}{3} Nu_h = 0.665 (ScGr_h)^{1/4}$$

At the cathode $c_c = 0$, at the anode $c_e = c_s$ under limiting current condition. i_{lim} is then the passivating c.d. at the anode.

Case II (normal electrolysis)

$$\Delta c = 1.59 j \left(\frac{v x}{D^2 g \alpha j} \right)^{1/5}$$

$$\delta_{d0.99} = 3.09 \left(\frac{D^2 v x}{g \alpha j} \right)^{1/5}$$

$$\delta_N = 0.51 \delta_{d0.99}$$

$$u_{\text{max}} = 1.1 \left(\frac{g \alpha j}{v} \right)^{2/5} D^{1/5} x^{3/5}$$

$$Nu_x = 0.558 (ScGr_x)^{1/4}$$

$$Nu_{\text{av}} = \frac{6}{5} Nu_h = 0.670 (ScGr_h)^{1/4}$$

In the presence of a conducting inert electrolyte, a correction term appears in α . The correction derived by Wilke and co-workers³ for case I is applicable also in case II.

1. Wagner, C. *Trans. Electrochem. Soc.* **95** (1949) 161.
2. Wilke, C. R., Tobias, C. W. and Eisenberg, M. *J. Electrochem. Soc.* **100** (1953) 513; *Chem. Eng. Progr.* **49** (1953) 663.

3. Ostrach, S. *NACA Report* **1111** (1953).
4. Sparrow, E. M. and Gregg, J. L. *Trans. ASME* **78** (1956) 435.
5. Levich, B. *Acta Physiochim. URSS* **17** (1942) 257; **19** (1944) 117.
6. Wagner, C. *J. Electrochem. Soc.* **104** (1957) 129.

Received April 16, 1958.

Detection of Small Amounts of Δ^3 -Carene in α -Pinene

ERKKI PULKKINEN, EERO SILTANEN
and VEIKKO PIRILA

*Institute of Chemistry, University of Helsinki
and Institute of Occupational Health,
Helsinki, Finland*

In connection with investigations on the sensitization of the skin to oil of turpentine¹⁻³ it was necessary to detect small amounts of Δ^3 -carene in α -pinene. Widmark⁴ has investigated the purity of various terpenes with the microscorption method according to Blohm⁵. With this method he was able to show the index inhomogeneity of α -pinene into which 0.2 % or more Δ^3 -carene had been added⁶. When investigating the purity of various terpenes we have used the infrared spectrophotometry which has the advantage of being specific. As a criterion for purity we have used the spectra of the series of American Petroleum Institute Research Project 44*.

In order to purify different terpenes, fractional distillation with Podbielniak-column and displacement chromatography were used. The latter method was more practicable giving equal or better results in shorter time. The displacement was performed on a macro scale by jointing together some columns with different diameters^{7,8}, in order to gain sharp fronts. The fractions were analyzed with infrared spectrophotometry^{8,9}. For detection of Δ^3 -carene in α -pinene the absorption peak of wave number 714 cm^{-1} appeared to be most suitable and made it possible to show 0.39 % Δ^3 -carene (Fig. 1) with a liquid

* Serial No. 566 for α -pinene, 567 for β -pinene, 1469 for Δ^3 -carene and 462 for d -limonene.