$$Q_1 = 4\pi R\, D_1\, c_0 \left[R\sqrt{\frac{k}{D_1}}\left(cth\; R\sqrt{\frac{k}{D_1}}\right) - 1 \right] \tag{15}$$

The ratio Q/Q_1 is given therefore by

$$\varphi \equiv \frac{Q}{Q_1} = \frac{D}{D_1}\; \frac{(1-\epsilon)\left[R\sqrt{\frac{4\pi\, a\, \epsilon\, HED_1}{v(1-\epsilon)D}}\; cth\left(R\sqrt{\frac{4\pi\, a\, \epsilon\, HED_1}{v(1-\epsilon)D}}\right) - 1\right]}{R\sqrt{\frac{k}{D_1}}\; cth\left(R\sqrt{\frac{k}{D_1}}\right) - 1} \tag{16}$$

For illustration purposes we shall take $R = 0.5$ cm., $a = 10^{-2}$ cm., $H = 1$. In Figure 3, Q/Q_1 is plotted as a function of $a\sqrt{k/D_1}$ for various values of D/D_1 and for two values of ϵ.

From this figure one may conclude that in some conditions the diluted catalyst particle may be more active than a catalyst particle having the same radius and formed only from active material.

It is also possible to show that there exists an optimum value for ϵ.

We notice that a similar idea has been extended to the nonisothermic case and has been used in connection with adsorption and with ion exchange (*13*).

ACKNOWLEDGMENT

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NOTATION

a = the radius of a small active particle
c = concentration in the inert medium; c_0—value of c for $r = R$
D = diffusion coefficient in the particle formed only of inert material
D_0 = diffusion coefficient in the inert medium of the heterogeneous particle
D_1 = diffusion coefficient in the small active particle
E = quantity defined by Equation (8)
H = equilibrium constant defined by Equation (6)
k = surface reaction rate constant
m = number of particles per volume unit
n = concentration in the small particles; n_0—value of n for $r_1 = a$
q = $Q/4\pi R\, c_0 D$
Q = total reaction rate in the diluted particle [defined by Equation (14)]
Q_1 = total reaction rate in a particle formed only of active material and having the same radius as the diluted particle
r = distance at the center of the large sphere
r_1 = distance at the center of the small sphere
R = the radius of the nonhomogeneous particle
v = the volume of the small sphere
ϵ = the fraction of volume occupied by active particles
η = $a\sqrt{k/D_1}$
φ ≡ Q/Q_1

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On Transient Heat Transfer in a Porous Medium

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In a recent communication, Kohlmayr (*1*) derived infinite series solutions to a transient heat transfer problem which are computationally more useful than Schumann's (*2*) solution. Kohlmayr used a double Laplace transform method to obtain a transform which was expanded into infinite series using a binomial expansion, and he used a term-by-term inversion to obtain infinite series solutions. He then demonstrated convergence of the series by giving two sequences of upper and lower bounds with some numerical demonstrations and concluded that it was no longer necessary to resort to finite-difference methods when computing theoretical response functions.

The purposes of this communication are twofold: to show that the infinite series solutions and two sequences of bounds given by Kohlmayr follow naturally from the two forms of integral (analytical) solutions which are obtained directly from the inversion of the transform and hence avoids the laborious analysis given by Kohlmayr, and to bring attention to a large number of pertinent literature which was not cited by Kohlmayr. Some of these give, by various methods, either one or the other form of the integral solution given here and also the infinite series solutions of Kohlmayr. Hence, it had not been necessary to resort to finite-difference methods since the appearance of these references.

In addition to those references given by Kohlmayr (*1*), there are a large number of pertinent references (*3* to *16*). Klinkenberg (*11*) presented a list of different processes which can be described by the same equations and a critical survey of various methods of evaluating the solutions in series or integral forms and asymptomatic approximations, including, Equation (18) of Kohlmayr. Equation (12) of Kohlmayr was derived by a different method by Kronig and Van Gijn (*5*).

Since these references give either one or the other form of integral solutions and infinite series solutions, it may be instructive to show how these two integral form solutions result and how these two reduce to Kohlmayrs infinite series solutions and two sequences of upper and lower bounds.

DERIVATION OF TWO FORMS OF INTEGRAL SOLUTION

The problem as given by Kohlmayr is

$$\frac{\partial G}{\partial z} = S - G = -\frac{\partial S}{\partial \tau}, \quad S(z, 0) = 1, \quad G(0, \tau) = 0 \tag{1}$$

Kohlmayr used a double Laplace transform method to obtain

$$\overline{G}\,(p, q) = 1/[p(pq + p + q)] \tag{2}$$

Equation (2) can be inverted in two ways to obtain two forms of solution: first, with respect to q and then with respect to p, or second, first with respect to p and then q. Taking the first case, we get

$$\overline{G}\,(p, \tau) = \mathcal{L}_q^{-1}\left[\frac{1}{p(p+1)} \cdot \frac{1}{q + 1 - \dfrac{1}{p+1}}\right]$$

$$= e^{-\tau}\,(1/p)\,[e^{\tau/(p+1)}/(p+1)]$$

The inversion with respect to p can be made by recognizing that the inverse of $e^{\tau/p}/p$ is $I_0\,(2\sqrt{\tau z})$ (zero-order modified Bessel's function of the first kind) and by using the shift and convolution theorems to obtain

$$G(z, \tau) = e^{-\tau}\int_0^z e^{-u}\, I_0(2\sqrt{\tau u})\; du \tag{3}$$

Thiele (*6*) gave an equivalent form.

The second approach yields another form of the solution:

$$\overline{G}\,(z, q) = \mathcal{L}_p^{-1}\left\{\frac{1}{q}\left[\frac{1}{p} - \frac{1}{p + q/(q+1)}\right]\right\}$$

$$= \frac{1}{q}\,[1 - e^{-z}\, e^{z/(q+1)}] = \frac{1}{q}$$

$$- e^{-z}\left[\frac{1}{q}\,\frac{e^{z/(q+1)}}{q+1} + \frac{e^{z/(q+1)}}{q+1}\right]$$

And, finally, the inversion with respect to q yields

$$G(z, \tau) = 1$$

$$- e^{-z}\left[\int_0^\tau e^{-u} I_0(2\sqrt{zu})\; du + e^{-\tau} I_0(2\sqrt{z\tau})\right] \tag{4}$$

This form of solution has been reported (for instance, *5, 10, 16*). Equations (3)and (4) are, then, two forms of solutions which have been reported previously (not together but separately). The corresponding forms for $S(z, \tau)$ are obtained from Equations (3) and (4) by noting that

$$S(z, \tau) - G(z, \tau) = e^{-\tau - z} I_0(2\sqrt{\tau z}) \tag{5}$$

FORMAL EQUIVALENCE WITH THE KOHLMAYR SOLUTIONS

We now derive and demonstrate that the solutions given by Kohlmayr are equivalent to taking infinite series expansions and finite series approximations, respectively, of $I_0(x)$ in evaluating the integral in Equations (3) and (4); that is

$$I_0(2\sqrt{xy}) = \sum_{i=0}^{\infty} \frac{(xy)^i}{(i!)^2} \tag{6}$$

Substitution of Equation (6) (absolutely and uniformly conversant series) into Equation (3) and term-by-term integration yield

$$G(z, \tau) = e^{-\tau} \sum_{i=0}^{\infty} \frac{\tau^i}{i!}\left(1 - e^{-z} \sum_{j=0}^{i} \frac{z^j}{j!}\right)$$

$$= 1 - e^{-\tau - z} \sum_{i=0}^{\infty} \frac{\tau^i}{i!} \sum_{j=0}^{i} \frac{z^j}{j!} \tag{7}$$

which is the same as Equation (12) of Kohlmayr and has been presented elsewhere (*5*). Equation (14) of Kohlmayr, the so-called *sequence of lower bounds,* is equivalent to taking only an n (finite) number of terms in the first expression of Equation (7), since the partial sums are monotonically increasing with n. The same process with Equation (4) leads to Equation (18) of Kohlmayr:

$$G(z, \tau) = 1 - \lim_{N \to \infty} e^{-z}\left[\sum_{i=0}^{N} \frac{z^i}{i!}\right.$$

$$\left. - e^{-\tau} \sum_{i=0}^{N-1} \frac{z^{i+1}}{(i+1)!} \sum_{j=0}^{i} \frac{\tau^j}{j!}\right] \tag{8a}$$

$$= e^{-\tau - z} \sum_{k=0}^{\infty} \frac{z^{k+1}}{(k+1)!} \sum_{j=0}^{k} \frac{\tau^j}{j!} \tag{8b}$$

An equivalent form was reported previously (*11*). The upper bounds, Equation (20) of Kohlmayr, are equivalent to taking only an N (finite) number of terms in Equation (8*a*), since the partial sums of the infinite series in the bracket are monotonically increasing with N. Note that new sequences of upper and lower bounds can be obtained by taking a finite number of terms in the last expression in Equations (7) and (8*b*), respectively.

NOTATION

G = normalized fluid temperature
p = parameter of the double Laplace transform (with respect to z)
q = parameter of the double Laplace transform (with respect to τ)
S = normalized solid temperature
z = dimensionless reduced length
$\mathcal{L}_p^{-1}$ = inverse Laplace transform with respect to z
$\mathcal{L}_q^{-1}$ = inverse Laplace transform with respect to τ
τ = dimensionless reduced time

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INFORMATION RETRIEVAL*

Saturated-liquid and vapor densities for polar fluids, Halm, Roland L., and Leonard I. Stiel, **AIChE Journal, 16,** No. 1, p. 3 (January, 1970).

Key Words: Thermodynamic Properties-8, Compressibility Factor-8, Density-8, Normal Fluids-9, Polar Fluids-9, Saturated Fluids-9, Acentric Factor-10, Fourth Parameter-10.

Abstract: Relationships have been developed for the saturated-liquid density and the compressibility factor of saturated vapors by an extension of Pitzer's acentric factor approach. The fourth parameter for polar fluids defined previously by the authors in terms of the vapor pressure was utilized. For the saturated-liquid density and the critical compressibility, factor quadratic terms were necessary to accurately represent the data for a wide range of normal and polar fluids including large polar molecules. Comparisons for substances not used in the development of the relationships indicate that good results can be obtained for polar fluids by the method of this study.

An analytical investigation of the flow in the saturated zone of ice counterwashers, Barak, Amitzur, and Gedeon Dagan, **AIChE Journal, 16,** No. 1, p. 9 (January, 1970).

Key Words: Washing-8, Desalination-8, Freezing-10, Flow-8, Brine-9, Ice-5, Counterwashers-10, Drained-Top-0, Flooded-0, Complex Variables-10, Conformal Mapping-10.

Abstract: The flow of brine through the ice bed in gravitational counterwashers is investigated by analytical methods. Two types of counterwashers are considered: a drained top counterwasher and a flooded one. Only counterwashers of rectangular cross section and two-dimensional flows are investigated. By assuming that the ice crystals move vertically upwards with a uniform velocity and that the relative flow of brine and wash water with respect to the ice bed obeys Darcy's law, the differential equations and the boundary conditions of the flow are derived. The solutions are obtained by using complex variables and conformal mapping. The solutions are presented as formulas, which make possible the rational design of counterwashers and the optimization of their dimensions and operation parameters.

On integration of the coexistence equation for binary vapor-liquid equilibrium, Van Ness, H. C., **AIChE Journal, 16,** No. 1, p. 18 (January, 1970).

Key Words: A. Vapor-Liquid Equilibria-8, Mathematical Analysis-8, Stability-8, Calculation-8, Isothermal-0, Numerical-0, Coexistence Equation-10, Binary Mixtures-9, Computer-10, Data-1, Vapor Pressures-1, Liquid Composition-1, Vapor Composition-2.

Abstract: Numerical integration of the coexistence equation for isothermal P—x data can be carried out by standard techniques. Two questions are considered with respect to this procedure: Do continuous, analytic P—x relations exist which fail to provide thermodynamically acceptable results? Does it matter from what point one starts the numerical integration? It is the purpose of this paper to demonstrate in each case that the answer is affirmative.

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