

# SIMULTANEOUS MASS AND HEAT TRANSFER TO A PLATE ELECTRODE IN THE REGION OF FREE CONVECTION WITH ANTIPARALLEL FLUXES OF MASS AND HEAT

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Simultaneous transfer of heat and ions to a vertical plate electrode in the region of free convection was treated mathematically by solving the Navier–Stokes, convective diffusion, and convective heat transfer equations. The direction of flow due to heat flux was considered opposite to that due to flux of ions. A criterion equation was proposed for the calculation of the Sherwood criterion with an error smaller than 2%. This was verified experimentally by measuring the limiting current densities for electrolytes containing  $K_4Fe(CN)_6$  and  $K_3Fe(CN)_6$  with KOH as base electrolyte.

All the published equations for the calculation of the Sherwood criterion<sup>1-4</sup> were derived for parallel flow velocity profiles formed by the fluxes of heat and ions to a plate electrode. In the counter-current case, Marchiano and Arvia<sup>2</sup> simply assume that the contributions of the fluxes of heat and mass can be subtracted from one another. This case has not been solved hitherto with a sufficient accuracy, and therefore it forms the subject of the present work. With respect to simplifications in the basic equations, only the cases  $Gr_T \ll Gr_M$  and  $Gr_T \gg Gr_M$  are considered. If  $Gr_T \approx -0.1Gr_M$ , turbulence takes place in the boundary layer and simple differential equations are not valid. Based on the solution of the differential equations, a criterion equation was proposed for the calculation of the Sherwood criterion in the whole region of Grashoff numbers including the turbulent one. This equation was verified experimentally in the whole range of validity. Experiments carried out for the co-current case substantiated the criterion equation proposed earlier<sup>4</sup>.

## THEORETICAL

We shall consider a vertical plate electrode placed in a semiinfinite space in the  $x - z$  plane, where the  $x$  is parallel to the acceleration of gravity. The orientation of the velocity components  $v_x$  and  $v_y$  and other quantities is apparent from Fig. 1. We denote  $c_0$  the concentration of electroactive ions; their solution contains a supporting

electrolyte in a large excess. Streaming at the electrode is a result of the electrode reaction and heat transfer. We assume that these effects counteract each other and that the liquid is incompressible with a constant density. In a stationary state, the system can be described as follows.

The convective diffusion equation

$$v \cdot \text{grad } c = D \Delta c, \quad (1)$$

the convective heat transfer equation

$$\varrho(v \cdot \text{grad } T) = \lambda_{\tau} \Delta T, \quad (2)$$

the Navier-Stokes equation

$$\varrho(v \cdot \text{grad } v) = \varrho g - \text{grad } p + \mu \Delta v, \quad (3)$$

and the continuity equation

$$\text{div } v = 0. \quad (4)$$

This system of partial differential equations can be transformed to a system of ordinary ones by neglecting certain terms and using a suitable transformation. This method was elaborated by Prandtl<sup>5,7</sup> and Pohlhausen<sup>6</sup> and consists in introducing dimensionless parameters and comparing their magnitudes.

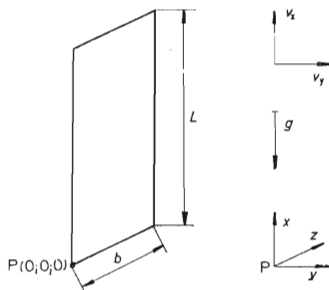


FIG. 1

Orientation of the electrode:  $x, y, z$  coordinate axes,  $P(0, 0, 0)$  origin of coordinates,  $b$  electrode width,  $L$  electrode length,  $v_x$  and  $v_y$  velocity components of electrolyte,  $g$  acceleration of gravity

Equations (1) and (2) can be simplified to the form

$$v_x \frac{\partial c}{\partial x} + v_y \frac{\partial c}{\partial y} = D \frac{\partial^2 c}{\partial y^2}, \quad (5)$$

$$v_x \frac{\partial T}{\partial x} + v_y \frac{\partial T}{\partial y} = a_T \frac{\partial^2 T}{\partial y^2}. \quad (6)$$

For streaming due to a density gradient, the Navier–Stokes equation for the boundary layer can be simplified<sup>8</sup> by setting  $\text{grad } p \approx \rho_0 g$  to the form

$$v_x \frac{\partial v_x}{\partial x} + v_y \frac{\partial v_x}{\partial y} = \nu \frac{\partial^2 v_x}{\partial y^2} + g(\rho - \rho_0)/\rho_0. \quad (7)$$

Equations (5)–(7) were derived on the assumption that  $D$ ,  $a_T$ , and  $\nu$  are independent of the composition and temperature of the electrolyte. Their values in the bulk of the electrolyte are used in numerical calculations. The last equation is obtained from Eq. (4)

$$\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} = 0. \quad (8)$$

The boundary conditions are as follows.

$$y = 0: x \in \langle 0, L \rangle: c = c_s, \quad T = T_s, \quad v_x = v_y = 0;$$

$$y \rightarrow \infty: c = c_0, \quad T = T_0, \quad v_x = 0.$$

If  $c_s = 0$ , we have to deal with the limiting current density on the electrode at constant temperature. Eqs (5)–(8) can be transformed to ordinary differential equations as follows. We introduce dimensionless parameters

$$\varphi = \frac{c - c_0}{c_s - c_0}, \quad \alpha = (c_s - c_0) \frac{1}{\rho_0} \frac{\partial \rho}{\partial c}, \quad (9), (10)$$

$$\Theta = \frac{T - T_0}{T_s - T_0}, \quad \beta = (T_s - T_0) \frac{1}{\rho_0} \frac{\partial \rho}{\partial T}. \quad (11), (12)$$

The dependence of the density on the temperature and concentration of electroactive ions can be approximated as

$$\varrho = \varrho_0(1 + \alpha\varphi + \beta\Theta). \quad (13)$$

We introduce the stream function  $\psi$ , which fulfils identically the equation of continuity (8)

$$v_x = \partial\psi/\partial y, \quad v_y = -\partial\psi/\partial x. \quad (14), (15)$$

For  $\alpha > 0$  and  $\beta < 0$ , we use transformation A

$$\psi = 4\nu Ax^{3/4} f(\eta), \quad (16)$$

where

$$\eta = Ay/x^{1/4}, \quad A = (g\alpha/4\nu^2)^{1/4}. \quad (17), (18)$$

For  $\alpha < 0$  and  $\beta > 0$ , we use transformation B

$$\psi = 4\nu Bx^{3/4} f(\eta), \quad (19)$$

$$\eta = By/x^{1/4}, \quad B = (g\beta/4\nu^2)^{1/4}. \quad (20), (21)$$

The transformations A and B differ only by the numerical coefficient. It follows from Eqs (14) and (16) or (14) and (19) that the value of  $df/d\eta$  is proportional to the velocity of flow  $v_x$ . On combining Eqs (5)–(21), we obtain a system of ordinary differential equations (primes denote differentiation with respect to  $\eta$ )

$$\varphi'' + 3cf(\eta)\varphi' = 0, \quad \Theta'' + 3Prf(\eta)\Theta' = 0, \quad (22), (23)$$

$$f''' + 3ff'' - 2f'^2 + \varphi + (\beta/\alpha)\Theta = 0 \quad (\alpha > 0, \beta < 0) \quad (24)$$

$$f''' + 3ff'' - 2f'^2 + (\alpha/\beta)\varphi + \Theta = 0 \quad (\beta > 0, \alpha < 0). \quad (25)$$

(Eq. 24) is valid for transformation (A), Eqs (16)–(18), while Eq. (25) is valid for transformation (B), Eqs (19)–(21). The boundary conditions are

$$\eta = 0: \quad f = f' = 0, \quad \varphi = \Theta = 1;$$

$$\eta \rightarrow \infty: \quad f' = 0, \quad \varphi = \Theta = 0.$$

The ratio of  $\beta/\alpha$  can be set equal to  $Gr_T/Gr_M$ , since

$$Gr_M = g\alpha L^3/\nu^2, \quad Gr_T = g\beta L^3/\nu^2. \quad (26), (27)$$

The Sherwood criterion is defined as

$$Sh = iL/nFD(c_s - c_0). \quad (28)$$

Since the local mass flux to the electrode surface fulfils the equations

$$j_{y=0} = -D(\partial c/\partial y)_{y=0}, \quad j_{y=0} = i/nF, \quad (29), (30)$$

Eqs (17)–(30) lead to the following relations between  $Sh$  (referred to the characteristic length  $L$  of the electrode) and  $\varphi'(0)$ :

$$Sh/Gr_M^{1/4} = \frac{2}{3}\sqrt{2}\varphi'(0) \quad (\alpha > 0, \beta < 0) \quad (31)$$

$$Sh/|Gr_M|^{1/4} = -\frac{2}{3}\sqrt{2}|Gr_T/Gr_M|^{1/4}\varphi'(0) \quad (\alpha < 0, \beta > 0). \quad (32)$$

The system of differential equations (22)–(24) or (25) was solved for different values of  $Pr$ ,  $Sc$ , and  $Gr_T/Gr_M$  to obtain the values of  $\varphi'(0)$ . Use was made of the orthogonal collocation method<sup>9,10</sup>; the detailed procedure was described earlier<sup>4</sup>. The rate profile  $f'(\eta)$  estimated from the work of Ostrach<sup>11</sup> for the same value of  $Pr$  without regard to the flux of ions was used as initial approximation in the iterative calculations.

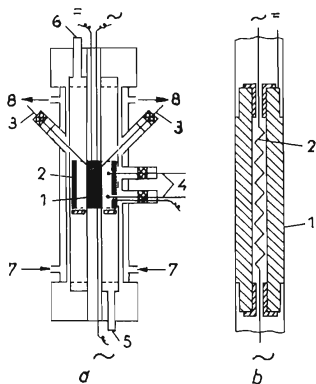


FIG. 2

Experimental set-up for measurement of the limiting current on a heated electrode: *a* 1 cylindrical indicator electrode; 2 counter-electrode; 3 thermistors for measurement of the electrode surface temperature; 4 thermistors for measurement of the bulk electrolyte temperature; 5, 6 inlet and outlet of electrolyte for tempering of the system; 7, 8 inlet and outlet of air to thermostat. *b* 1 cylindrical indicator electrode; 2 heating element

## EXPERIMENTAL.

To verify the calculated values of  $Sh$ , we used a redox system consisting of an equimolar mixture of  $K_3Fe(CN)_6$  and  $K_4Fe(CN)_6$  at a concentration of 0.01, 0.03, and 0.06 mol/l and 0.5M-KOH as a supporting electrolyte. The temperatures of measurement were 18, 25, and 35°C. If the studied electrode is warmer than the electrolyte and functions as cathode, the buoyancy forces due to heat and mass flux are of opposite directions (the case of counter-current), whereas if the electrode functions as anode, the mentioned forces act in the same direction (the case of co-current).

The electrolyser electrodes were made of nickel in the form of a cylinder, 1.8 cm in diameter and 2.5, 5, or 10 cm in length. The thickness of the diffusion is negligible against the electrode diameter, so that the electrode can be treated mathematically as a plate. A resistance heating element was placed in the center of the cylindrical electrode, which was hollow, the remaining space being filled up with a silicon oil (Fig. 2b). The electrolytic cell was in the form of an organic glass tube, 8 cm in inner diameter. The counter-electrode was placed on the inner wall of the cell with the working electrode placed coaxially. The temperature of this system was maintained by an air thermostat (Fig. 2a). Before the electrolysis started, the electrolyte of a constant temperature passed through the tubular cell. As soon as the whole system acquired a constant temperature, the electrolyte flow was stopped and the electrolysis commenced. To prevent parasitic streaming (due to a temperature difference of the electrolyte in the place of measurement and elsewhere), a separator of a diameter of 3 cm was placed under the working electrode. The tempera-

TABLE I  
Values of kinematic viscosity for solutions 1–3

Temp. °C	$\nu, \text{cm}^2 \text{s}^{-1}$		
	1	2	3
18	0.01070	0.01079	0.01090
25	0.00916	0.00925	0.00935
35	0.00745	0.00748	0.00752

TABLE II  
Values of diffusion coefficient of oxidised ( $D_2$ ) and reduced ( $D_1$ ) form for solution I

Temp., °C	Diffusion coefficient, $\text{cm}^2 \text{s}^{-1}$	
	$10^6 D_1$	$10^6 D_2$
18	5.68	6.39
25	6.85	7.73
35	8.70	9.75

ture of the working electrode surface and of the surrounding liquid was measured by thermistors of a diameter of 0.02 cm. With the use of a potentiostat, the stationary value of the limiting current was measured with an accuracy to within  $\pm 0.5\%$ . A smooth platinum electrode placed in a solution of the same composition as that used in the experiment served as reference.

#### Determination of Transport Parameters

The kinematic viscosity was calculated from the dynamic viscosity measured by the Engler viscosimeter and from the electrolyte density measured pycnometrically. The values of  $\nu$  for the three electrolyte solutions used are given in Table I, where the concentrations of both the reduced and oxidised forms were 0.01 mol/l for solution 1, 0.03 mol/l for solution 2, and 0.06 mol/l for solution 3 (containing 0.5 mol/l KOH in each case).

The diffusion coefficients were determined for solution 1 by three methods: by measuring the limiting current on a rotating disc electrode<sup>12</sup>, on a rotating cylindrical electrode<sup>13</sup>, and by the Cottrell method<sup>14</sup>. The values in Table II are averages from three measurements; the mean error is  $\pm 4\%$ . For solutions 2 and 3, the same diffusion coefficients were used.

The values of the density coefficient  $\beta$  for 0.5M-KOH were obtained by interpolation or extrapolation of the data published by Forche<sup>15</sup> and were used for all the three solutions. The values

TABLE III

Values of temperature conductivity  $a_T$  for solutions 1–3

Temp. °C	$a_T, \text{cm}^2 \text{s}^{-1}$		
	1	2	3
18	0.001404	0.001380	0.001377
25	0.001436	0.001422	0.001408
35	0.001479	0.001465	0.001450

TABLE IV

Values of density coefficient  $\alpha'$  for oxidation and reduction in solutions 1–3

Temp., °C	$10^3 \alpha' (\text{ox.})$ $\text{cm}^3 \text{mol}^{-1}$	$10^3 \alpha' (\text{red.})$ $\text{cm}^3 \text{mol}^{-1}$
18	13.67	15.14
25	16.85	15.79
35	19.25	17.38

TABLE V

Calculated values of  $Sh/|Gr_M|^{1/4}$  for various values of  $Sc$ ,  $Pr$ , and  $Gr_T/Gr_M$  and relative errors of criterion equation (36),  $\Delta$

$Sc$	$Pr$	$Gr_T/Gr_M$	$Sh/ Gr_M ^{1/4}$	$\Delta, \%$
500	5	-0.001	3.1106	1.67
		-0.002	3.1032	1.45
		-0.004	3.0879	1.04
		-0.008	3.0547	0.22
		-0.500	3.7504	-0.63
		-1.000	4.7704	-3.24
		-2.000	5.8282	-0.59
		-4.000	7.0169	0.64
		-7.813	8.3431	1.23
		-15.625	9.9511	1.53
		-31.250	11.8513	1.68
		-62.500	14.1039	1.76
		-125.000	16.7786	1.80
		-250.000	19.9568	1.82
		-500.000	23.7350	1.83
		-1 000,000	28.2271	1.84
	10	-0.008	3.0687	1.05
		-125.000	15.8802	1.0
	20	-0.008	3.0826	1.82
		-125.000	14.9566	0.71
1 000	5	-0.008	3.6285	-0.44
		-125.000	21.3139	1.95
	10	-0.001	3.7182	2.18
		-0.002	3.7089	1.93
		-0.004	3.6896	1.47
		-0.008	3.6464	0.50
		-2.000	7.0278	-0.44
1 000	10	-4.000	8.4564	0.74
		-7.813	10.0521	1.29
		-15.625	11.9878	1.58
		-31.250	14.2759	1.73
		-62.500	16.9888	1.80
		-125.000	20.2102	1.84
		-250.000	24.0383	1.86
		-500.000	28.5890	1.87
		-1 000,000	33.0007	1.88
			20	-0.008
-125.000	19.0808			1.29



TABLE V  
(Continued)

$Sc$	$Pr$	$Gr_T/Gr_M$	$Sh/ Gr_M ^{1/4}$	$\Delta, \%$
2 000	5	-0.001	4.4319	2.22
		-0.002	4.4148	1.67
		-0.004	4.3788	0.64
		-0.008	4.2975	-1.51
		-0.500	6.4106	5.60
		-1.000	7.8704	-0.78
		-2.000	9.4908	0.61
		-4.000	11.3608	1.28
		-7.813	13.4724	1.60
		-15.625	16.0473	1.77
		-31.250	19.0989	1.85
		-62.500	22.7216	1.89
		-125.000	27.0261	1.92
		-250.000	32.1428	1.93
		-500.000	38.2263	1.94
-1 000.000	45.4601	1.94		
10	10	-0.008	4.3141	-0.58
		-125.000	25.6629	1.95
20	20	-0.008	4.3470	0.64
		-125.000	24.2732	1.59

of the temperature coefficient of the density,  $\beta' = (\partial\rho/\partial T)\rho_0^{-1}$  (33) are as follows:

$$\begin{array}{rcccl}
 \text{Temperature, } ^\circ\text{C} & 18 & 25 & 35 & (33) \\
 \beta' \cdot 10^4, \text{ K}^{-1} & 2.36 & 2.95 & 3.65 &
 \end{array}$$

The temperature conductivity  $\alpha_T$  was calculated for 0.5M-KOH from the heat conductivity  $\lambda_T$  ( $\text{J/m s K}$ )<sup>16</sup>, specific heat capacity<sup>17</sup>, and density determined pycnometrically. The results are given in Table III.

Since the density coefficient  $\alpha$  is difficult to calculate, it was measured on an apparatus for the isothermal case with the use of the equation<sup>1</sup>

$$Nu = 0.66Gr_M^{0.25}Sc^{0.25}M_{1,2}. \quad (34)$$

The values of  $\alpha' = \alpha/(c_0 - c_s)$ , i.e.,

$$\alpha' = -\frac{1}{\rho_0} \frac{\partial \rho}{\partial c}. \quad (35)$$

depend mainly on the temperature and to some extent on the composition of the solutions 1–3. They were determined both for oxidation and reduction at different temperatures (Table IV). The same apparatus was used in further measurements with a heated electrode, and the values of  $\alpha'$  apparently involve an error due to parasitic streaming (recirculation) in the given cell. Eq. (34) involves a correction for migration ( $M_1$  for oxidation,  $M_2$  for reduction). In the presence of a large excess of supporting electrolyte,  $M_1 = M_2 = 1$ . For electrolytes 1–3, these correction factors were calculated<sup>3</sup> as follows:

Solution No	1	2	3
$M_1$ (ox.)	1.0134	1.0302	1.0442
$M_2$ (red.)	0.9896	0.9777	0.9687

### RESULTS AND DISCUSSION

The Sherwood criterion was calculated by using seven collocation points with an accuracy<sup>4</sup> of less than 1%, and this for 58 variants comprising various combinations of the values of  $Sc$ ,  $Pr$ , and  $Gr_T/Gr_M$ . The results enabled us to propose the following criterion equation describing the dependence of  $Sh$  on  $Gr_T/Gr_M$  for the counter-

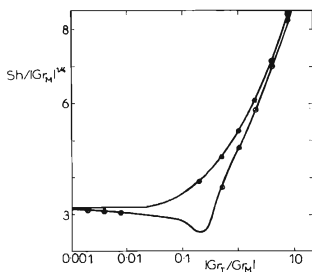


FIG. 3

Calculated values of  $Sh/|Gr_M|^{1/4}$  from the solution of Eqs (22)–(25) in dependence of  $|Gr_T/Gr_M|$  for  $Sc = 500$  and  $Pr = 5$  for counter-current (⊙) and co-current (●) and the corresponding data from criterion equations (36) and (37) (solid line)

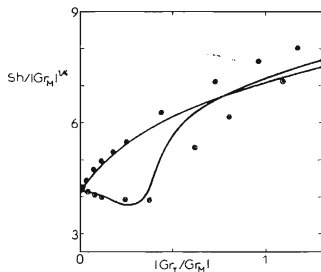


FIG. 4

Experimental values of  $Sh/|Gr_M|^{1/4}$  as function of  $|Gr_T/Gr_M|$  for  $Sc = 1\,689$ ,  $Pr = 7.76$ , and  $|Gr_M| = 4.64 \cdot 10^5$  for counter-current (⊙);  $Sc = 1\,364$ ,  $Pr = 6.64$ ,  $|Gr_M| = 1.07 \cdot 10^7$  for co-current (●) and the corresponding data from criterion equations (36) and (37) (solid lines)

TABLE VI  
 Calculated values of  $\varphi'(0)$ ,  $\Theta'(0)$ ,  $f''(0)$  for counter-current case; transformations A, B

$Sc$	$Pr$	$Gr_T/Gr_M$	$\varphi'(0)$	$\Theta'(0)$	$f''(0)$	Tr.	
500	5	-0.001	-3.2993	-0.3539	0.1707	A	
		-0.002	-3.2914	-0.3473	0.1700	A	
		-0.004	-3.2752	-0.3328	0.1688	A	
		-0.008	-3.2399	-0.2968	0.1660	A	
		-0.500	-4.7305	-0.9112	0.2666	B	
		-1.000	-5.0598	-0.9339	0.3799	B	
		-2.000	-5.1982	-0.9437	0.4318	B	
		-4.000	-5.2626	-0.9483	0.4568	B	
		-7.813	-5.2930	-0.9505	0.4688	B	
		-15.625	-5.4088	-0.9516	0.4750	B	
		-31.250	-5.3165	-0.9522	0.4782	B	
		-62.500	-5.3204	-0.9524	0.4797	B	
		-125.000	-5.3224	-0.9526	0.4805	B	
		-250.000	-5.3233	-0.9526	0.4809	B	
		-500.000	-5.3238	-0.9527	0.4811	B	
	-1 000.000	-5.3240	-0.9527	0.4812	B		
	10	-0.008	-3.2549	-0.4957	0.1670	A	
		-125.000	-5.0374	-1.1662	0.4175	B	
		20	-0.008	-3.2696	-0.7574	0.1680	A
			-125.000	-4.7444	-1.4169	0.3600	B
1 000	5	-0.008	-3.8486	-0.2221	0.1396	A	
		-125.000	-6.7610	-0.9526	0.4807	B	
	10	-0.001	-3.9438	-0.4582	0.1448	A	
		-0.002	-3.9339	-0.4505	0.1442	A	
		-0.004	-3.9134	-0.4330	0.1430	A	
		-0.008	-3.8675	-0.3805	0.1405	A	
		-2.000	-6.2681	-1.1556	0.3778	B	
		-4.000	-6.3423	-1.1611	0.3983	B	
	10	-7.813	-6.3774	-1.1638	0.4081	B	
		-15.625	-6.2953	-1.1651	0.4132	B	
-31.250		-6.4042	-1.1658	0.4158	B		
-62.500		-6.4087	-1.1661	0.4170	B		
-125.000		-6.4109	-1.1663	0.4177	B		
-250.000		-6.4120	-1.1664	0.4180	B		
-500.000		-6.4126	-1.1664	0.4181	B		
-1 000.000		-6.4128	-1.1664	0.4182	B		
20	-0.008	-3.8903	-0.6271	0.1416	A		
	-125.000	-6.0526	-1.4170	0.4601	B		

TABLE VI  
(Continued)

$Sc$	$Pr$	$Gr_T/Gr_M$	$\varphi'(0)$	$\theta'(0)$	$f''(0)$	Tr.
2 000	5	-0.001	-4.7007	-0.2542	0.1217	A
		-0.002	-4.6826	-0.2435	0.1196	A
		-0.004	-4.6445	-0.2196	0.1196	A
		-0.008	-4.5581	-0.1582	0.1165	A
		-0.500	-8.0860	-0.9387	0.3623	B
		-1.000	-8.3478	-0.9463	0.4240	B
		-2.000	-8.4649	-0.9496	0.4531	B
		-4.000	-8.5206	-0.9512	0.4673	B
		-7.813	-8.5472	-0.4741	0.4741	B
		-15.625	-8.5610	-0.9523	0.4777	B
		-31.250	-8.5678	-0.9535	0.4795	B
		-62.500	-8.5713	-0.9526	0.4804	B
		-125.000	-8.5730	-0.9527	0.4808	B
		-250.000	-8.5738	-0.9527	0.4810	B
		-500.000	-8.5742	-0.9527	0.4811	B
	-1 000.000	-8.5745	-0.9527	0.4812	B	
	10	-0.008	-4.5758	-0.2603	0.1171	A
		-125.000	-8.1406	-1.1664	0.4178	B
	20	-0.008	-4.6106	-0.4768	0.1182	A
		-125.000	-7.5997	-1.4171	0.3603	B

-current case:

$$Sh/|Gr_M|^{1/4} = [1 - 0.3e^{-30(Gr_T/Gr_M + 0.3)^2}] 0.66Sc^{1/4} [e^{10Gr_T/Gr_M} + |Gr_T/Gr_M|^{0.856} Sc^{0.319} Pr^{-0.2577}]^{7/24} \quad (36)$$

This equation can be used for  $Sc \in \langle 500, 2\,000 \rangle$  and  $Pr \in \langle 5, 20 \rangle$  with an accuracy better than 2% (with respect to the values of  $Sh/|Gr_M|^{1/4}$  calculated from Eqs (22) to (25)) for  $|Gr_T| \ll |Gr_M|$  and  $|Gr_T| \gg |Gr_M|$ . Table V gives the values of  $Sh/|Gr_M|^{1/4}$  calculated by the collocation method, and the errors of Eq. (36) on the assumption that the mentioned values are considered as correct. The calculations were not done for  $Gr_T \approx -0.1Gr_M$ , since in this region the influence of the heat flux is about the same as that of the mass flux; turbulence takes place in the boundary layer, the simplified differential equations (22)–(25) cease to be valid, and the calculation does not converge. The validity of Eq. (36) in this region was checked experimentally.

Outside the mentioned region, the orthogonal collocation method converges rapidly. The calculation of one variant on the ICL 4-72 type computer took 1-2 min with 3-6 iterations and with the required accuracy of  $10^{-8}$  in the value of  $Sh/|Gr_M|^{1/4}$ . Values of  $Sh|Gr_M|^{1/4}$  for  $Sc = 500$  and  $Pr = 5.5$  as function of the ratio of  $|Gr_T/Gr_M|$  for the counter-current case are shown in Fig. 3, where also the corresponding values calculated for the co-current case, taken from ref.<sup>4</sup>, are shown for comparison

TABLE VII

Calculated values of  $\varphi'(0)$ ,  $\Theta'(0)$ , and  $f''(0)$  for co-current case, transformation A

$Sc$	$Pr$	$Gr_T/Gr_M$	$\varphi'(0)$	$\Theta'(0)$	$f''(0)$	
500	5	0.2	-4.1774	-0.6739	0.2705	
		0.5	-4.8250	-0.8247	0.3940	
		1.0	5.5480	-0.9890	0.5745	
		2.0	6.4710	-1.1446	0.8884	
		4.0	-7.6141	-1.3563	1.4273	
		8.0	-9.0038	-1.6092	2.3431	
	10	1.0	-5.2950	-1.1958	0.5151	
	20	1.0	-5.0400	-1.4700	0.4612	
	1 000	5	1.0	-6.9839	-0.9632	0.5537
			10	0.2	-4.9746	-0.8243
0.5				-5.7958	-1.0080	0.3377
1.0				-6.6687	-1.1859	0.4943
2.0				-7.7821	-1.4018	0.7670
4.0				-9.1609	-1.6605	1.2352
8.0		-10.8366	-1.9685	2.0312		
20		1.0	-6.3511	-1.4525	0.4403	
2 000		5	0.2	-6.3721	-0.6495	0.2257
			0.5	-7.5567	-0.8095	0.3521
	1.0		-8.7761	-0.9582	0.5352	
	2.0		-10.3144	-1.1371	0.8541	
	4.0		-12.2034	-1.3517	1.4014	
	8.0		-14.4764	-1.6069	2.3276	
	10	1.0	K8.3793	-1.1776	0.4754	
	20	1.0	-7.9814	-1.4387	0.4220	

along with the curves calculated from the criterion equation (36) for counter-current and

$$Sh/Gr_M^{1/4} = 0.66Sc^{1/4}[1 + (Gr_T/Gr_M)^{0.856}Sc^{0.319}Pr^{-0.2577}]^{7/24} \quad (37)$$

TABLE VIII

Experimental values of  $Sh/|Gr_M|^{1/4}$  for counter-current (reduction) and relative errors,  $\Delta$ , of Eq. (36). Electrolyte 1 at 35°C;  $L = 5$  cm,  $c_2 = 1.130 \cdot 10^{-5}$  mol/cm<sup>3</sup>,  $Sc = 765$ ,  $Pr = 5.04$ ,  $Gr_M = 3.570 \cdot 10^5$

$\Delta T$ K	$i$ mA cm <sup>-2</sup>	$Gr_T/Gr_M$	$Sh/ Gr_M ^{1/4}$	$\Delta$ , %
0.00	0.196	0	3.477	2.23
0.06	0.191	-0.1355	3.383	5.45
0.14	0.190	-0.3162	3.371	11.59
0.37	0.244	-0.8358	4.324	-20.67
0.50	0.287	-1.1294	5.073	-13.68
0.80	0.318	-1.8071	5.637	-14.73
1.08	0.343	-2.4395	6.075	-14.73
1.54	0.371	-3.4786	6.578	-15.51
2.06	0.407	-4.6532	7.204	-13.96
2.59	0.442	-5.8504	7.830	-11.69
3.20	0.478	-7.2283	8.456	-9.54

TABLE IX

Experimental values of  $Sh/|Gr_M|^{1/4}$  for counter-current (reduction) and relative errors,  $\Delta$ , of Eq. (36). Electrolyte 3 at 25°C;  $L = 10$  cm,  $c_2 = 6.25 \cdot 10^{-5}$  mol/cm<sup>3</sup>,  $Sc = 1210$ ,  $Pr = 6.64$ ,  $Gr_M = 1.003 \cdot 10^7$

$\Delta T$ K	$i$ mA cm <sup>-2</sup>	$Gr_T/Gr_M$	$Sh/ Gr_M ^{1/4}$	$\Delta$ , %
0.00	1.034	0	3.944	3.41
0.05	1.026	-0.0165	3.909	2.51
0.10	1.034	-0.0330	3.944	3.94
0.22	1.079	-0.0726	4.112	9.48
0.44	1.132	-0.1452	4.313	18.52
0.96	1.202	-0.3169	4.583	32.30
1.38	1.238	-0.4555	4.719	2.72
2.37	1.459	-0.7823	5.561	-9.50
3.80	1.742	-1.2543	6.639	-4.01

TABLE X

Experimental values of  $Sh/|Gr_M|^{1/4}$  for counter-current (reduction) and relative errors,  $\Delta$ , of Eq. (36). Electrolyte 2 at 18°C;  $L = 5$  cm,  $c_2 = 3.081 \cdot 10^{-5}$  mol/cm<sup>3</sup>,  $Sc = 1689$ ,  $Pr = 7.76$ ,  $Gr_M = 4.641 \cdot 10^5$

$\Delta T$ K	$i$ mA cm <sup>-2</sup>	$Gr_T/Gr_M$	$Sh/ Gr_M ^{1/4}$	$\Delta$ , %
0.00	0.424	0	4.281	3.26
0.07	0.410	-0.0375	4.138	- 0.22
0.15	0.403	-0.0803	4.065	- 1.39
0.22	0.396	-0.1178	3.996	- 2.00
0.46	0.389	-0.2464	3.923	4.73
0.70	0.389	-0.3750	3.923	- 7.52
1.15	0.531	-0.6160	5.351	-15.34
1.49	0.612	-0.7981	6.171	- 9.84
2.04	0.707	-1.0928	7.133	- 3.67
2.82	0.807	-1.5106	8.130	1.26
4.00	0.930	-2.1427	9.809	11.85

TABLE XI

Experimental values of  $Sh/|Gr_M|^{1/4}$  for counter-current (reduction) and relative errors,  $\Delta$ , of Eq. (36). Electrolyte 3 at 25°C;  $L = 2$  cm,  $c_2 = 5.89 \cdot 10$  mol/cm<sup>3</sup>,  $Sc = 1210$ ,  $Pr = 6.64$ ,  $Gr_M = 7.561 \cdot 10^4$

$\Delta T$ K	$i$ mA cm <sup>-2</sup>	$Gr_T/Gr_M$	$Sh/ Gr_M ^{1/4}$	$\Delta$ , %
0.00	1.415	0	3.885	1.86
0.02	1.406	-0.0070	3.861	1.02
0.10	1.388	-0.0350	3.811	0.49
0.18	1.370	-0.0630	3.762	- 0.08
0.35	1.353	-0.1226	3.713	0.68
0.50	1.326	-0.1751	3.639	2.25
0.73	1.326	-0.2557	3.639	7.87
1.00	1.326	-0.3502	3.639	- 0.09
1.33	1.379	-0.4658	3.787	-19.31
1.61	1.830	-0.5674	5.022	- 8.27
2.02	2.122	-0.7075	5.828	- 2.57
2.44	2.413	-0.8546	6.627	5.47

TABLE XII

Experimental values of  $Sh/Gr_M^{1/4}$  for co-current (oxidation) and relative errors,  $\Delta$ , of Eq. (37). Electrolyte 3 at 35°C;  $L = 5$  cm,  $c_1 = 6.15 \cdot 10^{-5}$  mol/cm<sup>3</sup>,  $Sc = 864$ ,  $Pr = 5.19$ ,  $Gr_M = 2.146 \cdot 10^6$

$\Delta T$ K	$i$ mA cm <sup>-2</sup>	$Gr_T/Gr_M$	$Sh/Gr_M^{1/4}$	$\Delta$ , %
0.00	1.563	0	3.954	10.50
0.05	1.595	0.0184	4.035	7.34
0.11	1.655	0.0405	4.187	6.92
0.22	1.740	0.0811	4.401	6.15
0.62	1.910	0.2286	4.832	2.23
0.86	1.995	0.3170	5.046	1.26
1.24	2.098	0.4571	5.035	-0.25
1.40	2.144	0.5161	5.423	-0.34
2.00	2.267	0.7373	5.736	-1.74
2.39	2.342	0.8810	5.923	-2.19
3.75	2.554	1.3824	6.461	-3.15

TABLE XIII

Experimental values of  $Sh/Gr_M^{1/4}$  for co-current (oxidation) and relative errors,  $\Delta$ , of Eq. (37). Electrolyte 1 at 25°C;  $L = 2$  cm,  $c_1 = 1.041 \cdot 10^{-5}$  mol/cm<sup>3</sup>,  $Sc = 1336$ ,  $Pr = 6.38$ ,  $Gr_M = 1.523 \cdot 10^4$

$\Delta T$ H	$i$ mA cm <sup>-2</sup>	$Gr_T/Gr_M$	$Sh/Gr_M^{1/4}$	$\Delta$ , %
0.00	0.151	0	4.076	2.15
0.04	0.166	0.0724	4.481	-2.95
0.09	0.179	0.1629	4.807	-5.53
0.20	0.207	0.3621	5.572	-3.74
0.32	0.224	0.5793	6.021	-4.85
0.53	0.248	0.9595	6.673	-4.99
0.87	0.279	1.5751	7.500	-4.24
1.24	0.302	2.2449	8.143	-4.11
1.73	0.332	3.1320	8.953	-2.46
2.20	0.357	3.9829	9.522	-0.97
2.85	0.380	5.1597	10.238	-0.96



TABLE XIV

Experimental values of  $Sh/Gr_M^{1/4}$  for co-current (oxidation) and relative errors,  $\Delta$ , of Eq. (37). Electrolyte 3 at 18°C;  $L = 5$  cm,  $c_1 = 5.892 \cdot 10^{-5}$  mol/cm<sup>3</sup>,  $Sc = 1919$ ,  $Pr = 7.92$ ,  $Gr_M = 9.774 \cdot 10^5$

$\Delta T$ K	$i$ mA cm <sup>-2</sup>	$Gr_T/Gr_M$	$Sh/Gr_M^{1/4}$	$\Delta$ , %
0.00	0.952	0	4.683	7.20
0.08	1.098	0.0199	4.964	7.03
0.14	1.093	0.0349	5.381	12.40
0.35	1.174	0.0872	5.782	11.35
0.68	1.273	0.1695	6.269	10.78
1.12	1.372	0.2791	6.757	10.27
1.43	1.440	0.3564	7.087	10.75
1.91	1.514	0.4760	6.454	10.31
2.06	1.528	0.5134	7.525	9.73
2.51	1.609	0.6255	7.923	11.05
3.73	1.740	0.9296	8.568	10.53

TABLE XV

Experimental values of  $Sh/Gr_M^{1/4}$  for co-current (oxidation) and relative errors,  $\Delta$ , of Eq. (37). Electrolyte 3 at 25°C;  $L = 10$  cm,  $c_1 = 5.93 \cdot 10^{-5}$  mol/cm<sup>3</sup>,  $Sc = 1364$ ,  $Pr = 6.64$ ,  $Gr_M = 1.071 \cdot 10^7$

$\Delta T$ K	$i$ mA cm <sup>-2</sup>	$Gr_T/Gr_M$	$Sh/Gr_M^{1/4}$	$\Delta$ , %
0.00	0.939	0	4.187	4.39
0.05	0.958	0.0154	4.274	1.74
0.11	1.001	0.0340	4.462	2.18
0.23	1.066	0.0711	4.753	2.65
0.38	1.116	0.1174	4.975	1.64
0.59	1.165	0.1823	5.197	0.04
0.82	1.238	0.2534	5.505	0.68
1.42	1.411	0.4388	6.293	4.48
2.36	1.595	0.7292	7.112	6.82
3.10	1.721	0.9579	7.673	8.83
3.80	1.804	1.1742	8.044	9.17

for co-current<sup>4</sup>. The latter equation is valid for  $Sc \in \langle 500, 2000 \rangle$ ,  $Pr \in \langle 5, 20 \rangle$ , and  $Gr_T/Gr_M \in \langle 0.2, 8 \rangle$ . The values of  $\varphi'(0)$ ,  $\Theta'(0)$ , and  $f''(0)$  for various values of  $Sc$ ,  $Pr$ , and  $Gr_T/Gr_M$  for the counter-current case are given in Table VI for illustration. Analogous values for the co-current case are given in Table VII.

To verify the proposed criterion equations (36) and (37), we measured 140 values of the limiting current density for reduction and 300 for oxidation. Eq. (36) gives values of  $Sh$  for the counter-current case with an accuracy better than  $\pm 20\%$  in the whole region: for  $|Gr_T| \gg |Gr_M|$  or  $|Gr_T| \ll |Gr_M|$ , the accuracy is better than  $\pm 5\%$ . Examples of measured values for various values of the experimental parameters are given for the counter-current case in Tables VIII–XI together with the relative errors of Eq. (36) referred to experimental results. Analogous data for the co-current case are given in Tables XII–XV. It follows that Eq. (37) gives values of  $Sh$  with an accuracy better than  $\pm 10\%$  in the whole studied region.

Typical measured dependences of  $Sh/|Gr_M|^{1/4}$  on  $|Gr_T/Gr_M|$  and those calculated from Eqs (36) and (37) for the same parameters are shown graphically in Fig. 4. From this and Fig. 3 it is seen that the proposed Eq. (36) describes well both the experimental and theoretical results and can be used to calculate the Sherwood criterion in the region of  $Sc \in \langle 500, 2000 \rangle$  and  $Pr \in \langle 5, 20 \rangle$ . For  $|Gr_T/Gr_M| \geq 1$ , Eq. (36) can be simplified to the form

$$Sh/|Gr_M|^{1/4} = 0.66|Gr_T/Gr_M|^{1/4} Sc^{0.343} Pr^{-0.0652}. \quad (38)$$

#### LIST OF SYMBOLS

$a_T$	temperature conductivity ( $m^2/s$ )
$A$	parameter defined by Eq. (18)
$b$	width of operating electrode (m)
$B$	parameter defined by Eq. (21)
$c$	concentration of electroactive ions ( $mol/m^3$ )
$c_p$	specific heat capacity at constant pressure ( $J kg^{-1} K^{-1}$ )
$D$	diffusion coefficient of electroactive substance ( $m^2/s$ )
$f(\eta)$	auxiliary function, Eq. (16) or (19)
$F$	Faraday's constant ( $96487 C/mol$ )
$g$	acceleration of gravity ( $9.81 m/s^2$ )
$Gr_M$	Grashof's criterion for mass, Eq. (26)
$Gr_T$	Grashof's criterion for heat, Eq. (27)
$i$	current density ( $A/m^2$ )
$\bar{i}$	mean current density ( $A/m^2$ )
$j$	ionic flux ( $mol m^2/s$ )
$L$	electrode length (m)
$M_1, M_2$	migration factor
$n$	number of exchanged electrons
$p$	pressure in electrolyte (Pa)
$Pr$	Prandtl's criterion, equal to $\nu/a_T$

$Sc$	Schmidt's criterion, equal to $\nu/D$
$Sh$	Sherwood's criterion, Eq. (28)
$T$	absolute temperature (K)
$v$	velocity of flow of electrolyte (m/s)
$x, y, z$	coordinates (m)
$\alpha, \alpha'$	coefficients defined by Eqs (10) and (35)
$\beta, \beta'$	coefficients defined by Eqs (12) and (33)
$\eta$	dimensionless parameter
$\theta$	dimensionless temperature
$\lambda_T$	heat conductivity ( $\text{J m}^{-1} \text{s}^{-1} \text{K}^{-1}$ )
$\mu$	dynamic viscosity ( $\text{kg m}^{-1} \text{s}^{-1}$ )
$\nu$	kinematic viscosity ( $\text{m}^2/\text{s}$ )
$\rho$	density of solution ( $\text{kg}/\text{m}^3$ )
$\varphi$	dimensionless concentration
$\psi$	stream function, Eqs (14) and (15)

## Subscripts

0 bulk phase,  $s$  electrode surface,  $x$   $x$ -component of vector,  $y$   $y$ -component of vector,  
 1  $\text{K}_4\text{Fe}(\text{CN})_6$ , 2  $\text{K}_3\text{Fe}(\text{CN})_6$ .

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