

SIMULTANEOUS FLOW OF IONS AND HEAT TO A PLATE ELECTRODE IN THE REGION OF NATURAL CONVECTION*

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The Sherwood criterion was calculated for a flow of ions to the surface of a plate electrode during natural convection by solving the Navier-Stokes, convective diffusion, and convective heat transfer equations. The solution for the boundary layer region was performed by the collocation method using orthogonal exponential polynomials. Values of the Sh criterion were obtained for $Sc \in \langle 500; 2000 \rangle$, $Pr \in \langle 5; 20 \rangle$, and $Gr_T/Gr_M \in \langle 0.2; 8.0 \rangle$. A comparison with literature data revealed the best agreement with average errors of +2.0 and -1.4%. Another equation with an error of only +0.5% is proposed.

Relations for the calculation of the Sherwood criterion given in the literature can be expressed by the general equation

$$Sh/Gr_M^{1/4} = \xi Sc^{1/4} [1 + (Gr_T/Gr_M)^\omega Sc^\gamma Pr^\delta]^\varepsilon. \quad (1)$$

The values of the constants ξ , ω , γ , δ , and ε according to different authors¹⁻³ are given in Table I together with the validity intervals, in which the equations hold.

Neither of the equations (1a-d) in Table I was derived from a simultaneous solution of all relevant differential equations. It was the aim of the present work to carry out such a solution and on its basis to judge the correctness of Eqs (1a-d) in the region $Pr \approx 10$ and $Sc \approx 10^3$. The calculations led to a more exact equation (1e).

FORMULATION OF THE PROBLEM

An electrode in the form of a vertical plate is placed in a semiinfinite space in the $x-z$ plane, the x axis is vertical; the orientation of the velocity components v_x and v_z and other quantities are illustrated in Fig. 1.

The concentration of electroactive ions around the electrode is c_0 ; they undergo an electrode reaction $Ox + ne = Red$. The solution contains a supporting electrolyte in a large excess against the electroactive ions. During the electrode reaction and heat

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transfer, streaming in the same direction takes place. We shall not consider the case where the streaming due to the electrode reaction has an opposite direction than that due to the heat transfer.*

TABLE I
Parameters for the Equations for the Calculation of Sh

Equation	ξ	ω	γ	δ	ε	Ref.	Note
(1a)	0.67	1	1/2	-1/2	1/4	2	$Sc \in \langle 1, 10 \rangle$ $Pr \sim 1$ $Gr_M/Gr_T \in \langle 0, 1 \rangle$
(1b)	0.66	3/4	1/4	-1/4	1/3	3	$Sc \sim 10^3$ $Pr \sim 10$
(1c)	0.66	1	0.3722	-0.3006	1/4	1	$Sc \in \langle 800, 10^4 \rangle$ $Pr \in \langle 1, 80 \rangle$ $Gr_T > Gr_M$
(1d)	0.66	3/4	0.2791	-0.2255	1/3	1	$Sc \in \langle 800, 10^4 \rangle$ $Pr \in \langle 1, 80 \rangle$ $Gr_T > Gr_M$
(1e)	0.66	0.8570	0.3190	-0.2577	7/24	present work	$Sc \in \langle 500, 2000 \rangle$ $Pr \in \langle 5, 20 \rangle$ $Gr_T/Gr_M \in \langle 0.2, 8.0 \rangle$

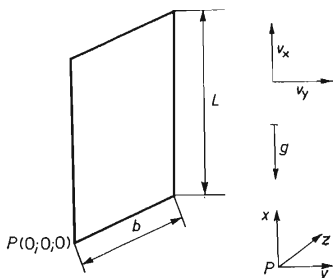


FIG. 1
Orientation of Electrode
 x, y, z Axes of coordinates; $P(0,0,0)$ origin of the coordinate system; b electrode width; L electrode length; v_x, v_y velocity components of electrolyte; g acceleration of gravity.

* In both cases, during the electrode reaction as well as heat transfer, there is a change in the electrolyte density at the electrode surface, hence the streaming is in either case due to a density gradient at the electrode surface.

If we consider an incompressible liquid with a constant density in a stationary state, the system can be described as follows: Convective diffusion and convective heat transfer:

$$v \cdot \text{grad } c = D \Delta c, \quad \rho C_p (v \cdot \text{grad } T) = \lambda_T \Delta T. \quad (2), (3)$$

Navier-Stokes and continuity equations:

$$\rho (v \cdot \text{grad } v) = \rho g - \text{grad } p + \mu \Delta v, \quad \text{div } v = 0. \quad (4), (5)$$

The system of partial differential equations (2)–(5) can be transformed into ordinary differential equations by neglecting certain terms and using a suitable transformation. This method elaborated by Prandtl^{4,5} and Pohlhausen⁶ consists in introducing dimensionless quantities and comparing their magnitude.

Eq. (2) can be rewritten as

$$v_x \partial c / \partial x + v_y \partial c / \partial y = D \partial^2 c / \partial y^2. \quad (6)$$

A similar equation holds for the convective heat transfer:

$$v_x \partial T / \partial x + v_y \partial T / \partial y = a_T \partial^2 T / \partial y^2. \quad (7)$$

For a streaming effected by a density gradient, the Navier-Stokes equation for the boundary layer is simplified by setting $\text{grad } p \approx \rho_0 g$ (compare¹⁰) to a single equation:

$$v_x \partial v_x / \partial x + v_y \partial v_x / \partial y = \nu \partial^2 v_x / \partial y^2 + g(\rho - \rho_0) / \rho_0. \quad (8)$$

In deriving Eqs (6)–(8), we considered D , a_T and ν as constants independent of the composition and temperature of the electrolyte. For the purpose of the calculations we set these quantities equal to their values in the bulk phase. The equation of continuity is:

$$\partial v_x / \partial x + \partial v_y / \partial y = 0. \quad (9)$$

The boundary conditions are:

$$c = c_s; \quad T = T_s; \quad v_y = v_x = 0 \quad \text{for } y = 0; \quad x \in \langle 0; L \rangle$$

$$c = c_0; \quad T = T_0; \quad v_x = 0 \quad \text{for } y \rightarrow \infty.$$

We shall consider the case corresponding for $c_s = 0$ to the case of limiting current density with a constant wall temperature, and we shall transform Eqs (6)–(9) into ordinary differential equations. We introduce the following dimensionless quantities:

$$\varphi = (c - c_0) / (c_s - c_0), \quad \alpha = (c_s - c_0) (\partial \rho / \partial c) / \rho_0, \quad (10), (11)$$

$$\theta = (T - T_0) / (T_s - T_0), \quad \beta = (T_s - T_0) (\partial \rho / \partial T) / \rho_0. \quad (12), (13)$$

We define the dependence of the density on the temperature and concentration of electroactive ions as follows:

$$\rho = \rho_0 (1 + \alpha \varphi + \beta \theta). \quad (14)$$

Further we introduce a stream function ψ so as to fulfil Eq. (9) identically:

$$v_x = \partial\psi/\partial y, \quad v_y = -\partial\psi/\partial x \quad (15), (16)$$

and we shall assume that this function has the following form:

$$\psi = 4vAx^{3/4}f(\eta), \quad (17)$$

where

$$\eta = Ay/x^{1/4}, \quad A = (g\alpha/4v^2)^{1/4}. \quad (18), (19)$$

On introducing (17) into (15) it follows that the value of $df/d\eta$ is proportional to the rate of electrolyte flow v_x . If we combine Eqs (6)–(19) we obtain the final system of differential equations, where primes denote differentiation with respect to η :

$$\varphi'' + 3 \text{Sc} \cdot f \cdot \varphi' = 0, \quad \theta'' + 3 \text{Pr} \cdot f \cdot \theta' = 0, \quad (20), (21)$$

$$f''' + 3f \cdot f'' - 2f'^2 + \varphi + (\beta/\alpha)\theta = 0. \quad (22)$$

The boundary conditions are:

$$f = f' = 0, \quad \varphi = \theta = 1 \quad \text{for } \eta = 0,$$

$$f' = 0, \quad \varphi = \theta = 0 \quad \text{for } \eta \rightarrow \infty.$$

The ratio of β/α can be expressed as Gr_T/Gr_M since according to the definition

$$\text{Gr}_M = g\alpha L^3/v^2, \quad \text{Gr}_T = g\beta L^3/v^2. \quad (23), (24)$$

The Sherwood's criterion is defined as

$$\text{Sh} = iL/nFD(c_s - c_0). \quad (25)$$

If we consider the local mass flow at the electrode surface

$$j_{(y=0)} = -D(\partial c/\partial y)_{y=0}, \quad j_{y=0} = i/nF, \quad (26), (27)$$

we can derive the following relation between Sh (referred to the characteristic electrode length L) and $\varphi'(0)$ from Eqs (18)–(27):

$$\text{Sh}/\text{Gr}_M^{1/4} = -\frac{2}{3}\sqrt{2}\varphi'(0). \quad (28)$$

Further we solve the system of differential equations (20)–(22) to obtain values of $\varphi'(0)$ for various values of Pr, Sc, and Gr_T/Gr_M .

METHOD OF CALCULATION

The mentioned differential equations were solved by the collocation method^{7,8} using orthogonal exponential polynomials. The collocation is carried out always in the zero points of a polynomial whose degree is by one higher than the highest degree used in the calculation. It follows from the theory that the solution will be in this

case most accurate, *i.e.*, the integral from the square of the deviation between the accurate and approximate solution in the given interval of η from zero to infinity will be a minimum.

The orthogonal exponential polynomial $W_N(\eta)$ of the N -th degree is defined as

$$W_N(\eta) = \sum_{K=1}^N b_{NK} \exp(-K\eta). \quad (29)$$

The coefficients b_{NK} according to ref.⁹ for $N = 5-10$ are given in the Appendix (Table AI); we calculated their zero points which are given in Table AII. The mentioned method is based on an approximation of the unknown function f by a sum of the polynomials $W_N(\eta)$ which are multiplied with constants to be determined.

In our case we used the following approximation:

$$f' = \sum_{N=1}^J C_N W_N(\eta), \quad f = \sum_{N=1}^J C_N Z_N(\eta), \quad (30), (31)$$

$$f'' = -\sum_{N=1}^J C_N Y_N(\eta), \quad f''' = \sum_{N=1}^J C_N X_N(\eta). \quad (32), (33)$$

To simplify the notation, we set:

$$Z_N(\eta) = \sum_{K=1}^N K^{-1} b_{NK} (1 - e^{-K\eta}), \quad (34)$$

$$Y_N(\eta) = \sum_{K=1}^N K b_{NK} e^{-K\eta}, \quad X_N(\eta) = \sum_{K=1}^N K^2 b_{NK} e^{-K\eta}. \quad (35), (36)$$

From the boundary conditions for $f'(0)$ and $f'''(0)$ it follows that

$$\sum_{N=1}^J C_N = 0; \quad \sum_{N=1}^J C_N \left(\sum_{K=1}^N K^2 b_{NK} \right) = -1 - Gr_T / Gr_M. \quad (37), (38)$$

In deriving Eq. (37) we used the relation $\sum_{N=1}^K b_{NK} = 1$. Eq. (20) can be rearranged as

$$\varphi'(0) = -1/P; \quad P = \int_0^\infty \exp\left(-\int_0^\eta 3 Sc f d\eta\right) d\eta. \quad (39), (40)$$

Similarly we define

$$S(\eta) = \int_0^\infty \exp\left(-\int_0^\eta 3 Sc f d\eta\right) d\eta \quad (41)$$

so that

$$\varphi = 1 - S(\eta)/P. \quad (42)$$

The integral of f is given by the equation

$$\int_0^\eta f \, d\eta = \sum_{N=1}^J C_N \left[\sum_{K=1}^N b_{NK} K^{-2} (K\eta + e^{-K\eta} - 1) \right]. \quad (43)$$

Similarly we obtain for Eq. (21)

$$\theta'(0) = -1/R; \quad \theta = 1 - Q(\eta)/R, \quad (44), (45)$$

where

$$R = Q(\infty), \quad Q(\eta) = \int_0^\eta \exp\left(-\int_0^\eta 3 \operatorname{Pr} f \, d\eta\right) d\eta. \quad (46), (47)$$

After introducing the above expressions into Eq. (22) we obtain

$$\begin{aligned} & \sum_{N=1}^J C_N X_N(\eta) - 3 \left(\sum_{N=1}^J C_N Z_N(\eta) \right) \left(\sum_{N=1}^J C_N Y_N(\eta) \right) - S(\eta)/P + 1 - \\ & - 2 \left(\sum_{N=1}^J C_N W_N(\eta) \right)^2 + (G_{T1}/G_{T2}) (1 - Q(\eta)/R) = 0. \end{aligned} \quad (48)$$

We require the fulfilment of Eq. (48) only in $J-2$ predetermined points with respect to the boundary conditions (37) and (38). These points are zero points of an orthogonal exponential polynomial whose degree is by one higher than the highest degree of the polynomials used for the collocation. Together with the boundary conditions (37) and (38) we then obtain J nonlinear equations for J unknown constants C_N .

The system of equations (37), (38) and (48) was linearized by expanding in series in the points C_N and neglecting the terms of higher orders. We thus obtained a system of J linear equations for the corrections ΔC_N of the coefficients C_N , whose values were found by an iterative procedure. We have

$$C_N^{k+1} = C_N^k + \Delta C_N^k, \quad k = 0, 1, 2, \dots \quad (49)$$

The initial approximation C_N^0 was calculated by solving the following equations on the basis of a velocity profile $f'(\eta)$ estimated from ref.⁸ for the same value of Pr :

$$\sum_{N=1}^J C_N^0 W_N(\eta) = f'; \quad \sum_{N=1}^J C_N^0 = 0, \quad (50), (51)$$

$$\sum_{N=1}^J C_N^0 \left(\sum_{K=1}^N K^2 b_{NK} \right) = -1 - G_{T1}/G_{T2}. \quad (52)$$

After calculation of the constants C_N we calculated the values of $\varphi'(0)$ and $\theta'(0)$ from Eqs (39) and (44). The results for $J = 7$ are given in Table II. The constants C_N are given in Table III for the first five variants. It is seen that the absolute values

TABLE II

Calculated Values of $\varphi'(0)$ and $\theta'(0)$ for Given Values of Sc, Pr, and Gr_T/Gr_M with the Use of Orthogonal Exponential Polynomials of the First to Seventh Degree

Sc	Pr	Gr_T/Gr_M	$\varphi'(0)$	$\theta'(0)$	Calc. No
500	5	0.2	-4.1474	-0.6739	1
		0.5	-4.8250	-0.8247	2
		1.0	-5.5480	-0.9890	3
		2.0	-6.4710	-1.1446	4
		4.0	-7.6141	-1.3563	5
		8.0	-9.0038	-1.6092	6
	10	1.0	-5.2950	-1.1958	7
		20	1.0	-5.0400	-1.4700
1 000	5	1.0	-6.9839	-0.9632	9
		0.2	-4.9746	-0.8243	10
		0.5	-5.7958	-1.0080	11
		1.0	-6.6687	-1.1859	12
		2.0	-7.7821	-1.4018	13
		4.0	-9.1609	-1.6605	14
	20	8.0	-10.8366	-1.9685	15
		1.0	-6.3511	-1.4525	16
2 000	5	0.2	-6.3721	-0.6495	17
		0.5	-7.5567	-0.8095	18
		1.0	-8.7761	-0.9582	19
		2.0	-10.3144	-1.1371	20
		4.0	-12.2034	-1.3517	21
		8.0	-14.4764	-1.6069	22
	10	1.0	-8.3793	-1.1776	23
		20	1.0	-7.9814	-1.4387

TABLE III

Multiplicative Constants C_N for Calculations No 1-5
Values of the criteria are given in Table II.

Calc. No	C_1	C_2	C_3	C_4	C_5	C_6	C_7
1	0.09449	-0.11762	0.03992	-0.01999	0.00594	0.00399	0.00125
2	0.14389	-0.16722	0.03351	-0.01057	0.00277	-0.00353	0.00115
3	0.19737	-0.20485	0.00537	0.00497	-0.00104	-0.00268	0.00086
4	0.26925	-0.23825	-0.04812	0.01995	-0.00022	-0.00327	0.00067
5	0.36498	-0.26298	-0.12736	0.01932	0.01158	-0.00610	0.00054

of C_N decrease with increasing N beginning with the second term, hence the orthogonal exponential polynomials were suitably chosen for the given problem.

The calculated values of $\varphi'(0)$ were introduced into Eq. (28) and the values of $Sh/Gr_M^{1/4}$ were compared with those obtained from Eqs (1a-d). The relative deviation for all these equations was calculated and on this basis a new equation (1e) was proposed; the relative deviations are summarized in Table IV.

Typical velocity profiles, $f'(\eta)$, calculated from Eq. (30) are shown in Fig. 2. The concentration and temperature profiles, $\varphi(\eta)$ and $\theta(\eta)$, calculated from Eqs (42) and (45) are exemplified in Fig. 3. The problems of the heat transfer are noted in Appendix II.

TABLE IV
Relative Errors of Eqs (1a-e) in Percent

Sc	Pr	Gr_T/Gr_M	(1a)	(1b)	(1c)	(1d)	(1e)		
500	5	0.2	-6.63	0.35	2.29	-3.47	-0.55		
		0.5	-9.00	2.38	2.28	-3.58	-0.07		
		1.0	-10.30	4.02	2.16	-1.62	0.38		
		2.0	-11.16	5.42	2.01	-0.70	0.79		
		4.0	-11.67	6.50	1.90	0.05	1.10		
	10	8.0	-11.96	7.27	1.82	0.62	1.33		
		1.0	-6.98	3.66	1.92	-2.21	-0.04		
		2.0	-4.35	2.85	1.26	-3.23	-0.88		
		1 000	5	1.0	-12.87	5.17	2.20	-1.17	0.63
			10	0.2	-5.72	1.20	2.44	-3.28	-0.37
0.5	-7.91			3.36	2.34	-2.45	0.02		
1.0	-9.13			5.04	2.15	-1.54	0.42		
2.0	-9.92			6.48	1.98	-0.66	0.78		
20	4.0	-10.38	7.59	1.87	0.08	1.10			
	8.0	-10.63	8.38	1.81	0.64	1.33			
	1.0	-6.05	4.48	1.74	-2.32	-0.17			
	2 000	5	0.2	-11.52	2.49	2.61	-2.75	-0.01	
			0.5	-14.53	4.53	2.17	-1.90	0.24	
1.0			-15.92	6.00	1.90	-1.07	0.54		
2.0			-16.59	7.29	1.84	-0.20	0.95		
10		4.0	-16.82	8.32	1.91	0.56	1.34		
		8.0	-16.93	9.01	1.95	1.09	1.61		
		1.0	-11.87	6.01	1.98	-1.31	0.46		
		2.0	-8.43	5.65	1.72	-1.91	0.03		

DISCUSSION

The calculations were done for $J = 7$; their accuracy was checked by comparing with those obtained by Ostrach⁸ by numerical integration for $Gr/Gr_M = 0$. The deviation against the value of $\varphi'(0)$ obtained numerically was $+0.3\%$ for $Sc = 2$ or 10 and $+0.6\%$ for $Sc = 100$. Another calculation was done for $Sc = 1000$, $J = 5$ or 6 and the deviation was in both cases $+1.1\%$. Hence, the method gives systematically slightly higher values than the numerical calculations.

The method of calculation is very rapid and converges well. The calculation of one variant took about a minute on an ICL-4-72 type computer, the number of iterations was 3–6 for the desired accuracy of 10^{-8} in the value of $\varphi'(0)$.

It is seen from Table IV that of the equations given in the literature Eqs (1c) and (1d) are satisfactory in the considered region of the criteria, the average error being $+2.0$ and -1.4% , which is always higher than the error of the method of calculation. Further it is seen that the optimum results correspond to the arithmetic mean of the Sh values from Eqs (1c) and (1d), *i.e.*

$$\begin{aligned} Sh/Gr_M^{1/4} = & 0.33 Sc^{1/4} \{ [1 + (Gr_T/Gr_M) Sc^{0.3722} Pr^{-0.0306}]^{1/4} + \\ & + [1 + (Gr_T/Gr_M)^{3/4} Sc^{0.2791} Pr^{-0.2255}]^{1/3} \}. \end{aligned} \quad (53)$$

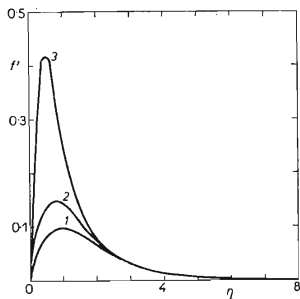


FIG. 2

Velocity Profiles $f'(\eta)$

$Sc = 2000$, $Pr = 5$. Gr_T/Gr_M : 1 0.2;
2 1.0; 3 3.0.

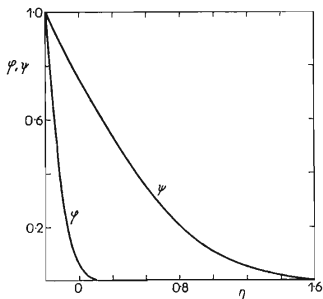


FIG. 3

Concentration, $\varphi(\eta)$, and Temperature, $\psi(\eta)$,
from Left to Right Profiles for $Sc = 1000$,
 $Pr = 10$, and $Gr_T/Gr_M = 1$

Eq. (1e) is a good approximation of (53). Eq. (1a) is practically useless (errors up to 10%). It is also seen from the Table IV that Eq. (1b) has the smallest deviations in the region of $Gr_T/Gr_M \rightarrow 0$.

Accordingly, we propose Eq. (1e) with an average error of +0.45%. This gives the most accurate results for $Gr_T/Gr_M \in \langle 0; 2 \rangle$, as is seen from Table IV. For higher values of Gr_T/Gr_M Eq. (1d) is preferable.

LIST OF SYMBOLS

a_T	parameter equal to $\lambda_T/\rho C_p$ (cm^2/s)
b_{NK}	coefficient of orthogonal exponential polynomial
c	concentration of electroactive substance (mol/cm^3)
C_N	constant to be determined
C_N^0	first estimate of C_N
C_N^{k+1}	more accurate value of C_N
ΔC_N^k	correction of C_N
C_p	specific heat at constant pressure ($cal/K \cdot g$)
D	diffusion coefficient of electroactive substance (cm^2/s)
$f(\eta)$	auxiliary function, see Eq. (17)
F	Faraday's constant, 96487 C/mol
g	acceleration of gravity, 981 cm/s^2
Gr_M	Grashof's number for mass, see Eq. (23)
Gr_T	Grashof's number for heat, see Eq. (24)
i	current density (A/cm^2)
\bar{i}	mean current density on electrode of length L (A/cm^2)
j	flux of ions ($mol/cm^2 \cdot s$)
J	number of equations
L	length of electrode (cm)
n	number of electrons in electrode reaction
Pr	Prandtl's number equal to ν/a_T
Sc	Schmidt's number equal to ν/D
Sh	Sherwood's number, see Eq. (25)

TABLE AI

Values of b_{NK} for Orthogonal Exponential Polynomials⁹ W_N

$N \setminus K$	1	2	3	4	5
5	5	-60	210	-280	126
6	-6	105	-560	1 260	-1 260
7	7	-168	1 260	-4 200	6 930
8	-8	252	-2 520	11 550	-27 720
9	9	-360	4 620	-27 720	90 090
10	-10	495	-7 920	60 060	-252 252

T	electrolyte temperature (K)
v_x	x -component of velocity of electrolyte
v_y	y -component of electrolyte velocity
x, y, z	coordinates (cm)
α	coefficient defined by Eq. (11)
β	coefficient defined by Eq. (13)
$\gamma, \delta, \varepsilon, \xi, \omega$	constants of Eq. (1)
η	dimensionless parameter
θ	dimensionless temperature
λ_T	heat conductivity (cal/cm . s . K)
μ	dynamic viscosity (g/cm . s)
ν	kinematic viscosity (cm ² /s)
ρ	density of solution (g/cm ³)
φ	dimensionless concentration
ψ	stream function, see Eqs (15) and (16)

Subscripts o and s refer to bulk phase and electrode surface, respectively.

APPENDIX

Heat Flow to a Plate Electrode

The calculated values of $\theta'(0)$ enable to calculate the Nusselt's criterion Nu for the heat flow,

$$\text{Nu} = k_T L / \lambda_T, \quad (A1)$$

where k_T is the heat transfer coefficient in cal/cm² s units. The heat flow, Q , at the electrode surface is given as

$$Q = -\lambda_T b \int_0^L (\partial T / \partial y)_{y=0} dy, \quad (A2)$$

hence

$$Q = k_T b L (T_s - T_0). \quad (A3)$$

TABLE AI
(Continued)

6	7	8	9	10
—	—	—	—	—
462	—	—	—	—
—5 544	1 716	—	—	—
36 036	—24 024	6 435	—	—
—168 168	180 180	—102 960	24 310	—
630 630	—960 960	875 160	—437 580	92 378

TABLE AII
Zero Points of Orthogonal Exponential Polynomials

N = 5	N = 6	N = 7	N = 8	N = 9	N = 10
0-058800	0-040624	0-029755	0-022736	0-017940	0-014517
0-324129	0-220663	0-160261	0-121805	0-095766	0-077299
0-876086	0-576209	0-410957	0-308960	0-241191	0-193726
1-967830	1-188967	0-817966	0-603026	0-465107	0-370582
—	2-317343	1-466350	1-042351	0-787868	0-619842
—	—	2-616552	1-713462	1-248884	0-962642
—	—	—	2-877726	1-935402	1-438949
—	—	—	—	3-109260	2-136402
—	—	—	—	—	3-317100

If we combine these equations with (12), (18), and (19), we obtain

$$\text{Nu}/\text{Gr}_T^{1/4} = -\frac{2}{3}\sqrt{2}(\text{Gr}_M/\text{Gr}_T)^{1/4} \theta'(0). \quad (A4)$$

The values of Nu obtained from this equation were compared with those from the equation given by Mathers and coworkers²:

$$\text{Nu}/\text{Gr}_T^{1/4} = 0.67 \text{Pr}^{1/4} [1 + (\text{Pr}/\text{Sc})^{1/2} (\text{Gr}_M/\text{Gr}_T)]^{1/4}. \quad (A5)$$

The relative error of eq. (A5) with respect to (A4) is -4 to -16% in the studied region of the criteria Pr, Sc, Gr_M, and Gr_T.

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