A Heuristic Method for the Inversion of Certain Laplace Transforms to Produce Initially Valid Approximations

MIKAYEL SEMERCIYAN and GEORGE THODOS

Department of Chemical Engineering
Northwestern University, Evanston, Illinois 60201

Based on a Lagrangian interpolation, a heuristic scheme is developed for the inversion of certain types of Laplace transforms and is applied to the solution of problems of interest to chemical engineers for which the exact solution is either very difficult or impossible to obtain. The solutions thus obtained are in good agreement with exact values, when available, for initial values of the transformed independent variable and may therefore be used as approximations. Three illustrative examples are presented.

Salzer (1961) proposes an approximate analytical method for the inversion of the Laplace transform

$$F(s) = \frac{1}{s^p}\phi(s) \quad p > 0 \tag{1}$$

using a Lagrangian interpolation on the function $\phi(s)$, producing a polynomial in inverse powers of the transform variable s followed by a term-by-term inversion of the resulting expression. In this treatment, Salzer assumes that $\phi(s)$ is analytic in the right-half plane where it is also bounded away from zero as $s \to \infty$. It should also be pointed out that other inversion methods are available which approximate $\phi(s)$ by rational functions.

In the present approach, the singular factor $1/s^p$ of Equation (1) is replaced by $1/e^{\mu\sqrt{s}}$ and the function $\phi(s)$ is approximated by a polynomial in powers of $1/\sqrt{s}$. This adaptation of Salzer's method enables the inversion of some Laplace transforms obtained in the course of the solution of partial differential equations encountered in diffusional and heat transfer studies. This proposed method is not mathematically rigorous and no mathematical proofs can be presented. However, for cases for which exact solutions are available, good approximations have been obtained through the application of this method.

INTERPOLATING FUNCTIONS FOR INVERSE LAPLACE TRANSFORM

The following section introduces functions which can be used for the proposed inversion method. Defining $\chi_n(t)$ as the inverse transform,

$$\chi_n(t) = \mathcal{L}^{-1}\left[\frac{e^{-\sqrt{s}}}{s^{n/2}}\right] \quad (n = -1, 0, 1, 2, 3 \ldots.) \tag{2}$$

it is possible to show that

$$\chi_{-1}(t) = \frac{\frac{1}{t} - 2}{4\sqrt{\pi t^3}} \exp\left(-\frac{1}{4t}\right) \tag{2a}$$

$$\chi_0(t) = \frac{1}{2\sqrt{\pi t^3}} \exp\left(-\frac{1}{4t}\right) \tag{2b}$$

$$\chi_1(t) = \frac{1}{\sqrt{\pi t}} \exp\left(-\frac{1}{4t}\right) \tag{2c}$$

$$\chi_{n+2}(t) = (4t)^{\frac{n}{2}}\, i^n \operatorname{erfc} \frac{1}{2\sqrt{t}} \quad (n = 0, 1, 2, \ldots) \tag{2d}$$

The functions $\chi_n(t)$ were computed to 12 significant digits using the algorithm of Gautschi (1961) for $0 < t \leq 0.25$. For $t > 0.25$, the truncated infinite series was used to generate $\chi_2(t)$, and the recursion relation for the integrals of error functions was used to generate the remaining $\chi_n(t)$ functions.

APPROXIMATION OF $\varphi(s)$ THROUGH A LAGRANGIAN INTERPOLATION

The Lagrangian interpolation polynomial in $1/s$ at the distinct interpolating points $1/s_k > 0$ $(k = 0, 1, 2, \ldots, n)$ is

$$l_k\left(\frac{1}{s}\right) = \frac{\omega_k\left(\frac{1}{s}\right)}{\omega_k\left(\frac{1}{s_k}\right)} \tag{3}$$

where

$$\omega_k\left(\frac{1}{s}\right) = \frac{\omega\left(\frac{1}{s}\right)}{\frac{1}{s} - \frac{1}{s_k}} \tag{4}$$

with

$$\omega\left(\frac{1}{s}\right) = \prod_{i=0}^{n}\left(\frac{1}{s} - \frac{1}{s_i}\right) \tag{5}$$

Thus

$$l_k\left(\frac{1}{s_m}\right) = \begin{cases} 1 & \text{if} \quad m = k \\ 0 & \text{if} \quad m \neq k \end{cases} \quad \text{for } k = 0, 1, 2, \ldots, n \tag{6}$$

Correspondence concerning this paper should be addressed to G. Thodos.

Using these Lagrangian interpolating polynomials, $\phi(s)$ can be approximated as follows:

$$\phi(s) \approx \sum_{k=0}^{n} \phi(s_k)\, l_k\left(\frac{1}{s}\right) \tag{7}$$

In certain cases, it may prove more advantageous to use $1\sqrt{s}$ or $1/\sqrt{s+\lambda}$ as the argument of the interpolation polynomial instead of $1/s$. However, for simplicity of presentation, the form in $1/s$ will be retained for further treatment. Expressing the polynomial explicitly,

$$l_k\left(\frac{1}{s}\right) = a_{k0} + \frac{a_{k1}}{s} + \frac{a_{k2}}{s^2} + \ldots\ldots\ldots + \frac{a_{kn}}{s^n} = \sum_{j=0}^{n} a_{kj}\, s^{-j} \tag{8}$$

where the coefficients a_{kj} depend only on the interpolating points $1/s_k$. Recursion relations for the establishment of a_{kj} are presented by Semerciyan (1972). For the equally spaced case ($s_k = k + 1$, $k = 0, 1, \ldots, n$), Krylov and Skoblya (1969) present values a_{kj} up to ten significant figures for $n = 1, 2, 3, \ldots\ldots, 15$.

From $F(s) = e^{-\mu\sqrt{s}}\,\phi(s)$, the approximation follows,

$$F(s) \approx e^{-\mu\sqrt{s}} \sum_{k=0}^{n} \phi(s_k)\, l_k\left(\frac{1}{s}\right) = e^{-\mu\sqrt{s}} \sum_{k=0}^{n} \phi(s_k) \sum_{j=0}^{n} a_{kj}\, s^{-j} \tag{9}$$

Interchanging the summations of Equation (9), it follows that

$$F(s) \approx \sum_{j=0}^{n} \sum_{k=0}^{n} [a_{kj}\, \phi(s_k)]\, e^{-\mu\sqrt{s}}\, s^{-j} \tag{10}$$

The term by term inversion yields

$$f(t) \approx \sum_{j=0}^{n} \sum_{k=0}^{n} [a_{kj}\, \phi(s_k)]\, \mathcal{L}^{-1}\left[\frac{e^{-\mu\sqrt{s}}}{s^j}\right] = \sum_{j=0}^{n} \sum_{k=0}^{n} [a_{kj}\, \phi(s_k)]\, \mu^{2j-2}\, \chi_{2j}\left(\frac{t}{\mu^2}\right) \tag{11}$$

For the case $F(s) = e^{-\mu\sqrt{s+\lambda}}\,\phi(s)$, with $\phi(s)$ approximated by

$$\phi(s) \approx \sum_{k=0}^{n} \phi(s_k)\, l_k\left(\frac{1}{\sqrt{s+\lambda}}\right) \tag{12}$$

the approximate inverse is given by

$$f(t) = \sum_{j=0}^{n} \sum_{k=0}^{n} [a^*_{kj}\, \phi(s_k)]\, \mathcal{L}^{-1}\left\{\frac{e^{-\mu\sqrt{s+\lambda}}}{(s+\lambda)^{j/2}}\right. = \sum_{j=0}^{n} \sum_{k=0}^{n} [a^*_{kj}\, \phi(s_k)]\, e^{-\lambda t}\, \mu^{j-2}\, \chi_j\left(\frac{t}{\mu^2}\right) \tag{13}$$

where a^*_{kj} is the coefficient of $1/(s+\lambda)^{j/2}$ in the expansion of $l_k(1/\sqrt{s+\lambda})$.

Although no specific choice of the interpolating points is suggested in this study, an attempt has been made by Krylov and Skoblya (1969) to select the optimum distribution of the interpolating points.

The coefficients a_{kj} ($k, j = 0, 1, 2, \ldots\ldots, n$) increase rapidly with n. Moreover, if any two interpolating points are close together, the coefficients a_{kj} become large, and consequently the loss of significant figures becomes sufficiently important to effect the accuracy of the computed value of the inverse transform.

In certain cases, the inversion of the Laplace transform may be facilitated by incorporating an asymptotic behavior into the expansion. This is only possible when such an asymptotic behavior is known a priori for the specific problem, as in Examples 1 and 2.

ILLUSTRATIVE EXAMPLES

Example 1

For transient creeping flow around solid spheres, Sy, Taunton, and Lightfoot (1971) develop for the Laplace transform of the dimensionless velocity of a sphere falling freely from rest in a viscous medium, the expression

$$\overline{V_s^*} = \frac{1}{s\left[s + \frac{9}{2\alpha}\sqrt{s} + \frac{9}{2\alpha}\right]} \tag{1a}$$

where

$$V_s^* = \frac{V}{a^2 \frac{\hat{\rho} - \rho}{\alpha\mu} g} \tag{1b}$$

The inverse transform of Equation (1a) is

$$V_s^* = \frac{1}{QR} + \frac{1}{Q(Q-R)}\,[e^{Q^2 t^*} \operatorname{erfc} Q\sqrt{t^*}] - \frac{1}{R(Q-R)}\,[e^{R^2 t^*} \operatorname{erfc} R\sqrt{t^*}] \tag{1c}$$

where

$$Q = \frac{9}{4\alpha}\left[1 + \sqrt{\frac{5\rho - 8\hat{\rho}}{9\rho}}\right] \tag{1d}$$

and

$$R = \frac{9}{4\alpha}\left[1 - \sqrt{\frac{5\rho - 8\hat{\rho}}{9\rho}}\right] \tag{1e}$$

In Equations (1d) and (1e), $\hat{\rho}$ denotes the density of the sphere, ρ the density of the fluid, and

$$\alpha = \frac{1}{2} + \frac{\hat{\rho}}{\rho} \tag{1f}$$

where $8\hat{\rho} < 5\rho$ is assumed to hold.

The asymptotic behavior of the transform is found to be

$$\overline{V_s^*} \sim \frac{1}{s^2} \quad \text{as} \quad s \to \infty \tag{1g}$$

Assuming that

$$\overline{V_s^*} = \frac{1}{s^2} + \beta(s) \tag{1h}$$

$$\beta(s) = \overline{V_s^*} - \frac{1}{s^2} = \frac{1}{s\left[s + \frac{9}{2\alpha}\sqrt{s} + \frac{9}{2\alpha}\right]} - \frac{1}{s^2} \tag{1i}$$

Simplifying, Equation (1i) becomes

$$\beta(s) = \frac{-\frac{9}{2\alpha}\sqrt{s} - \frac{9}{2\alpha}}{s^2\left[s + \frac{9}{2\alpha}\sqrt{s} + \frac{9}{2\alpha}\right]} \tag{1j}$$

velocity of such a sphere, initially at rest,

$$\frac{1}{s\overline{V}^*} = \alpha s + \frac{9}{2}(\sqrt{s}+1)\left[1 - \frac{(\sqrt{s}+1)}{(3+\sqrt{s}) + \frac{\hat{\mu}}{\mu}\frac{e^{\sqrt{s}}(s^{3/2}-3s+6\sqrt{s}-6)+e^{-\sqrt{s}}(s^{3/2}+3s+6\sqrt{s}+6)}{e^{\sqrt{s}}(s-3\sqrt{s}+3)-e^{-\sqrt{s}}(s+3\sqrt{s}+3)}}\right] \quad (2a)$$

The asymptotic form of Equation (1j) as $s \to \infty$ is

$$\beta(s) \sim -\frac{9}{2\alpha}\frac{1}{s^{5/2}} \quad (1k)$$

Terminating this process at this point,

$$\beta(s) = \frac{1}{s^{5/2}}\phi(s) \quad (1l)$$

where $\phi(s)$ is bounded as $s \to \infty$. Using the proposed method

$$\phi(s) \approx \sum_{j=0}^{n}\frac{c_j}{s^{j/2}} \quad (1m)$$

where $c_j = \sum_{j=0}^{n} a_{kj}\,\phi(s_k)$. Therefore

$$V_s^* \approx \frac{1}{s^2} + \frac{1}{s^{5/2}}\sum_{j=0}^{n}\frac{c_j}{s^{j/2}} \quad (1n)$$

$$V_s^* \approx \frac{1}{s^2} + \sum_{j=0}^{n}\frac{c_j}{s^{\frac{j+5}{2}}} \quad (1o)$$

The term by term inversion yields

$$V_s^* \approx t^* + \sum_{j=0}^{u} c_j \frac{t^{*\frac{j+3}{2}}}{\Gamma\left(\frac{j+5}{2}\right)} \quad (1p)$$

The limiting velocity V_∞^* is found from Equation (1a), by the final value theorem, to be

$$V_\infty^* = \lim_{s\to 0} sV_s^* = \frac{2\alpha}{9}$$

Exact and approximate values of V_s^*/V_∞^* have been calculated using Equations (1b) and (1p) respectively for different times t^*

V_s^*/V_∞^*

t^*	exact	approximate
0.0001	4.351145×10^{-4}	4.351147×10^{-4}
0.001	4.051668×10^{-3}	4.051670×10^{-3}
0.01	0.032726717	0.032726715
0.1	0.18385046	0.18385047
1.0	0.5358	0.5350
2.0	0.6435	0.4352

The interpolating points for these calculations were chosen to be $s_k = (k+1)^2$ for $k = 0, 1, \ldots\ldots, 10$. The values calculated by this method are in good agreement with the exact values up to and including $t^* = 1.00$. For $t^* > 1.00$, the approximation is no longer useful. Therefore, the approximate relationship of Equation (1p) is capable of predicting reliable normalized velocities up to $V_s^*/V_\infty^* \approx 0.500$.

Example 2

For the transient creeping flow around liquid spheres, falling or rising within a viscous liquid medium, Sy and Lightfoot (1971) develop the Laplace transform for the velocity of such a sphere, initially at rest,

where

$$V^* = \frac{V}{a^2\frac{\rho-\hat{\rho}}{\mu}g} \quad (2b)$$

Equation (2a) requires in addition to parameter α of Equation (1a) the viscosity parameter $\hat{\mu}/\mu$, the viscosity ratio for the liquid in the sphere and the surrounding liquid medium, respectively.

To invert Equation (2a), Sy and Lightfoot (1971) have used the Bellman method (1) and tabulate calculated values of V^*/V_∞^* for $\frac{1}{2} < \alpha < 2\frac{1}{2}$, $0 < \hat{\mu}/\mu < \infty$, and $0.00319 < t^* < 0.2578$, where $t^* = \nu t/a^2$. These investigators also treat the short time behavior of the velocity using a tedious expansion procedure to arrive at an expression involving iterated integrals of the error function. It appears that the validity of this expansion of Sy and Lightfoot (1971) is limited.

For large values of s, the asymptotic form of Equation (2a) becomes

$$V^* \sim \frac{1}{\alpha s^2} \quad \text{as} \quad s \to \infty \quad (2c)$$

Following the approach outlined in Example 1

$$V^* = \frac{1}{\alpha s^2} + \beta(s) \quad (2d)$$

where the remainder can be expressed as

$$\beta(s) = \frac{1}{s^{5/2}}\Omega(s) \quad (2e)$$

in which $\Omega(s)$ is bounded as $s \to \infty$. This treatment produces the relationship

$$V^* = \frac{t^*}{\alpha} + \sum_{j=0}^{n} c_j \frac{t^{*\frac{j+3}{2}}}{\Gamma\left(\frac{j+5}{2}\right)} \quad (2f)$$

The asymptotic value of this velocity is found to be

$$V_\infty^* = \frac{1+\frac{\hat{\mu}}{\mu}}{3+\frac{9}{2}\frac{\hat{\mu}}{\mu}} \quad (2g)$$

Dimensionless velocities V^*/V_∞^* have been calculated with Equations (2f) and (2g) to produce values which have been used to establish the relationships of Figure 1 for $\hat{\mu}/\mu = 1.00$. A comparison of calculated values of V^*/V_∞^* between the method proposed in this study and that suggested by Sy and Lightfoot (1971) indicated that good agreement exists in the range $0.001 < t^* < 1.0$. The limit of the applicability of the proposed method is $t^* \approx 1.0$. It is worth noting that whereas Bellman's method produces values which apparently exhibit slight fluctua-

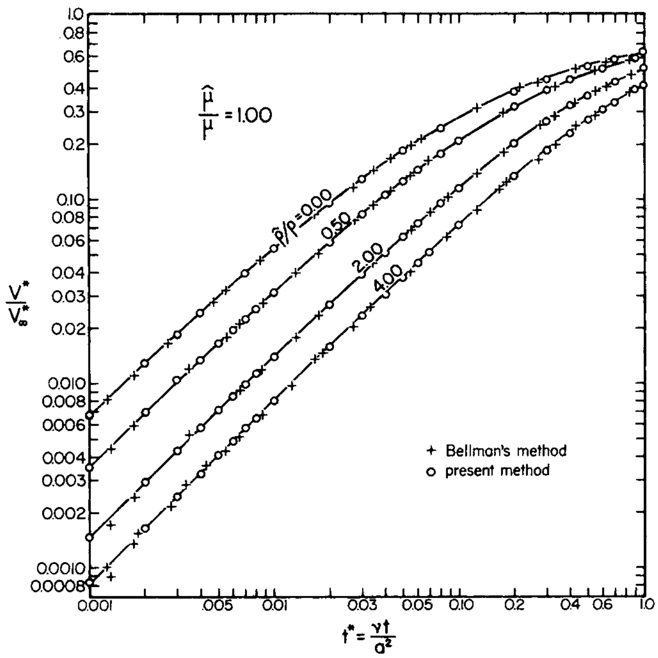

Fig. 1. Normalized velocity-time relationships of different density ratios for liquid spheres falling or rising in a viscous liquid ($\hat{\mu}/\mu$ = 1.00).

tions, the results forthcoming from the present study are smooth.

Example 3

In the adsorption of a component present in a solution flowing through a packed column, Rosen (1952) considered the case of a linear equilibrium isotherm on the surface $q_s = Kc_s$ between the diffusing and adsorbed phases and also the existence of film mass transfer coupled along with solid diffusion for which the diffusion coefficient was constant. Using this basic information, Rosen (1952) obtained the Laplace transform for the concentration of the solution at distance x

$$\bar{c}(x, s) = \frac{c_0}{s} e^{-xY_T(s)} \tag{3a}$$

where

$$Y_T(s) = \frac{Y_D(s)}{1 + R_f Y_D(s)} \tag{3b}$$

and

$$Y_D(s) = \gamma \left[\sqrt{\frac{2s}{\sigma}} \coth \sqrt{\frac{2s}{\sigma}} - 1 \right] \tag{3c}$$

In Equation (3c), $\sigma = 2D/b^2$ and $R_f = b/3h$, where h is the film mass transfer coefficient. Also, in Equation (3c), $\gamma = 3DK/b^2$ where D is the solid diffusion coefficient and b is the radius of the sphere.

For the special case $R_f = 0$ and $\gamma x = 1$, Equation (3a) becomes

$$\bar{u}(s) = \frac{\bar{c}(s)}{c_0} = \frac{1}{s} e^{-\left[\sqrt{\frac{2s}{\sigma}} \coth \sqrt{\frac{2s}{\sigma}} - 1\right]} \tag{3d}$$

In order to eliminate the parameter σ, time is normalized to produce the dimensionless quantity $t^* = \sigma t$ which changes the transform of Equation (3d) into

$$F(s) = \frac{1}{\sigma} u\left(\frac{s}{\sigma}\right) = \frac{1}{s} e^{-[\sqrt{2s} \coth \sqrt{2s} - 1]} \tag{3e}$$

Rosen (1952) evaluated the inverse transform of Equation (3e), using a quadrature involving an improper integral and also presented an asymptotic approximation of the inverse transform.

The proposed method of this study was applied to Equation (3e). As $s \to \infty$, the transform becomes asymptotically

$$F(s) \sim \frac{1}{s} e^{-(\sqrt{2s} - 1)} \tag{3f}$$

Hence, the proper factorization becomes

$$F(s) = \frac{e^{-\sqrt{2s}}}{s} \phi(s) \tag{3g}$$

where

$$\phi(s) = e^{1 - \sqrt{2s}\,(\coth \sqrt{2s} - 1)} \tag{3h}$$

The function $\phi(s)$ satisfies the requirements outlined for this method and can be expressed as follows:

$$\phi(s) \approx \sum_{j=0}^{n} \frac{c_j}{s^{j/2}} \tag{3i}$$

The term-by-term inversion of Equation (3g) involving the approximation of Equation (3i) becomes

$$f(t^*) \approx \sum_{j=0}^{n} \left[\sum_{k=0}^{n} a_{kj}\, \phi(s_k) \right] 2^{\frac{j}{2}} \chi_{j+2}\left(\frac{t^*}{2}\right) \tag{3j}$$

where a_{kj} has been calculated using the points $s_k = \{\delta^2, (2\delta)^2, (3\delta)^2, \ldots, (n+1)^2\delta^2\}$. Different values of δ and n were used to produce results which indicate that $\delta = 1$ is probably the best value for this parameter.

For the purpose of comparison, Bellman's method (1966) was also applied to Equation (3e) using a 5 × 5 and a 10 × 10 inversion matrix.

In order to check the calculated values of $f(t^*)$ obtained by these three methods, the method of Dubner and Abate (1968), which is considered to be more exacting, has been used. For the application of the Dubner-Abate method, the infinite series

$$f(t^*) \approx 2 \frac{e^{at^*}}{T} \left\{ \frac{1}{2} Re[F(a)] + \sum_{k=1}^{\infty} Re\left[F\left(a + \frac{k\pi}{T} i\right) \right] \cos \frac{k\pi}{T} t^* \right\} \tag{3k}$$

has been used, where $T \geqq 2t_{\max}$. Equation (3k) has an easily calculated error bound and approximations for $f(t^*)$ were obtained using 100 and 5,000 terms, respectively, for each value of $t^* = 1$ and $t^* = 1.5$. The resulting values of $f(t^*)$ are summarized in Table 1 and indicate that Rosen's reported exact value at $t^* = 1.00$ differs from the Dubner-Abate calculation by 0.814 − 0.808 = 0.006.

A comparison of these calculated values of $f(t^*)$ indicates that for $\delta = 1.00$ and $n = 5$, the proposed method is capable of producing, in general, values that are in good agreement with the values reported by Rosen up to $t^* = 1.0$.

DISCUSSION OF RESULTS

An estimate of error, as suggested by Salzer (1958, 1961) for the numerical inversion of the Laplace transform is too complex to be of practical value. Consequently,

Table 1. Comparison of Calculated Values of $f(t^*)$ for Rosen's Adsorption Problem

t^*	Rosen's values	Bellman's method (5 × 5 matrix)	Bellman's method (10 × 10 matrix)	$\delta = 0.10$ $n = 3$	$\delta = 0.10$ $n = 5$	Present method $\delta = 1.00$ $n = 3$	Present method $\delta = 1.00$ $n = 5$	$\delta = 10$ $n = 3$	$\delta = 10$ $n = 5$	(1968) Dubner and Abate $n = 100$	(1968) Dubner and Abate $n = 5000$
0.0	0.000	—	—	0.000	0.000	0.000	0.000	0.000	0.000	—	—
0.1	0.004	0.008	0.004	0.004	0.005	0.004	0.004	0.004	0.004		
0.3	0.185	0.185	0.184	0.156	0.206	0.185	0.185	0.185	0.184		
0.5	0.427	0.425	0.427	0.352	0.444	0.426	0.426	0.428	0.427		
0.7	0.622	0.623	0.622	0.506	0.617	0.618	0.622	0.631	0.628		
1.0	0.808	0.816	0.815	0.669	0.783	0.816	0.820	0.863	0.856	0.814	0.814
1.5	—	0.951	0.951	—	—	—	—	—	—	0.952	0.952
∞	1.000	—	—	—	—	—	—	—	—		

no attempt was made in this study to make any error estimates.

The present method produces a C^∞ function approximating the inverse transform thereby combining the functions of interpolation and inversion. Hence, the results may readily be used for analytical applications. Moreover, this method is capable of accommodating the asymptotic forms of the function for $t \to 0$. Furthermore, the use of $1/e^{\mu\sqrt{s}}$ as the singular factor produces solutions in the form of error functions and their integrals. This form of solution appears to be well suited for diffusion and heat transfer applications where such functions are commonly encountered in analytical solutions.

A major advantage of this method is its applicability to chemical engineering problems in the diffusion and heat transfer fields, using a relatively small amount of computational time. This is indicated by the fact that only $n + 1$ evaluations are required when n terms are considered. In the examples illustrated above, $n = 5$ and $n = 10$ were sufficient for obtaining reasonably good approximations.

A number of other problems of interest to chemical engineers have been developed and solved elsewhere (Semerciyan, 1972).

Since this method is not mathematically rigorous, care should be taken in using it and whenever more exact methods are available, these should be used as guidelines.

Computations for this study were carried out at the Vogelback Computing Center of Northwestern University using a CDC-6400 digital computer.

ACKNOWLEDGMENT

Thanks are extended to Whirlpool Corporation for financial assistance during the period of this study.

NOTATION

a = radius of sphere, cm. (examples 1 and 2)
a = real number associated with the Dubner-Abate method
a_{kj} = coefficient of s^{-j} in the expansion of $l_k(1/s)$
a^*_{kj} = coefficient $1/(s+\lambda)^{j/2}$ in the expansion of $l_k(1/\sqrt{s+\lambda})$
b = radius of sphere, cm, Example 3
c_j = coefficient, Equation (1m)
c_0 = initial concentration, g-moles/cm^3
c_s = liquid concentration on surface, g-moles/cm^3
C^∞ = class of infinitely differentiable functions
$c(x, t)$ = concentration at distance x and time t, g-moles/cm^3
$\bar{c}(x, s)$ = Laplace transform of $c(x, t)$
D = solid diffusion coefficient, cm^2/sec
e = base of natural logarithm, 2.71828...
$F(s)$ = Laplace transform of $f(t)$
g = gravitational acceleration, 980 cm/sec^2
h = film mass transfer coefficient, g-moles/ sec cm^2 (g-moles/cm^3)
i, j, k, n = indices, 0, 1, 2, 3 ...
K = slope of equilibrium isotherm, q_s/c_s
$l_k(1/s)$ = Lagrange polynomial in $1/s$
p = exponent, Equation (1)
q_s = concentration of diffusing component on solid surface, grams/gram solid
Q = parameter defined by Equation (1d)
R = parameter defined by Equation (1e)
R_f = film resistance to mass transfer, $b/3h$
Re = real part of a complex number
s = transform variable
s_k = interpolating points
t = time, sec.
t^* = normalized time, $\nu t/a^2$, Equation (1p)
t^* = normalized time, σt
T = real number greater than or equal to twice the largest value of the independent variable
$\bar{u}(s)$ = ratio $\bar{c}(s)/c_0$
V = velocity, cm/sec
V_s^* = normalized velocity
V_∞^* = normalized limiting velocity
$\bar{V}_s^*$ = Laplace transform of the normalized velocity
x = distance, cm
$Y_D(s)$ = function defined by Equation (3c)
$Y_T(s)$ = function defined by Equation (3b)

Greek Letters

α = parameter, defined by Equation (1f), $1/2 + \hat{\rho}/\rho$
$\beta(s)$ = function defined by Equations (1i) and (2d)
γ = parameter, $3DK/b^2$, cm^3/sec g
$\Gamma(x)$ = gamma function of x
δ = parameter defining the spacing of the points of interpolation
λ = non-negative number
μ = exponent
μ = viscosity of liquid medium, dynes sec/cm^2
$\hat{\mu}$ = viscosity of liquid sphere, dynes sec/cm^2
ν = kinematic viscosity, cm^2/sec
ρ = density of liquid medium, g/cm^3
$\hat{\rho}$ = density of liquid sphere, g/cm^3
σ = parameter, $2D/b^2$, 1/sec
$\phi(s)$ = well behaving factor of the Laplace transform
$\chi_n(t)$ = inverse transform defined by Equation (2)
$\omega(1/s)$ = function defined by Equation (5)
$\omega_k(1/s)$ = function defined by Equation (4)
$\Omega(s)$ = function defined by Equation (2e)

LITERATURE CITED

Bellman, R., R. E. Kalaba, and J. A. Lockett, Numerical Inversion of the Laplace Transform, American Elsevier, New York (1966).

Dubner, H., and J. Abate, "Numerical Inversion of Laplace Transforms by Relating them to the Finite Fourier Cosine Transform," *J. Assoc. Comput. Mach.*, **15**, 115 (1968).

Gautschi, W., "Recursive Computation of the Repeated Integrals of the Error Functions," *Math. Comp.*, **15**, 227 (1961).

Krylov, V. I., and N. S. Skoblya, Handbook of Numerical Inversions of Laplace Transforms, Israel Program for Scientific Translations, Daniel Davey, Jerusalem (1969).

Rosen, J. B., *J. Chem. Phys.*, **20**, 387 (1952).

Salzer, H. E., "Tables for the Numerical Calculation of Inverse Laplace Transform," *J. Math and Phys.*, **37**, 89 (1958).

———., "Additional Formulas and Tables for Orthogonal Polynomials Originating from Inversion Integrals", *ibid.*, **40**, 72 (1961).

Semerciyan, Mikayel, Ph.D. dissertation, Northwestern Univ., Evanston, Illinois (1972).

Sy, F., and E. N. Lightfoot, "Transient Creeping Flow Around Fluid Spheres," *AIChE J.*, **17**, 177 (1971).

Sy, F., J. W. Taunton, and E. N. Lightfoot, "Transient Creeping Flow Around Spheres," *AIChE J.*, **16**, 386 (1970).

Manuscript received December 8, 1971; revision received April 27, 1972; paper accepted April 29, 1972.

Mass Transfer into Dilute Polymeric Solutions

D. T. WASAN, M. A. LYNCH, K. J. CHAD, and N. SRINIVASAN

Department of Chemical Engineering
Illinois Institute of Technology, Chicago, Illinois 60616

Mass transfer into dilute polymeric solutions was studied by using a short wetted-wall column. Oxygen was absorbed into thin films of water and aqueous polymeric solutions. The polymer systems studied included dilute solutions of carboxymethylcellulose, polyethylene oxide, Carbopol, and Cyanamer. All of the above systems were moderately non-Newtonian with power law indexes less than unity. Methocel (a Newtonian fluid with a power law index of one) was also studied. The flow of liquid films was well within the laminar flow regime.

The rheological properties of these solutions as well as equilibrium solubility of oxygen in these solutions were determined. In all of the polymer systems studied except Polyox the equilibrium solubility of oxygen decreased with an increase in polymer concentration. In Polyox solutions, however, the equilibrium solubility of oxygen increased with an increase in polymer concentration.

For all of the systems investigated (including Polyox) the mass transfer coefficient for absorption of oxygen at a given flow rate decreased with an increase in polymer concentration. The mass transfer coefficient was highest for water at all flow rates.

The diffusivity of oxygen in all of the systems considered except Polyox was lower than that in water. This was attributed to the increased viscosity of the polymeric solutions. The diffusivity of oxygen in Polyox solutions was higher than it was in water. This was found to be due to the complex chemical reactions which occur in this system. In all of the pseudoplastic systems studied the diffusivity of oxygen increased with increasing wall shear rate (decreasing viscosity).

The diffusive transport rates of low molecular weight solutes such as gases in polymeric or macromolecular solutions and colloidal suspensions are of great interest not only in the chemical industry but also in processes involving biological media. A number of investigators have reported data on the diffusion of low molecular weight solutes in both aqueous and nonaqueous media (*2* to *5*, *8*, *9*, *13* to *21*, *23*, *27*, *28*, *30*, *32*, *36*, *39*). However, there have been only a few determinations of the diffusivity of gases in dilute polymeric non-Newtonian solutions. Furthermore, data on the equilibrium solubility of gases in such systems are scanty. Most recently, Caskey and Barlage (*6*) presented a review of the existing literature and their new data on the diffusion of carbon dioxide in aqueous solutions of carboxymethylcellulose. The diffusion coefficient data measured with the liquid laminar jet method were opposite those obtained with a quiescent liquid contactor. These investigators gave no definite reason for this difference in results obtained from the two different experimental techniques. Since different techniques for diffusivity measurements such as laminar jet (*2*, *10*, *27*, *39*), quiescent liquid contactor (*6*, *23*, *26*), rotating disk (*13*), etc. involve different kinds of fluid mechanical behavior which are not completely understood for non-Newtonian polymeric systems it is apparent that further work is needed before diffusive transport rates in these systems can be accurately discerned from such measurement methods.

In the work presented here, a short wetted-wall column was selected because it is one of the best and simplest pieces of equipment for gas-liquid contacting. The hydrodynamics of such columns have been thoroughly studied and are well understood (*29*). A second advantage is that the area for mass transfer is constant and known, a feature

M. A. Lynch is with DuPont Co., Louisville, Kentucky. K. J. Chad is with Universal Oil Products, Des Plaines, Illinois. N. Srinivasan is with India Cements Ltd., Madras, India.