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ELECTROPHORETIC THERMAL THEORY

III. STEADY-STATE TEMPERATURE GRADIENTS IN RECTANGULAR SECTION COLUMNS

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SUMMARY

Temperature gradients in the steady state are calculated for columns of electrolyte solution having rectangular section, and uniform bore, for various power dissipations. Wall thickness and material are allowed for. Fillings having zero, positive, and negative temperature coefficients of resistivity are calculated, correction being made for non-uniform current density. For negative coefficients, central-peripheral gradients are more severe than simple theory suggests, especially at higher powers, but this tendency is very much less than in circular section columns.

INTRODUCTION

Central-peripheral temperature gradients have been calculated previously, assuming a zero temperature coefficient of resistivity and uniform density of current through the lumen section. In this paper, these gradients are recalculated without these simplifying assumptions. For negative coefficients, gradients are more severe, increasingly so at high power dissipations. But the case is far more favourable than in circular section tubes, even more so than simple theory indicates. Wall thickness, however, has a larger influence for thick walls than is the case for cylindrical columns. Similar calculations, using Bessel functions, are given in a previous paper of this series[1]. A discussion of the anticipated effects of these gradients in electrophoresis, and a comparison of results of digitally computed gradients, in the context of factors determining the ideal column shapes and thermal properties, are given in a preceding paper[2]. A further paper[3] describes programming and digital computation of the

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gradients calculated here and in ref. 1. The results of this work were briefly reported at a symposium in 1971, by the second author[4], at whose instigation this project was undertaken for the reasons outlined in refs. 1 and 2. The treatment has subsequently been extended at the second author's suggestion to the unsteady state by Coxon and Binder[5].

THEORY

For an electrolyte of zero temperature coefficient of resistivity[2]

Consider a rectangular-section column filled with electrolyte. Assume it to be long enough to neglect end effects in a medial and uniform region. Assume the ratio of lengths of adjacent sides of the rectangle to be large enough to neglect edge effects. Assume that heat is uniformly generated in the electrolyte, and that there is no thermal convection or other internal fluid movement. Assume a zero temperature coefficient of resistivity and thermal conductivity[2]. Assume that a steady state pertains, and the column exterior is perfectly cooled and thermostatted. Using the listed symbols, which refer to the tube section normal to the long axis

$$\frac{d^2 t}{dx^2} = -\frac{W_0}{k_1}$$

Solving by Laplace transforms, the subsidiary equation is

$$p^2 \bar{t} = -\frac{W_0}{k_1 p}$$

so

$$\bar{t} = -\frac{W_0}{k_1 p^3}$$

and

$$t = -\frac{W_0}{k_1}\frac{x^2}{2} \quad (1)$$

For the column material

$$\frac{W_t}{2(2a+b)} = \frac{k_2 (T_2 - T_1)}{d}$$

so

$$T_2 = T_1 + \frac{W_t d}{2(2a+b) k_2} \quad (2)$$

The limits for eqn. 1 are

$$x = a,\ t = T_2$$

and

$$x = 0,\ \frac{dt}{dx} = 0$$

Using these and eqn. 2, we obtain

$$T_1 + \frac{W_t\, d}{2\,(2a + b)\, k_2} = A - \frac{W_t}{2\, a\, b\, k_1} \cdot \frac{a^2}{2}$$

so

$$A = T_1 + \frac{W_t}{2} \left[\frac{d}{(2a + b)\, k_2} + \frac{a^2}{2\, a\, b\, k_1}\right]$$

Substituting into the original equation

$$T = T_1 + \frac{W_t}{2} \left[\frac{d}{(2a + b)\, k_2} + \frac{a^2 - x^2}{2\, a\, b\, k_1}\right] \tag{3}$$

When $x = 0$

$$T_3 = T_1 + \frac{W_t}{2} \left[\frac{d}{(2a + b)\, k_2} + \frac{a}{2\, b\, k_1}\right] \tag{4}$$

For positive and negative coefficients

$$\frac{d^2 t}{dx^2} = -\frac{W_0\,(1 + \alpha\, t)}{k_1} \tag{5}$$

so

$$\frac{d^2 t}{dx^2} + \frac{W_0\, \alpha\, t}{k_1} = -\frac{W_0}{k_1}$$

Solving by Laplace transforms, the subsidiary equation is

$$\left(p^2 + \frac{W_0\, \alpha}{k_1}\right) \bar{t} = -\frac{W_0}{k_1\, p}$$

so

$$\bar{t} = -\frac{1}{\alpha\, p} + \frac{p}{\alpha \left(p^2 + \frac{W_0\, \alpha}{k_1}\right)}$$

Inverting

$$t = \frac{1}{\alpha} \left[\cos\left(x \sqrt{\frac{W_0\, \alpha}{k_1}}\right) - 1\right] \tag{6}$$

For the tube material

$$\frac{W_t}{2\,(2a + b)} = \frac{k_2\,(T_2 - T_1)}{d}$$

so

$$T_2 = T_1 + \frac{W_t\, d}{2\,(2a + b)\, k_2} \tag{7}$$

For eqn. 5 the limits

$$x = a, \; t = T_2$$

and

$$x = 0, \; \frac{dt}{dx} = 0$$

apply. Using these and eqn. 7

$$T_2 = T_1 + \frac{W_t\, d}{2\,(2a + b)\, k_2} = \frac{1}{\alpha}\left[A \cos\left(a \sqrt{\frac{W_0\, \alpha}{k_1}}\right) - 1\right]$$

so

$$A = \left[\alpha\left(T_1 + \frac{W_t\, d}{2\,(2a + b)\, k_2}\right) + 1\right] \frac{1}{\cos\left(a \sqrt{\frac{W_0\, \alpha}{k_1}}\right)}$$

Substituting in the original equation, and using

$$\beta = \sqrt{\frac{W_0\, \alpha}{k_1}}$$

then

$$t = \frac{\cos(\beta x)}{\cos(\beta a)}\left[T_1 + \frac{1}{\alpha} + \frac{W_t\, d}{2\,(2a + b)\, k_2}\right] - \frac{1}{\alpha} \tag{8}$$

This expression is valid for both positive and negative values of the coefficient α.

For negative coefficients

Where α is negative, we have to evaluate the cosines of imaginary numbers

$$\cos x = 1 - \frac{x^2}{2!} + \frac{x^4}{4!} - \frac{x^6}{6!} + \cdots$$

so

$$\cos(ix) = 1 + \frac{x^2}{2!} + \frac{x^4}{4!} + \frac{x^6}{6!} + \cdots$$

which is also the value of cosh (x), which series we may use in digital computation. So for negative α, the temperature expression becomes

$$t = \frac{\cosh(\gamma x)}{\cosh(\gamma a)}\left\{T_1 + \frac{1}{\alpha} + \frac{W_t\, d}{2\,(2a + b)\, k_2}\right\} - \frac{1}{\alpha} \tag{9}$$

where

$$\gamma = \sqrt{-\frac{W_0\, \alpha}{k_1}}$$

The relationship of W_t and W_0

Consider an element in the column section parallel to b, of width b, and thickness dx, a distance x from the central line of the tube section

$$W_t = 2\,W_0 \int_0^a (1 + a\,t)\,b\,dx$$

From eqn. 8

$$t = \frac{1}{a}\left\{\left[a\left(T_1 + \frac{W_t\,d}{2\,(2a + b)\,k_2}\right) + 1\right]\left[\frac{\cos(\beta\,x)}{\cos(\beta\,a)}\right] - 1\right\}$$

so

$$W_t = 2\,W_0 \int_0^a b\left[a\,T_1 + \frac{W_t\,da}{2\,(2a + b)\,k_2} + 1\right]\left[\frac{\cos(\beta\,x)}{\cos(\beta\,a)}\right]dx$$

$$= \frac{2\,W_0\,b}{\cos(\beta\,a)}\left[a\,T_1 + \frac{W_t\,da}{2\,(2a + b)\,k_2} + 1\right]\int_0^a \cos(\beta\,x)\,dx$$

$$= \left[\frac{2\,b\,W_0\,a\,(2a + b)\,k_2\tan(\beta\,a)}{(2a + b)\,k_2\,\beta - W_0\,b\,a\,d\tan(\beta\,a)}\right]\left(T_1 + \frac{1}{a}\right) \quad (10)$$

which is valid for positive a. Similarly for negative a

$$W_t = \left[\frac{2\,b\,W_0\,a\,(2a + b)\,k_2\tanh(\gamma\,a)}{(2a + b)\,k_2\,\gamma - W_0\,b\,a\,d\tanh(\gamma\,a)}\right]\left(T_1 + \frac{1}{a}\right) \quad (11)$$

Current density correction

The foregoing theory is valid only for uniform current density. But current density cannot be uniform for coefficients of resistivity other than zero[2,4]. To correct for this, modify eqn. 5 to

$$\frac{d^2t}{dx^2} = -\frac{W_0}{k_1}\cdot\frac{1}{1 + a\,t}$$

To render this more easily soluble, let

$$\frac{1}{1 + a\,t} = 1 + \mu\,t$$

and substitute negative μ for positive a and positive μ for negative a in eqns. 8–11. For positive a and negative μ

$$t = \frac{\cosh(\gamma\,x)}{\cosh(\gamma\,a)}\left[T_1 + \frac{1}{\mu} + \frac{W_t\,d}{2\,(2a + b)\,k_2}\right] - \frac{1}{\mu} \quad (12)$$

and

$$W_t = \left[\frac{2b\,W_0\,\mu\,(2a + b)\,k_2\tanh(\gamma\,a)}{(2a + b)\,k_2\,\gamma - W_0\,b\,\mu\,d\tanh(\gamma\,a)}\right]\left(T_1 + \frac{1}{\mu}\right) \quad (13)$$

and for negative a and positive μ

$$t = \frac{\cos(\beta\,x)}{\cos(\beta\,a)}\left[T_1 + \frac{1}{\mu} + \frac{W_t\,d}{2\,(2a + b)\,k_2}\right] - \frac{1}{\mu} \quad (14)$$

and

$$W_t = \left[\frac{2b\ W_0\,\mu\,(2a + b)\,k_2 \tan(\beta\,a)}{(2a + b)\,k_2\,\beta - W_0\,b\,\mu\,d \tan(\beta\,a)}\right]\left(T_1 + \frac{1}{\mu}\right) \tag{15}$$

Calculation of μ

In practice $(1 + \alpha t)$ is an approximation of a series $(1 + \alpha t + \beta t^2)$. Plotting the reciprocal of the latter against t, an approximately straight line is obtained, of gradient $\mu = 0.033$, using values for 0.1 mM KCl[6]. This value was therefore used in digital computation[3]. Above 34°, for T_1 of 4°, the relation is less linear and therefore less reliable.

CONCLUSIONS

Comparison of equations for zero and negative temperature coefficients of resistivity, in the latter case allowing for non-uniform current densities, shows that for electrolyte solutions there is an increase in central temperature not previously allowed for. This is less severe than in the case of circular column sections, dealt with in the previous paper. On the other hand, wall thickness has a greater influence. The comparison between circular and rectangular sections favours the latter more than was apparent from simple theory, particularly if the walls are thin compared to the lumen. As in circular sections, positive coefficients are palliative.

SYMBOLS AND UNITS

a = half-thickness of interior of column
x = values of a from zero to a
b = width of column
d = thickness of column wall
k_1 = thermal conductivity of electrolyte, cal·sec^{-1}·cm^{-1}·°C^{-1}
k_2 = thermal conductivity of wall material, cal·sec^{-1}·cm^{-1}·°C^{-1}
t, T = temperature
T_1 = temperature at wall exterior, °C
T_2 = temperature at lumen periphery, °C
T_3 = temperature at lumen section centre, °C
W_0 = nominal power dissipation assuming a zero value of α, or at switch-on at T_1, cal·cm^{-3}
W_t = actual power dissipation, per unit length of column, cal·cm^{-1}
$\bar{t}$, p = operators in Laplace transforms
α = temperature coefficient of resistivity of electrolyte, °C^{-1}

$\beta = \sqrt{\frac{\alpha W_0}{k_1}}$

$\gamma = \sqrt{-\frac{\alpha W_0}{k_1}}$

μ = a function of α

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REFERENCES

1 J. F. Brown and J. O. N. Hinckley, *J. Chromatogr.*, 109 (1975) 218.
2 J. O. N. Hinckley, *J. Chromatogr.*, 109 (1975) 209.
3 D. H. Jones and J. O. N. Hinckley, *J. Chromatogr.*, to be submitted.
4 J. O. N. Hinckley, in E. Reid (Editor), *Methodological Developments in Biochemistry*, Vol. 2, Longman, London, 1973, Ch. 21, p. 201.
5 M. Bier, J. O. N. Hinckley, A. J. K. Smolka, M. J. Binder, M. Coxon, T. W. Nee, M. O. Scully, H. S. T. Shih and R. S. Snyder, *Proc. 3rd Space Process. Symp. Skylab Results*, 2 (1974) 729.
6 F. Kohlrausch and L. Holborn, *Das Leitvermögen der Electrolyte insbesondere der Lösungen*, Teubner, Leipzig, 1898.