

are present in cyclic form so that a limiting degree of association is reached at low temperatures. Although hydrogen bond energies are nearly the same for all the alcohols, entropy values differ between four types: methanol, other normal alcohols, secondary alcohols, and tertiary alcohols (if steric effects are neglected). At low temperatures, the normal alcohols approach a degree of association of two while secondary and tertiary alcohols associate in larger rings.

The average entropy of association in the liquid was found to be about 8 cal./mole °K. for methanol and about 10 cal./mole °K. for the other alcohols from a model similar to the gaseous model described.

#### NOTATIONS

- $c_p$  = heat capacity  
 $c_p^o$  = heat capacity in the ideal gas state  
 $H$  = enthalpy  
 $n$  = number of moles of monomer and number of monomer units in the n-mer  
 $S$  = entropy  
 $T$  = temperature

#### Greek Letters

- $\Delta H_n$  = enthalpy change for the formation of n-mer from monomers  
 $\Delta S$  = entropy difference  
 $\Delta S_{\text{vap}}$  = entropy of vaporization  
 $\delta$  = deviation in degrees from a straight angle in the structure of the hydrogen bond  
 $\gamma$  = degree of association

#### LITERATURE CITED

1. Wiehe, I. A., and E. B. Bagley, *AIChE J* 13, 836 (1967).
2. Weltner, William, and K. S. Pitzer, *J. Am. Chem. Soc.*, 73, 2606 (1951).
3. Kretschmer, Carl N., and Richard Wiebe, *ibid.*, 76, 2579 (1954).
4. Barrow, Gordon M., *J. Chem. Phys.*, 20, 1739 (1952).
5. Mathews, J. F., and J. J. McKetta, *J. Phys. Chem.*, 65, 753 (1961).
6. Berman, N. S., C. W. Larkam, and J. J. McKetta, *J. Chem. Eng. Data*, 9, 218 (1964).
7. Hales, J. L., J. D. Cox, and E. B. Lees, *Trans. Faraday Soc.*, 59, 1544 (1963).
8. Berman, N. S., and J. J. McKetta, *J. Phys. Chem.*, 66, 1444 (1962).
9. Beynon, E. T., and J. J. McKetta, *ibid.*, 67, 2761 (1963).
10. Pauling, Linus, "The Nature of the Chemical Bond," 3rd. ed., Cornell Univer. Press, Ithaca, New York (1960).
11. Dunken, Heinz, and Hartmut Fritzsche, *Spectrochim. Acta*, 20, 785 (1964).
12. Thomas, L. H., *J. Chem. Soc.*, 1948, 1345 (1948).
13. *Ibid.*, 1948, 1349 (1948).
14. *Ibid.*, 1963, 1995 (1963).
15. ———, and R. Meatyard, *ibid.*, 1963, 1986 (1963).
16. Hildebrand, Joel H., and Robert L. Scott, "Regular Solutions," Prentice Hall, Englewood Cliffs, N.J. (1962).
17. Fiock, E. F., D. C. Ginnings, and W. B. Holton, *J. Res. Nat. Bur. Std.*, 6, 881 (1931).
18. Hermesen, R. W., and J. M. Prausnitz, *J. Chem. Phys.*, 34, 1081 (1961).
19. Hildebrand, J. H., and R. L. Scott, "Solubility of Non Electrolytes," 3rd ed., Reinhold, New York (1950).
20. Dannhauser, Walter, and Lowell W. Bahe, *J. Chem. Phys.*, 40, 3058 (1964).

## Properties of the Transient Heat Transfer (Single Blow) Temperature Response Function

G. F. KOHLMAYR

Pratt and Whitney Aircraft Division, United Aircraft Corporation, East Hartford, Connecticut

A theoretical analysis of the transient heat transfer to and from a liquid flowing through a porous medium has been provided by Anzelius (1), Nusselt (2), Hausen (3), and Schumann (4). Schumann's analytical solution of the so-called *single-blow problem* was used by Furnas (5), and by Saunders and Ford (6) to determine the heat transfer characteristics of porous media by matching experimental and theoretical temperature response curves. The value of Schumann's analytical solution of the single-blow problem is somewhat limited as it contains an infinite series of Bessel functions which makes it inconvenient to compute. Locke (7) observed that the number of terms of the series, which must be summed to obtain a good approximation, increases with the number of transfer units,

$N_{tu}$ . Locke's maximum slope method avoids the computation of the Schumann solution. In their work on the effectiveness of regenerators, Hausen (8) and Allen (9) have also shunned Schumann's solution and resorted to finite difference methods in solving the single-blow problem.

The purpose here is to derive a simple analytical solution of the single-blow problem which, although it is formally equivalent to the Schumann solution, is computationally much more useful. In our analysis we will use the double Laplace transform method. To exhibit the excellent convergence properties of the new representation of the solution, called *response function*, we will form two se-

quences of upper and lower bounds, which converge toward the solution.

## THE MATHEMATICAL MODEL

According to Hausen (3), and Schumann (4), the heat transfer to and from a fluid transfusing through a porous core can be described by the following system of two linear partial-differential equations:

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

$$\frac{\partial S}{\partial \tau} + S(z, \tau) = G(z, \tau) \quad (2)$$

For a derivation of these equations, a discussion of the basic assumptions made, and the definition of the so-called reduced variables  $z$  and  $\tau$ , we refer to the book by Jakob (10) and the paper by Pucci et al. (11).

The appropriate initial condition for the single-blow problem for normalized temperatures is

$$S(z, \tau)|_{\tau=0} = 1 \quad (3)$$

that is a constant temperature distribution in the porous core. The boundary condition, for a step change of the fluid temperature of the inlet cross section, is stipulated by

$$G(z, \tau)|_{z=0} = 0 \quad (4)$$

## ANALYTICAL SOLUTION

The analytical solution of the (characteristic initial value or Coursat) problem expressed by Equations (1) to (4) can be accomplished by using double Laplace transforms. Let the double Laplace transform (DLT) of  $G(z, \tau)$  be defined by

$$\overline{G}(p, q) = L\{G(z, \tau); p, q\} = \int_0^\infty \int_0^\infty G(z, \tau) e^{-pz - q\tau} dz d\tau \quad (5)$$

[see, for example, Sneddon (12)]. The DLT of  $S(z, \tau)$  is obtained analogously. The DLT formulation of the single-blow problem for a step change is then given by the following two algebraic equations

$$(p+1)\overline{G}(p, q) - \overline{S}(p, q) = 0 \quad (6)$$

$$-\overline{G}(p, q) + (q+1)\overline{S}(p, q) = \frac{1}{p} \quad (7)$$

and the DLT of the fluid temperature response function  $G(z, \tau)$  is found as

$$\overline{G}(p, q) = \frac{1}{p(pq + p + q)} \quad (8)$$

For the remaining task of inverting  $\overline{G}(p, q)$  one can substitute the algebraic identity

$$\frac{1}{p(p+1)^{i+1}} = \frac{1}{p} - \sum_{j=0}^i \frac{1}{(p+1)^{j+1}} \quad (9)$$

in the expression obtained by expanding  $\overline{G}(p, q)$  in a series:

$$\begin{aligned} \overline{G}(p, q) &= \sum_{i=0}^{\infty} \frac{1}{p(p+1)^{i+1} (q+1)^{i+1}} \quad (10) \\ &= \sum_{i=0}^{\infty} \frac{1}{(q+1)^{i+1}} \left[ \frac{1}{p} - \sum_{j=0}^i \frac{1}{(p+1)^{j+1}} \right] \end{aligned}$$

$$= \frac{1}{pq} - \sum_{i=0}^{\infty} \frac{1}{(q+1)^{i+1}} \sum_{j=0}^i \frac{1}{(p+1)^{j+1}}$$

The last expression can be inverted immediately once the elementary DLT pair

$$L \left\{ \frac{z^i}{i!} e^{-\alpha z} \frac{\tau^j}{j!} e^{-\beta \tau}; p, q \right\} = \frac{1}{(p+\alpha)^{i+1} (q+\beta)^{j+1}} \quad (11)$$

is known. Thus one finds the following representation of the fluid temperature response function:

$$\begin{aligned} G(z, \tau) &= 1 - e^{-z-\tau} \sum_{i=0}^{\infty} \frac{\tau^i}{i!} \sum_{j=0}^i \frac{z^j}{j!} \quad (12) \\ &= 1 - e^{-z-\tau} \left[ 1 + \tau(1+z) \right. \\ &\quad \left. + \frac{\tau^2}{2} \left( 1 + z + \frac{z^2}{2} \right) + \dots \right] \end{aligned}$$

The above expression can easily be computed as it converges rather fast and does not give rise to roundoff errors.

## UPPER AND LOWER BOUNDS

The numerical evaluation of the response function requires some approximation of  $G(z, \tau)$ . We demonstrate the convergence properties of consecutive approximations of  $G(z, \tau)$  by studying the inequality ( $n = 0, 1, 2, \dots$ )

$$\begin{aligned} [1 - G(z, \tau)] e^{z+\tau} &= \sum_{i=0}^{\infty} \frac{\tau^i}{i!} \sum_{j=0}^i \frac{z^j}{j!} \\ &= (1 - \delta_{n,0}) \sum_{i=0}^{n-1} \frac{\tau^i}{i!} \sum_{j=0}^i \frac{z^j}{j!} + \sum_{i=n}^{\infty} \frac{\tau^i}{i!} \sum_{j=0}^i \frac{z^j}{j!} \\ &\leq (1 - \delta_{n,0}) \sum_{i=0}^{n-1} \frac{\tau^i}{i!} \sum_{j=0}^i \frac{z^j}{j!} + e^z \left[ e^\tau - (1 - \delta_{n,0}) \sum_{i=0}^{n-1} \frac{\tau^i}{i!} \right] \\ &= [1 - G(z, \tau; n)] e^{z+\tau} \quad (13) \end{aligned}$$

which defines a sequence of lower bounds on  $G(z, \tau)$

$$\begin{aligned} G(z, \tau; n) &= (1 - \delta_{n,0}) \left[ e^{-\tau} \sum_{i=0}^{n-1} \frac{\tau^i}{i!} \right. \\ &\quad \left. - e^{-z-\tau} \sum_{i=0}^{n-1} \frac{\tau^i}{i!} \sum_{j=0}^i \frac{z^j}{j!} \right] \quad (14) \end{aligned}$$

These bounds are ordered according to the inequalities

$$\dots \leq G(z, \tau; n) \leq G(z, \tau; n+1) \leq \dots \leq G(z, \tau) \quad (15)$$

and can be used to approximate  $G(z, \tau)$ . It is evident that  $G(z, \tau; n) \rightarrow G(z, \tau)$  as  $n \rightarrow \infty$  (see Figure 1).

Turning now to upper bounds, we note first the algebraic identity

$$\begin{aligned} \overline{G}(p, q) &= \frac{1}{p(pq + p + q)} = \frac{1}{pq} - \frac{q+1}{q(pq + p + q)} \\ &= \frac{1}{pq} - \frac{1}{q(p+1)} - \sum_{i=0}^{\infty} \frac{1}{(p+1)^{i+2} q(q+1)^{i+1}} \end{aligned}$$

The identity (9), with  $q$  substituted for  $p$ , can be applied to the infinite series in Equation (16); there results

$$\bar{G}(p, q) = \frac{1}{pq} - \frac{1}{q(p+1)} - \frac{1}{pq(p+1)} \quad (17)$$

$$+ \sum_{i=0}^{\infty} \frac{1}{(p+1)^{i+2}} \sum_{j=0}^i \frac{1}{(q+1)^{j+1}}$$

a DLT which corresponds to another useful representation of the response function:

$$G(z, \tau) = e^{-z-\tau} \sum_{i=0}^{\infty} \frac{z^{i+1}}{(i+1)!} \sum_{j=0}^i \frac{\tau^j}{j!} \quad (18)$$

The above expression is equivalent to that given by Equation (12). Similarly the inequality ( $N = 0, 1, 2, \dots$ )

$$e^{z+\tau} G(z, \tau) = (1 - \delta_{N,0}) \sum_{i=0}^{N-1} \frac{z^{i+1}}{(i+1)!} \sum_{j=0}^i \frac{\tau^j}{j!}$$

$$+ \sum_{i=N}^{\infty} \frac{z^{i+1}}{(i+1)!} \sum_{j=0}^i \frac{\tau^j}{j!} \leq (1 - \delta_{N,0}) \sum_{i=0}^{N-1} \frac{z^{i+1}}{(i+1)!} \sum_{j=0}^i \frac{\tau^j}{j!}$$

$$+ e^{\tau} \left[ e^z - (1 - \delta_{N,0}) \sum_{i=0}^N \frac{z^i}{i!} \right] = e^{z+\tau} G(z, \tau; N) \quad (19)$$

establishes upper bounds on  $G(z, \tau)$ , namely

$$G(z, \tau; N) = 1 + (1 - \delta_{N,0}) \left[ e^{-z-\tau} \sum_{i=0}^{N-1} \frac{z^{i+1}}{(i+1)!} \sum_{j=0}^i \frac{\tau^j}{j!} \right.$$

$$\left. - e^{-z} \sum_{i=0}^N \frac{z^i}{i!} \right]$$

$$(20)$$

which are ordered according to

$$G(z, \tau) \leq \dots \leq G(z, \tau; N+1) \leq G(z, \tau; N) \leq \dots \quad (21)$$

and converge to  $G(z, \tau)$ , (see Figure 1).

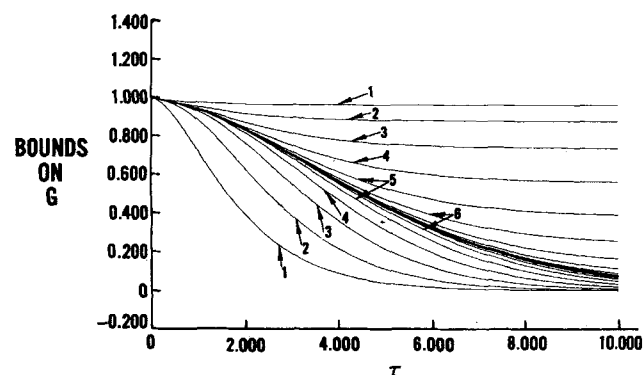


Fig. 1. Sequence of upper and lower bounds on the single-blow transient response function ( $z = 5.0$ ).

#### FORMAL EQUIVALENCE WITH THE SCHUMANN SOLUTION

It is a natural question to ask whether the two representations of the transient response function expressed by Equations (12) and (18) are formally equivalent to Schumann's analytical solution. The latter is usually stated for the case where the porous medium is heated. Below, it will be restated for the cooling case; the fluid temperature is then given by

$$G(z, \tau) = e^{-z-\tau} \sum_{n=1}^{\infty} z^n \frac{d^n}{d(z\tau)^n} \left( J_0(2\sqrt{z\tau}) \right) \quad (22)$$

where  $J_0(x) = \sum_{m=0}^{\infty} x^{2m}/2^{2m}(m!)^2$  denotes a Bessel function of order zero. For the above case, the formal equivalence is readily established. Consider first

$$\sum_{n=1}^{\infty} z^n \frac{d^n}{d(z\tau)^n} (J_0(2\sqrt{z\tau})) = \sum_{n=1}^{\infty} z^n \sum_{m=0}^{\infty} \frac{z^m \tau^m}{m! (m+n)!}$$

$$= \sum_{n=0}^{\infty} z^{n+1} \sum_{m=0}^{\infty} \frac{z^m \tau^m}{m! (m+n+1)!} \quad (23)$$

Upon the simple transformation of indexes  $i = m + n$ ,  $j = m$ , there follows

$$\sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \frac{z^{m+n+1} \tau^m}{(m+n+1)! m!} = \sum_{i=0}^{\infty} \frac{z^{i+1}}{(i+1)!} \sum_{j=0}^i \frac{\tau^j}{j!} \quad (24)$$

in agreement with the representation of the response function expressed by Equation (18).

#### CONCLUSION

In reducing transient heat transfer test data by the conceptually attractive curve matching method, the single-blow temperature response function is required. Two representations of the response function have been presented here, both lending themselves to more efficient computation than Schumann's analytical solution, with which they are formally equivalent. Thus it is no longer necessary to resort to finite-difference methods when computing theoretical response functions.

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#### NOTATION

- $G$  = normalized fluid (gas) temperature
- $S$  = normalized solid temperature
- $z$  = reduced length, dimensionless
- $\tau$  = reduced time, dimensionless
- $p$  = parameter of the double Laplace transform
- $q$  = parameter of the double Laplace transform
- $N_{tu}$  = number of transfer units, dimensionless
- $\delta_{i,j}$  = Kronecker symbol

#### LITERATURE CITED

1. Anzelius, A., *Z. Angew. Math. Mech.*, **6**, 291 (1926).
2. Nusselt, W., *Z. Ver. deut. Ing.*, **71**, 85 (1927).
3. Hausen, H., *Z. Angew. Math. Mech.*, **9**, 173 (1929).
4. Schumann, T. E. W., *J. Franklin Inst.*, **208**, 405 (1929).
5. Furnas, C. C., *U.S. Bur. Mines Bull. No. 361* (1932).
6. Saunders, O. A., and H. Ford, *J. Iron Steel Inst.*, **141**, 291 (1940).
7. Locke, G. L., *Tech. Rept. No. 10*, Dept. Mech. Eng., Stanford Univ., Calif. (June, 1950).
8. Hausen, H., *Z. Angew. Math. Mech.*, **11**, 105 (1931).
9. Allen, D. N. De G., *Quart. J. Mech. and Appl. Math.*, **5**, 455 (1952).
10. Jakob, M., "Heat Transfer," Vol. 2, pp. 261-341, Wiley, New York (1957).
11. Pucci, P. F., C. P. Howard, and C. H. Piersall, Jr., *Am. Soc. Mech. Engrs. Paper No. 66-GT-93* (1966).
12. Sneddon, I. N., "Functional Analysis," in *Encyclopedia of Physics*, S. Flügge, ed., Vol. 2, Springer-Verlag (1955).