DIFFUSIONAL FLOW UNDER NON-ISOTHERMAL LAMINAR FREE CONVECTION AT A THERMAL CONVECTIVE ELECTRODE*

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Abstract—A theoretical solution for the set of differential equations related to laminar free convection under simultaneous concentration and thermal gradients, at an ideal vertical plate electrode, is attempted.

The rate equation comprises the limiting case of isothermal free convection and presents a relationship between the maximum average flux and the temperature gradient that is qualitatively coincident with previous experimental results. Velocity and concentration distributions in the boundary layer are evaluated.

Résumé—On a tenté une solution théorique des équations différentielles compliquées par dans un électrode ideale plane et verticale avec convection libre et gradients thermique et de concentration simultanés. On a évalué les distributions de concentration et de vitesse dans des couches limites.

L'équation de débit comprend le cas limite de convection libre isothermique et elle présente une dépendence de la vitesse moyenne du procassus avec le gradient de température qui montre une concordance qualitative avec des données experimentales préalables.

Zusammenfassung—Es wird versucht, eine theoretische Lösung für die Differentialgleichungen der laminaren freien Konvektion an einer idealen senkrechten Plattenelektrode, an welcher gleichzeitige Konzentrations- und Wärmegradienten, vorhanden sind aufzustellen.

Die Geschwindigkeitsgleichung schliesst den Grenzfall der isothermien freien Konvektion ein und zeigt eine Beziehung zwischen dem maximalen mittleren Fluss und dem Temperaturgradienten, welche qualitativ mit vorhergehenden experimentellen Resultaten übereinstimmt.

Die Geschwindigkeits- und Konzentrationsverteilungen in der Grenzschicht wurden abgeschätzt.

Mass-transfer phenomena play an important part in electrochemical kinetics as well as in heterogeneous reactions in general, as described in the literature.[1,2] Generally the solutions of the differential mass-transfer equations applied to electrochemistry refer to isothermal systems.

In the case of isothermal laminar free convection the solutions of the differential mass-transfer equations have already been studied for a vertical plate, yielding local rate equations of the form[1,3–8]

$$j = KD \left(\frac{\nu}{D}\right)^{1/4} \left(\frac{g\alpha}{\nu^2}\right)^{1/4} C_0 x^{-1/4}. \tag{1}$$

The meaning of the symbols is given later; K is a numerical constant depending on the approximations made in the mathematical deductions.

Analogously, the differential heat-transfer equations for vertical plates under free convection have been solved by various authors[9–11] and the local flux equations, *mutatis mutandis*, have the same form as (1).

Buoyancy effects caused by both temperature and concentration gradients were considered in a recent publication in order to get a reasonable idea of the influence of relevant parameters to transport processes involved in binary diffusion and heat transfer in the laminar free convection boundary layer on a vertical plate.[12]

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Recently, experiments on the increase of the mass-transfer rate due to thermal convection were reported.[13] An attempt was made to present a new electroanalytical technique based on the so-called thermal convective electrode.

Some years ago the same effect had been observed in this laboratory,[14] but the results were not published since a solution of the non-linear set of coupled equations related to the problem involving simultaneous gradients of temperature and concentration, under laminar free convection and a fixed geometry, was not then found. The purpose of this paper is to present an approach to the theory of a thermal convective electrode.

DIFFERENTIAL EQUATIONS AND BOUNDARY CONDITIONS

To solve the mass-transfer problem under combined effect of temperature and concentration gradients, the simultaneous solution of the transfer equations related to momentum, energy and mass must be attempted.

For the particular case of a vertical plate under buoyancy forces only, the momentum-transfer equation is

$$v_x \frac{\partial v_x}{\partial x} + v_y \frac{\partial v_x}{\partial y} = v \frac{\partial^2 v_x}{\partial y^2} + g \frac{(\rho_0 - \rho)}{\rho_0}, \tag{2}$$

where x is the coordinate defined along the plate and y is the direction perpendicular to it, v_x and v_y are the velocity components in the x and y directions respectively, v is the kinematic viscosity, g the gravity, ρ_0 a reference density and ρ a density that is a function of the concentration and temperature.

The mass- and energy-transfer equations are respectively

$$v_x \frac{\partial C}{\partial x} + v_y \frac{\partial C}{\partial y} = D \frac{\partial^2 C}{\partial y^2} \tag{3}$$

and

$$v_x \frac{\partial T}{\partial x} + v_y \frac{\partial T}{\partial y} = \frac{k}{\rho C_p} \frac{\partial^2 T}{\partial y^2}, \tag{4}$$

where C is the concentration of the diffusing species, D its diffusion coefficient, T the temperature, k the thermal conductivity and C_p the specific heat at constant pressure. The boundary conditions for this set of differential equations are

$$
\left.
\begin{matrix}
y = 0 \begin{cases} v_x = v_y = 0 \\ C = 0 \\ T = T_1 \end{cases} \\
y = \infty \begin{cases} v_x = v_y = 0 \\ C = C_0 \\ T = T_0 \end{cases}
\end{matrix}
\right\}. \tag{5}
$$

Total differential equations

To solve (2), (3) and (4) we transform them into a set of total differential equations. By taking into account that the density is a weak function of concentration and temperature, it can be conveniently expressed by

$$\rho = \rho_0 + \frac{\partial \rho}{\partial C} (C - C_0) + \frac{\partial \rho}{\partial T} (T - T_0). \tag{6}$$

It is also convenient, for the subsequent analysis, to introduce the densification and expansion coefficients, α and β, respectively, as is usually done in dealing with the individual cases of isothermal free convection and free heat transfer. They are

$$\alpha = \frac{C_0}{\rho_0} \frac{\partial \rho}{\partial C} \tag{7}$$

and

$$\beta = \frac{\Delta T}{\rho_0} \frac{\partial \rho}{\partial T}, \tag{8}$$

where $\Delta T = T_0 - T_1$.

Following the procedure used to solve the mass-transfer differential equation under free convection,[1] we define now a new independent dimensionless variable, μ, by

$$\mu = \left(\frac{g}{4\nu^2}\right)^{1/4} \frac{y}{x^{1/4}}. \tag{9}$$

We also define a dimensionless concentration, φ, and temperature, τ, as

$$\varphi = \frac{C_0 - C}{C_0} \tag{10}$$

and

$$\tau = \frac{T_0 - T}{T_0 - T_1}. \tag{11}$$

The velocity component in terms of the streaming function ψ, is defined as a function of μ, in the following form,

$$\psi = 4\nu \left(\frac{g}{4\nu^2}\right)^{1/4} x^{3/4} f(\mu). \tag{12}$$

Then, we have

$$v_x = \frac{\partial \psi}{\partial y} = 4\nu \left(\frac{g}{4\nu^2}\right)^{1/2} x^{1/2} f'(\mu) \tag{13}$$

and

$$v_y = -\frac{\partial \psi}{\partial x} = \nu \left(\frac{g}{4\nu^2}\right)^{1/4} \left(\frac{\mu f'(\mu) - 3f(\mu)}{x^{1/4}}\right), \tag{14}$$

where $f(\mu)$ and $f'(\mu)$ are respectively functions of the variable μ and its first derivative, which satisfy

$$f''' + 3ff'' - 2f'^2 + \alpha\varphi + \beta\tau = 0. \tag{15}$$

Similarly, the new total differential equations for mass and energy transfer, in terms of φ and τ, are respectively

$$\varphi'' + 3Scf\varphi' = 0, \tag{16}$$

$$\tau'' + 3Prf\tau' = 0, \tag{17}$$

where the primes correspond to the order of the derivatives; Sc is the Schmidt number defined by

$$Sc = \frac{\nu}{D} \tag{18}$$

and Pr is the Prandlt number given by

$$Pr = \frac{\nu \rho C_p}{k}.$$ (19)

The boundary conditions related to (15), (16) and (17) are

$$\mu = 0 \begin{cases} f = f' = 0 \\ \varphi = 1 \\ \tau = 1 \end{cases} ; \qquad \mu = \infty \begin{cases} f' = 0 \\ \varphi = 0 \\ \tau = 0 \end{cases}.$$ (20)

Distribution functions

To obtain the distribution function related to mass transfer under thermal convection, let us first consider the following two limiting cases, (i) isothermal free convection under a concentration gradient and (ii) thermal free convection.

Case (i). For isothermal free convection, $\Delta T = 0$ and consequently the set of total differential equations is reduced to (15) and (16), which have been analysed by different authors.[1,6] To establish the concentration distribution Levich assumes that the function f can be expressed as a series expansion in powers of η, as follows:

$$f(\eta) = \frac{A_\eta}{2} \eta^2 - \frac{\eta^3}{6} + \left(\frac{A_\eta Sc}{2} \right)^{1/3} \frac{\eta^4}{24 \times 0.89},$$ (21)

where

$$\eta = \left(\frac{g\alpha}{4\nu^2} \right)^{1/4} \frac{y}{x^{1/4}}.$$ (22)

Taking into account the boundary conditions, the constant A_η is[1]

$$A_\eta = \frac{0.48}{Sc^{1/4}}.$$ (23)

The concentration distribution becomes

$$\varphi = 1 - \frac{\left(\frac{0.48}{2} \right)^{1/3} Sc^{1/4}}{0.89} \eta.$$ (24)

Case (ii). Analogously, when there is no concentration gradient, the set of equations is that of the corresponding heat-transfer problem. Following basically the assumptions of case (i), which means that the convergence of the integrals in τ may be in a first approximation, and for Pr number of about 10 or larger, comparable to that of φ,

$$f(\lambda) = \frac{A_\lambda}{2} \lambda^2 - \frac{\lambda^3}{6} + \left(\frac{A_\lambda Pr}{2} \right)^{1/3} \frac{\lambda^4}{24 \times 0.89},$$ (25)

where

$$\lambda = \left(\frac{g\beta}{4\nu^2} \right)^{1/4} \frac{y}{x^{1/4}}$$ (26)

and

$$A_\lambda = \frac{0.48}{Pr^{1/4}}.$$ (27)

Similarly as in case (i), the temperature distribution is

$$\tau = 1 - \frac{\left(\dfrac{0\cdot48}{2}\right)^{1/3} Pr^{1/4}}{0\cdot89} \lambda. \tag{28}$$

Case (iii). To attack the problem of combined contributions of gradients of concentration and temperature, we assume that its streaming function is the algebraic sum of the streaming functions of cases (i) and (ii). Then according to (12), (21) and (25), we have

$$\psi = 4\nu \left(\frac{g}{4\nu^2}\right)^{1/4} x^{3/4} \left\{ \left[A_\eta \alpha^{3/4} \pm A_\lambda \beta^{3/4} \right] \frac{\mu^2}{2} - \frac{\alpha \pm \beta}{6} \mu^3 \right.$$
$$\left. + \left[(A_\eta Sc)^{1/3} \alpha^{5/4} \pm (A_\lambda Pr)^{1/3} \beta^{5/4} \right] \frac{\mu^4}{2^{1/3} \times 24 \times 0\cdot89} \right\}. \tag{29}$$

By comparison of (29) with (12), the term in braces corresponds to $f(\mu)$. Consequently the distribution equation, for the velocity component in the x direction, is obtained immediately from (13) as

$$v_x = 4\nu \left(\frac{g}{4\nu^2}\right)^{1/2} x^{1/2} \left\{ 0\cdot48 \left[\frac{\alpha^{3/4}}{Sc^{1/4}} \pm \frac{\beta^{3/4}}{Pr^{1/4}} \right] \mu - \frac{\alpha \pm \beta}{2} \mu^2 + \frac{(0\cdot24)^{1/3}}{6 \times 0\cdot89} [Sc^{1/4} \alpha^{5/4} \right.$$
$$\left. \pm Pr^{1/4} \beta^{5/4}] \mu^3 \right\}. \tag{30}$$

It is interesting for the sake of comparison to evaluate the velocity profile in terms of v_x and y for cases (i), (ii) and (iii). The following calculations refer to an actual system at a constant length equal to unity having the properties indicated in Table 1, as well as the conditions of temperature and concentration used.

TABLE 1. PARAMETERS FOR NUMERICAL CALCULATIONS

ΔT °C	T_0 °C	T_1 °C	C M	$D \times 10^6$ cm²/s	$\nu \times 10^2$ cm²/s	Sc	Pr	$\alpha \times 10^4$	$\beta \times 10^4$
−15	12·5	5	0·05	3·16	1·760	5590	9·1	71·8	64·9
+15	27·5	35	0·05	6·60	0·826	1250	6·6	71·8	66·1
−15	12·5	5	0·005	3·16	1·760	5590	9·1	7·18	64·9
+15	27·5	35	0·005	6·60	0·826	1250	6·6	7·18	66·1

$x = 1$ cm.

Physiochemical properties are taken as concentration-independent for the sake of calculation. This situation is actually approached when C is the concentration of a diffusing ion in the presence of a large excess of a supporting electrolyte. The thermal dependence of the properties were taken from the literature.[15–17] The physiochemical properties entering the mass-transfer contribution are referred to the temperature of the plate (T_1) whereas those related to the heat-transfer contribution were taken at average temperature (T_0). This criterion was applied taking into account that the variation of those properties affecting the respective transport phenomena occur at widely different distances. After choosing a set of η, λ and μ, the functions f and their derivatives were calculated. Tables 2 and 3

TABLE 2

$$f(\eta) = \frac{0.24}{Sc^{1/4}}\,\eta^2 - \frac{\eta^3}{6} + \frac{(0.24)^{1/3}}{24 \times 0.89}\,Sc^{1/4}\eta^4 .$$

$$f'(\eta) = \frac{0.48}{Sc^{1/4}}\,\eta - \frac{\eta^2}{2} + \frac{(0.24)^{1/3}}{6 \times 0.89}\,Sc^{1/4}\eta^3 .$$

	$T_0 = T_1 = 5°C$		$T_0 = T_1 = 35°C$	
η	$f(\eta) \times 10^6$	$f'(\eta) \times 10^4$	$f(\eta) \times 10^6$	$f'(\eta) \times 10^4$
0	0	0	0	0
0·01	2·60	5·06	3·80	7·42
0·05	50·1	16·6	79·3	28·0
0·07	84·2	17·9	141	33·3
0·08	95·3	17·6	175	35·0
0·09	120	16·8	212	36·0
0·10	136	15·6	248	36·3
0·12	301	12·0	320	35·2
0·15	491	4·80	421	30·3
0·20	—	—	535	14·5
	$(\eta)_{\varphi=0} = 0.165$		$(\eta)_{\varphi=0} = 0.240$	

TABLE 3

$$f(\lambda) = \frac{0.24}{Pr^{1/4}}\,\lambda^2 - \frac{\lambda^3}{6} + \frac{(0.24)^{1/3}}{24 \times 0.89}\,Pr^{1/4}\lambda^4 .$$

$$f'(\lambda) = \frac{0.48}{Pr^{1/4}}\,\lambda - \frac{\lambda^2}{2} + \frac{(0.24)^{1/3}}{6 \times 0.89}\,Pr^{1/4}\lambda^3 .$$

λ	$T_1 = 5°C;\quad T_0 = 12.5°C$		$T_1 = 35°C;\quad T_0 = 27.5°C$	
	$f(\lambda) \times 10^4$	$f'(\lambda) \times 10^4$	$f(\lambda) \times 10^4$	$f'(\lambda) \times 10^4$
0	0	0	0	0
0·10	12·1	228	13·4	252
0·20	54·8	368	47·4	415
0·25	62·3	409	69·6	462
0·30	83·3	433	93·8	500
0·35	105	441	120	517
0·40	127	434	145	519
0·45	148	412	171	507
0·50	169	384	196	483
0·60	203	298	204	402
0·70	229	178	278	288
0·80	241	50	301	152
0·90	—	—	310	6

refer to cases (i) and (ii) and Tables 4 and 5 comprise case (iii) under two extreme situations as described later.

The velocity profiles are plotted in Figs. 1–3, showing various interesting features. The velocity profile for case (i) is shown in Fig. 1 for two different concentrations and temperatures. The curves exhibit the usual maxima, diminishing and shifting toward higher y at lower concentration of the diffusing species. The profiles are completely developed in the same range of y as the concentration profiles (y_0). Figure 2 corresponds to the velocity profiles for case (ii). The maximum velocities are much larger than for case (i) and the profiles extend to higher y values. In Fig. 3 velocity profiles for two different concentrations and temperatures are shown. For each concentration two particular cases are considered, one in which the buoyancy forces

TABLE 4

$$f(\mu) = 0.24\left(\frac{\alpha^{3/4}}{Sc^{1/4}} \pm \frac{\beta^{3/4}}{Pr^{1/4}}\right)\mu^2 - \frac{\alpha \pm \beta}{6}\mu^3 + \frac{(0.24)^{1/2}}{24 \times 0.89}(\alpha^{5/4}Sc^{1/4} \pm \beta^{5/4}Pr^{1/4})\mu^4.$$

$$f'(\mu) = 0.48\left(\frac{\alpha^{3/4}}{Sc^{1/4}} \pm \frac{\beta^{3/4}}{Pr^{1/4}}\right)\mu - \frac{\alpha \pm \beta}{2}\mu^2 + \frac{(0.24)^{1/2}}{6 \times 0.89}(\alpha^{5/4}Sc^{1/4} \pm \beta^{5/4}Pr^{1/4})\mu^3.$$

$C = 0.05$ M

μ	$T_1 = 5°C;$ $T_0 = 12.5°C$ $f(\mu) \times 10^4$	$f'(\mu) \times 10^4$	$T_1 = 35°C;$ $T_0 = 27.5°C$ $f(\mu) \times 10^4$	$f'(\mu) \times 10^4$
0	0	0	0	0
0.2	0.99	9.88	1.62	15.3
0.4	3.95	19.2	5.81	25.9
0.6	9.20	26.2	11.8	32.9
0.8	14.6	32.9	14.7	36.8
1.0	21.6	35.6	26.3	38.6
1.2	28.6	34.5	34.1	39.3
1.5	37.7	23.7	46.0	39.3
1.7	41.0	9.3	54.1	41.3
2.0	—	—	67.2	47.1
2.2	—	—	77.3	54.6
2.5	—	—	96.3	73.7

$(\mu)_{\varphi=0} = 0.373$ $\qquad\qquad$ $(\mu)_{\varphi=0} = 0.500$

TABLE 5

$C = 0.005$ M

μ	$T_1 = 5°C;$ $T_0 = 12.5°C$ $f(\mu) \times 10^4$	$f'(\mu) \times 10^4$	$T_1 = 35°C;$ $T_0 = 27.5°C$ $f(\mu) \times 10^4$	$f'(\mu) \times 10^4$
0	0	0	0	0
0.2	1.13	11.0	1.34	13.0
0.4	4.26	19.8	5.02	23.3
0.6	8.93	26.6	10.5	31.1
0.8	14.8	31.4	17.3	36.5
1.0	21.4	34.4	25.0	39.9
1.2	28.4	35.7	33.1	41.4
1.5	39.1	34.7	45.5	40.5
1.7	45.8	32.3	53.4	38.1
2.0	54.7	26.3	64.1	32.4
2.2	59.4	20.9	70.1	27.8
2.5	64.3	11.1	77.2	19.4
3.0	—	—	83.2	4.2

$(\mu)_{\varphi=0} = 0.347$ $\qquad\qquad$ $(\mu)_{\varphi=0} = 0.538$

arising from the existence of both temperature and concentration gradients are added, and another where they are substracted. For the former, when the factor α is about the same as β, the maximum becomes an inflexion point due to the influence of the function related to $f(\eta)$ for large values of y, which are not taken into account in the simpler case. In this particular case the boundary condition $f'(\mu) = 0$ when $\mu = \mu_0$ is actually not fulfilled. However, the concentration distribution is not affected to any great extent under such circumstances because for its evaluation only the first term of the series expansion of $f(\mu)$ is considered. Furthermore, Fig. 3 reveals a greater influence of the thermal gradient in the magnitude of the velocity component for the combined case.
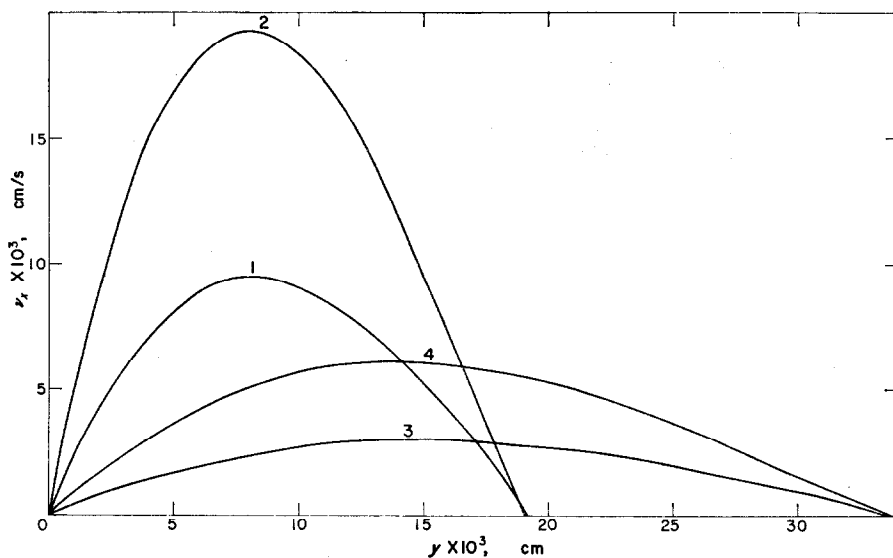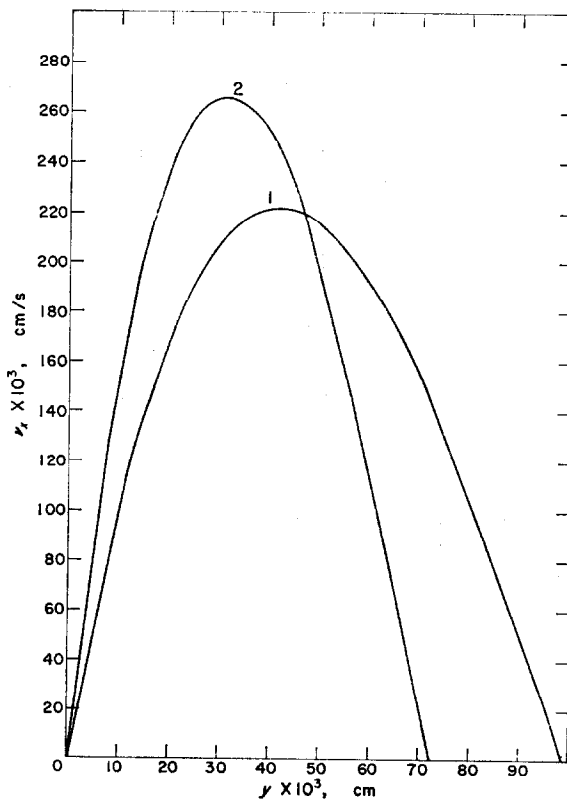
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FIG. 1. Velocity (v_x) distribution in boundary layer for isothermal laminar free convection, at $x = 1$ cm.

1, 5°C; C, 0·05 M   2, 35°C; C, 0·05 M
3, 5°C; C, 0·005 M   4, 35°C; C, 0·005 M.

FIG. 2. Velocity (v_x) distribution in boundary layer for thermal free convection, at $x = 1$ cm.
1, ΔT, −15°C; $T_0 = 12\cdot5$°C
2, ΔT, +15°C; $T_0 = 27\cdot5$°C.
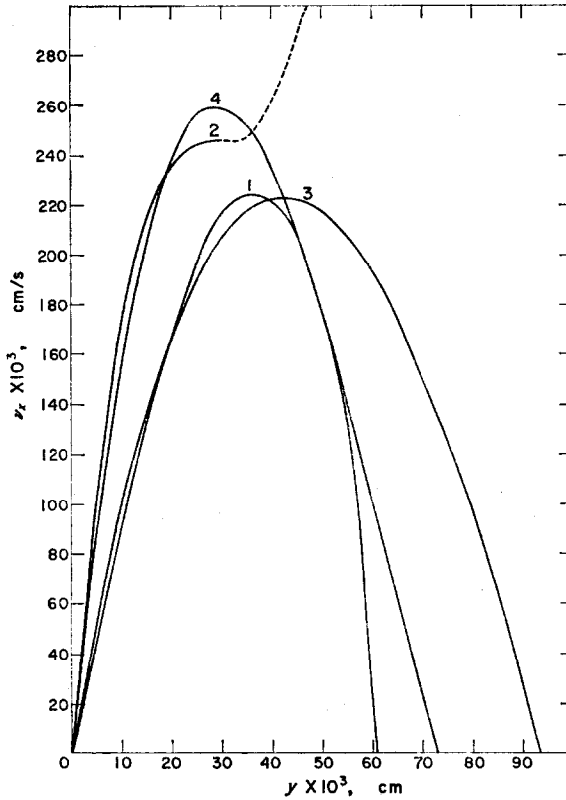
FIG. 3. Velocity (v_x) distribution in boundary layer for simultaneous
temperature and concentration gradients at $x = 1$ cm.
1, $\Delta T = -15°C$; $T_0 = 12\cdot5°C$; C, 0·05 M
2, $\Delta T = +15°C$; $T_0 = 27\cdot5°C$; C, 0·05 M
3, $\Delta T = -15°C$; $T_0 = 12\cdot5°C$; C, 0·005 M
4, $\Delta T = +15°C$; $T_0 = 27\cdot5°C$; C, 0·005 M.

By solving (16) taking into account the boundary conditions (20) we obtain

$$\varphi = 1 - \frac{\int_0^\mu \exp\left[-3Sc \int_0^\mu f(\mu)\,d\mu\right] d\mu}{\int_0^\infty \exp\left[-3Sc \int_0^\infty f(\mu)\,d\mu\right] d\mu}. \tag{31}$$

If $f(\mu)$ is substituted by the first term of (29) assuming that the type of approximation
formulated for case (i) and case (ii) is also permissible in the present circumstances,
we have

$$\varphi = 1 - \frac{(0\cdot24)^{1/3}\left(\dfrac{\alpha^{3/4}}{Sc^{1/4}} \pm \dfrac{\beta^{3/4}}{Pr^{1/4}}\right)^{1/3} Sc^{1/3}}{0\cdot89}\,\mu. \tag{32}$$

Returning now to the original variables, we obtain the following distribution equation
for concentration,

$$C = 0\cdot70C_0\left(\frac{\alpha^{3/4}}{Sc^{1/4}} \pm \frac{\beta^{3/4}}{Pr^{1/4}}\right)^{1/3} Sc^{1/3}\left(\frac{g}{4\nu^2}\right)^{1/4}\frac{y}{x^{1/4}}. \tag{33}$$

A plot of the concentration profile in terms of φ and y is shown in Fig. 4 for cases (i) and (iii). It becomes evident that the gradient of the concentration function is greater for the case of a combined contribution. Consequently the thickness of the diffusion layer for the latter ($[y]_{\varphi=0} = \delta_d$), at a constant electrode height, diminishes.
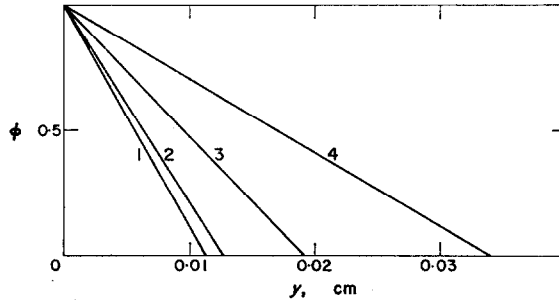

FIG. 4. Concentration distribution in boundary layers.
1, Case (iii), C, 0·05 M; $\Delta T = +15°C$; $T_0 = 27·5°C$
2, Case (iii), C, 0·005 M; $\Delta T = +15°C$, $T_0 = 27·5°C$
3, Case (i), C, 0·05 M; $\Delta T = 0°C$, $T_0 = 5°C$
4, Case (i), C, 0·005 M; $\Delta T = 0°C$, $T_0 = 5°C$.

The mass-transfer equation

The local maximum diffusional flux under the effect of simultaneous temperature and concentration gradients and laminar conditions in a vertical plate ($y = 0$), is obtained with Fick's law and (33) as follows,

$$j = D\left(\frac{\partial C}{\partial y}\right)_{y=0} = 0·70DC_0\left(\frac{\alpha^{3/4}}{Sc^{1/4}} \pm \frac{\beta^{3/4}}{Pr^{1/4}}\right)^{1/3} Sc^{1/3}\left(\frac{g}{4\nu^2}\right)^{1/4} x^{-1/4}. \tag{34}$$

Integrating (34) over the surface of the plate we obtain the total maximum flux

$$J = 0·90DC_0\left(\frac{\alpha^{3/4}}{Sc^{1/4}} \pm \frac{\beta^{3/4}}{Pr^{1/4}}\right)^{1/3} Sc^{1/3}\left(\frac{g}{4\nu^2}\right)^{1/4} X^{3/4}b, \tag{35}$$

where X is the electrode height and b is the width of the plate in the z direction. Hence the average maximum flux, $\bar{J}$, is

$$\bar{J} = 0·90DC_0\left(\frac{\alpha^{3/4}}{Sc^{1/4}} \pm \frac{\beta^{3/4}}{Pr^{1/4}}\right)^{1/3} Sc^{1/3}\left(\frac{g}{4\nu^2}\right)^{1/4} X^{-1/4}. \tag{36}$$

Equation (36) can be plotted taking $\bar{J}$ as a function of $\pm\Delta T$, as shown in Figs. 5 and 6 on the basis of Table 1. The curves are characterized by a very rapid initial increase of $\bar{J}$ with $\pm\Delta T$.

In Figs. 5 and 6, curves 1 are calculated with (36) for negative ΔT values and a simultaneous decrease of the temperature of the plate and the reference temperature of the system. Curves 2 are also given for negative ΔT values, at constant temperature of the plate and increasing reference temperature of the system. Curves 3 correspond to positive ΔT values, constant plate temperature and reference temperature decreasing. Finally curve 4 also corresponds to positive ΔT at increasing both the plate and reference temperature. Figures 5 and 6 show various remarkable features. When $\Delta T = 0$, the maximum flux is that corresponding to an isothermal free laminar
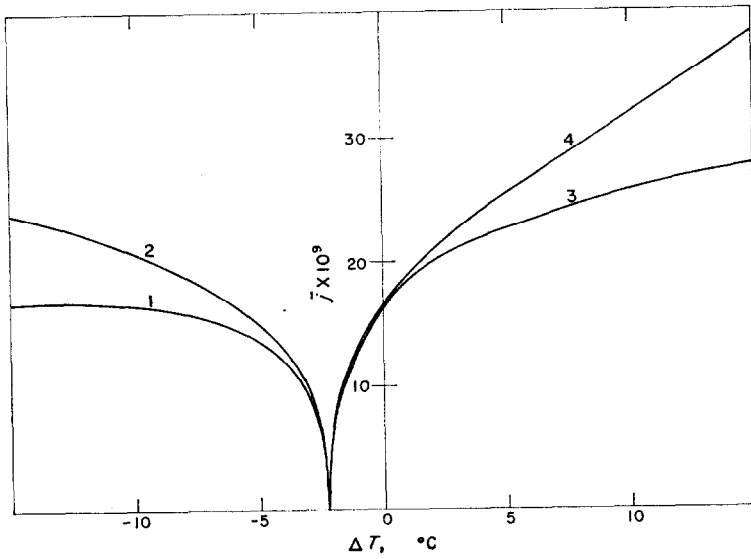
FIG. 5. Plot of J against ΔT.
C, 0·05 M. The conditions relating to each curve are given in the text.
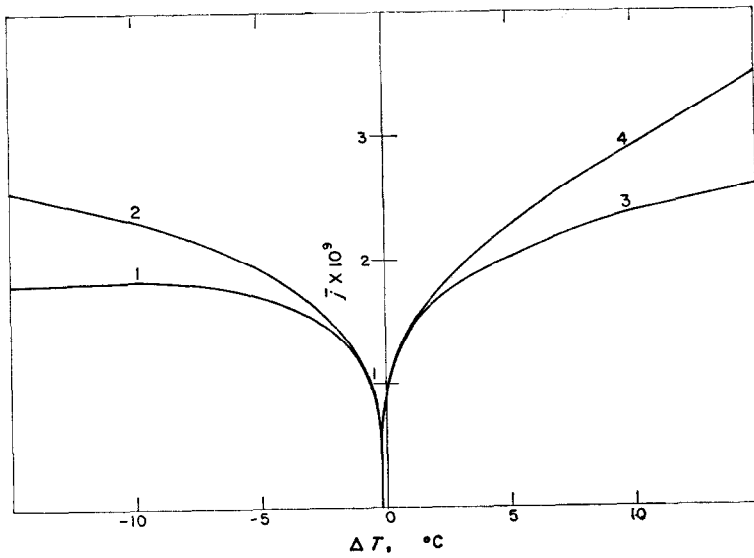

FIG. 6. Plot of J against ΔT.
C, 0·005 M. The conditions relating to each curve are given in the text.

convection process under a concentration gradient whose value results from Levich's equation. When ΔT decreases J decreases continuously, approaching zero at $(\Delta T)_{J=0}$. From (36), this situation arises when

$$\frac{\alpha^{3/4}}{Sc^{1/4}} = \frac{\beta^{3/4}}{Pr^{1/4}}. \tag{37}$$

The fact that J becomes zero means that at $(\Delta T)_{J=0}$, the velocity component in the x direction due to the thermal gradient is exactly compensated by that due to the concentration gradient. Consequently the process approaches an ideal diffusion process, for which no steady flux is obtained with the present ideal model.[18] At $\Delta T < (\Delta T)_{J=0}$, J begins to increase because under these circumstances there is again a net velocity component.

$(\Delta T)_{J=0}$ depends on the concentration of the reacting species and when the latter decreases, $(\Delta T)_{J=0}$ approaches zero. This is clearly shown in Fig. 6, where the concentration is ten times lower than that in Fig. 5.

Another feature of those curves, which is related both to those already analysed and to the change of the physicochemical properties of the fluid with temperature, is their asymmetry with respect to $(\Delta T)_{J=0}$. The latter effect also contributes to the appearance of a slight maximum in the plot of Figs. 5 and 6 for negative ΔT values, at decreasing reference and plate temperatures. The maximum is better defined at lower values of α.

APPLICATION TO A VERTICAL PLANE THERMAL CONVECTIVE ELECTRODE

For an electrochemical system involving a vertical plane working electrode, where the electrode reaction is under non-isothermal, free convection–diffusion control, we can write the average maximum flux in terms of the limiting cd i_L, as

$$i_L = 0.90zFDC_0\left(\frac{\alpha^{3/4}}{Sc^{1/4}} \pm \frac{\beta^{3/4}}{Pr^{1/4}}\right)^{1/3} Sc^{1/3} \left(\frac{g}{4\nu^2}\right)^{1/4} X^{-1/4}, \tag{38}$$

where z is the number of electrons entering the electrochemical reaction and F the Faraday constant.

Ducret and Cornet[13] have recently employed an electrochemical device called by the authors "electrode á convection thermique". In this set-up the stirring was induced by a thermal gradient and it was applied to different electrochemical systems. The results in principle fit qualitatively well within the predictions the equation here proposed. Unfortunately, the published data are not suitable for a quantitative test of the theoretical equation because of the arbitrary geometry of the cells employed. Besides, the authors plot the results taking the maximum flux (in terms of current) against the amount of heat exchanged per unit area. Nevertheless with the exception of a constant factor, their plot is directly comparable to those shown in Figs. 5 and 6

A detailed experimental test of the rate equation derived in the present work has been performed employing an electrolysis cell with a geometry approaching the ideality involved in the present derivation. The results will be reported in the near future.

Finally, the present study shows the importance of keeping a constant temperature over the whole electrochemical set-up when ionic-mass transfer rates are measured, particularly in free convection or at a low rate of stirring. The discrepancies of results

sometimes observed in this type of work may in part be due to temperature gradients originating in the systems.

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