integration of values on graphs of the $A$-series. In order to eliminate the real time in the dimensionless ordinate, $T_2^*\theta^*$ is used as the ordinate parameter for the solution of Equation (5). The solution of Equation (5) for a constant energy source is shown in graphs of series $B$.

From these graphs, temperature profiles for an instantaneous or continuous, constant disk source problem can be obtained. For a steady, variable disk source (that is, $w(t) \neq 1.0$) solution can be obtained by using the disk source energy profile and graphs of series $A$ in Equation (5). For an analogous mass transfer problem involving a disk source such as the diffusion of a pollutant, concentration profiles of the diffusing component can be obtained by using the graphs presented here.

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**NOTATION**

$C$ = heat capacity
$Q$ = instantaneous energy source
$q$ = continuous energy source
$R$ = radius of disk source
$r$ = radial distance
$T$ = temperature
$t$ = time
$z$ = distance from the interface
$\alpha$ = thermal diffusivity
$\rho$ = density
$\lambda, \xi$ = dummy variable

**LITERATURE CITED**

1. Carslaw, H. S., and J. C. Jaeger, "Conduction of Heat in Solids," p. 260, Oxford Press, London (1959).

# Limitations on the Generalized Differentiation Method for Obtaining Rheological Data from the Couette, Annular, and Falling Cylinder Rheometers

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In the January, 1967, issue of the *AIChE Journal,* Lescarboura, Eichstadt, and Swift (*1*) proposed a generalized method for analyzing rheological data on time independent fluids obtained from various rheometers. Implications are made that are not fully justified, and it is the purpose of this communication to discuss and clarify these matters from a theoretical standpoint.

One is led to believe from the aforementioned article that the equations obtained by the "generalized differentiation method" for the Couette, annular, and falling cylinder rheometers are valid and will lead to the *correct* flow curve, $\dot{\gamma} = f(\tau)$, for any time-independent fluid if the "flow is laminar; if there is no slip at the wall . . .; and if the rate of shear at a point depends only on the shear stress." (See the last sentence in each of the sections entitled, "The Coaxial Cylinder Rotational Rheometer," "The Concentric Annulus Rheometer," and "The Falling Cylinder Rheometer," and the remarks in the sections entitled "Discussion" and "Conclusions." It can be shown that the equations obtained for the Couette, annular, and falling cylinder rheometers by the "generalized differentiation method" of the authors are not rigorous from a theoretical standpoint unless the fluid behaves as a power law fluid over the range of shear stresses developed by the rheometer *on each run. For a fluid which* does not show this power law behavior, the equations developed are approximate in that one must assume power law behavior over ranges of shear stress as determined by each run, and thus the advantage stated for the differential over the integral technique in the first two paragraphs of (*1*) is nonexistent with the equations given for these rheometers.

On the other hand, Equation (7)* for the capillary viscometer is rigorous for any time-independent fluid characterized by the relationship

$$\tau = m''(\tau)\dot{\gamma}^{n''(\tau)} \tag{1a}$$

for a viscometric flow. For this instrument the differential technique does have the advantage of requiring no rheological model for the fluid. [Note: For the capillary rheometer $n'' \equiv n'$ as defined by Equations (1*a*) and (10), and similarly $m'' \equiv m'$, but for the other three rheometers the $n'$ and $m'$ defined in each case are not equivalent to the $n''$ and $m''$ defined by (1*a*). This distinction is important.]

In order to substantiate the above statements let us consider first the coaxial cylinder rotational rheometer. The shear stress-shear rate relationship which is to be used in the "generalized differentiation method" is not clearly stated in the article, and one must infer its form from Equation (10), which has been written for the capillary viscometer, and from Equation (16). Private communication with Swift has shown that the following relationship was used:

$$\tau = m'(T)\dot{\gamma}^{n'(T)} \tag{2a}$$

This relationship inherently requires that the power law describe the fluid over each shear rate range covered by a given run in the rheometer. That is, for any given torque, $T$, the rheometer covers a range of shear stress and shear rate values from $R_i$ to $R_o$, all of which must be related by the fixed values of $m'(T)$ and $n'(T)$ through Equation (2*a*). Clearly this means that one has applied the power law model from $\tau_o \rightarrow \tau_i$ for any given torque $T$. Further, Equation (2*a*) fails to be rigorous because the relationship between $\tau$ and $\dot{\gamma}$ must be unique, and Equation (2*a*) does not meet this requirement. For instance, one may easily envision making runs at two different torques so that the range of shear rates encountered in the two runs overlap considerably. Then unless the fluid is a true power law fluid over all the shear rates covered by the two runs, we will have two sets of constants $n'(T_1) \neq n'(T_2)$ and $m'(T_1) \neq m'(T_2)$ which we cannot expect to give us identical $\tau$ values for all values of $\dot{\gamma}$ occurring in both runs. Thus the inherent application of the power law model through the use of (2*a*) in deriving Equations (14), (19), and (20) excludes the generality and rigor claimed for these equations.

The same objections apply to the equations derived for the concentric annulus and falling cylinder rheometers, where $n'$ is defined as the slope of the logarithmic plot of $\Delta P$ vs. $Q$ and of the logarithmic plot of $(\sigma - \rho)$ vs. $v_t$, respectively. The result is that Equations (24) and (28) as well as (29) and (33) are rigorous only when the fluid is a power law fluid from the minimum $|\dot{\gamma}_o|$ to the maximum $|\dot{\gamma}_i|$ generated in the runs.

Let us consider now the capillary viscometer, which provided the ideas for the "generalized differentiation method," in order to discern how the confusion has arisen and to see whether a generalized differential approach may be set up. Equation (1*a*) may be applied to this rheometer, and thus it follows that

$$\tau_R = m''(\tau_R)\dot{\gamma}_R{}^{n''(\tau_R)} \tag{3a}$$

The equation of motion written for this system gives

$$\tau = r\Delta P/2L \tag{4}$$

so that

$$n''(\tau) = n''(r\Delta P/2L) = f_1(r\Delta P/L) \tag{4a}$$

and

$$n''(\tau_R) = f_1(R\Delta P/L) = f_2(\Delta P/L)$$

*only because R is being held constant.* Therefore the inference that $n''(\tau) = n''(\Delta P/L)$, without any restriction on the radial position at which $\tau$ is measured, is ambiguous and incorrect, and it appears that similar reasoning led to the analogous Equation (2*a*) for the Couette rheometer. The analogous equations implied for the concentric annulus and the falling cylinder rheometers will be equally fallacious.

In addition to this confusion, the uniqueness of the equation for $Q/\pi R^3$ in a capillary viscometer has led to another error. For a power law fluid it is easily shown (*2*) that

$$Q/\pi R^3 = [n/\{3n+1\}]\ [R\Delta P/2Lm]^{1/n} \tag{5a}$$

and for a time-independent fluid Equations (3*a*) and (4) of this communication and Equation (4) from reference *3*, with the proper changes in notation, give

$$Q/\pi R^3 = [n''(\tau_R)/\{3n''(\tau_R)+1\}]\ [R\Delta P/2Lm''(\tau_R)]^{1/n''(\tau_R)} \tag{6a}$$

so that the equation for a power law fluid and a time-independent fluid have the same form, but this is *uniquely so* for the capillary rheometer because it is a one-boundary system. One finds that the corresponding equations for the Couette, annular, or falling cylinder rheometers do not have the same form without ambiguity simply because they are two boundary systems with $|\tau_i| \neq |\tau_o|$ such that $n''(\tau_o)$, $n''(\tau_i)$, $m''(\tau_o)$, and $m''(\tau_i)$ all must occur in the equation for the general time-independent fluid. This is unfortunate because the "generalized differentiation technique" is based on the premise that the equation for time-independent fluids can be inferred from the power law equation for a given system.

To elucidate this point consider the Couette rheometer once again. An equation similar to (14), call it (14*a*), will be the proper starting point for a generalized differential analysis, but its form must be rigorously defined. The end result of the derivation we wish to attempt by a "generalized differential technique" is given by Mooney's equation, and thus we may use his equation to determine the proper form of Equation (14*a*).

For a Couette rheometer in which only the outer cylinder rotates, Mooney's equation becomes

$$2\Omega_o \frac{d \ln \Omega_o}{d \ln \tau_o} = 2\tau_i \frac{d\,\Omega_o}{d\,\tau_i} = \dot{\gamma}_i - \dot{\gamma}_o \tag{23}$$

From Equation (1*a*) one obtains

$$\dot{\gamma}_o = \left(\frac{\tau_o}{m''|_{\tau_o}}\right)^{\frac{1}{n''|_{\tau_o}}} \quad \text{and} \quad \dot{\gamma}_i = \left(\frac{\tau_i}{m''|_{\tau_i}}\right)^{\frac{1}{n''|_{\tau_i}}} \tag{7a}$$

and the equations of motion give

$$\tau_i = T/2\,\pi\,L\,R_i^2 \tag{17}$$

$$\tau_o = T/2\,\pi\,L\,R_o^2 \tag{18}$$

Substituting Equations (17) and (18) into (7*a*) and then Equation (7*a*) into (23) one obtains

* Equations given by number refer only to equations listed in the article by Swift et al., whereas equations given by a number followed by *a* refer to equations given in this communication.

$$\Omega_o = \frac{\left\{ \frac{d \ln \tau_o}{d \ln \Omega_o} \right\}}{2} \left[ \left\{ \frac{T/2\,\pi\,L\,R_i^2}{m''|_{\tau_i}} \right\}^{\frac{1}{n''|\tau_i}} - \left\{ \frac{T/2\,\pi\,L\,R_o^2}{m''|_{\tau_o}} \right\}^{\frac{1}{n''|\tau_o}} \right] \quad (14a)$$

Equation (14$a$) reduces to the power law form (2)

$$\Omega_o = \frac{n}{2} \left[ \frac{T}{2\pi L m} \right]^{1/n} \left\{ \left[ \frac{1}{R_i^2} \right]^{1/n} - \left[ \frac{1}{R_o^2} \right]^{1/n} \right\} \quad (8a)$$

if

$$n''|_{\tau_o} = n''|_{\tau_i} = n = \text{constant}$$
$$m''|_{\tau_o} = m''|_{\tau_i} = m = \text{constant}$$

which means we have a power law fluid. However, in order to apply this "generalized differentiation technique" one would have to infer Equation (14$a$) from the power law form, Equation (8$a$), by analogy, which does not seem possible.

Since the concentric annulus and falling cylinder rheometers are also two-boundary systems, with the boundaries being $R_i$ and $R_o$, one can expect that the same problem will occur for these rheometers when one attempts to deduce the starting equation from the corresponding equation for the power law fluid.

Viewing the "generalized differentiation technique" as an approximate one in which the fluid is assumed to display power law behavior *over a range of shear rates as determined by each run,* (but where $n$ and $m$ are allowed to vary from run to run), one finds that the equations given by Swift et al. for the Couette, annular, and falling cylinder rheometers are applicable. The excellent agreement of the exact results obtained from the capillary equations with the approximate results obtained from the equations for the other three rheometers, as shown in Figures 1 to 5 of the article (*1*) suggests that one consider this matter in greater detail.

First one should note that the fluids considered in Figures 3 and 5 are essentially power law fluids over the range of shear rates shown, and therefore one would expect good agreement. Enough curvature is detectable, however, in Figures 2 and 4 to suggest that some other explanation may be required for these cases.

In the case of the Couette rheometer Equation (14$a$) reveals that the accuracy of Equation (14) improves as $n''|_{\tau_o} \rightarrow n''|_{\tau_i}$ and $m''|_{\tau_o} \rightarrow m''|_{\tau_i}$. Further the equations of motion, (17) and (18), show that by a judicious selection of rheometer dimension one can make $\tau_i \rightarrow \tau_o$ and thus $n''|_{\tau_o} \rightarrow n''|_{\tau_i}$ and $m''|_{\tau_o} \rightarrow m''|_{\tau_i}$. That is

$$\tau_i/\tau_o = R_o^2/R_i^2 \quad (9a)$$

so that $\tau_i \rightarrow \tau_o$ as $R_i \rightarrow R_o$.

Table 1 indicates that the authors used a radius ratio of 0.8 to generate the data from the Couette rheometer equations for Figure 2. Thus the necessary assumption that the fluid behave as a power law fluid *over the range of* 0.64 $\tau_i \leq \tau \leq \tau_i$ *for any run* is quite good as can be seen by inspection of Figure 2.

A similar analysis to explain the good results for the concentric annulus rheometer can be developed as follows. One cannot obtain a rigorous solution for $Q$ by a differential procedure (*4*) similar to that used for the Couette and capillary rheometers to obtain Equations (6$a$) and (14$a$), but by using the defining equation for the flow rate in an annulus

$$Q = -\pi \int_{R_i}^{R_o} r^2\, \dot{\gamma}\, dr \quad (10a)$$

and the equation of motion

$$\tau = \frac{R_o\, \Delta P}{2L} \left( \frac{r}{R_o} - \frac{R_o\, \lambda^2}{r} \right) \quad (11a)$$

one obtains the integral equation

$$\frac{-Q\tau_o^3}{\pi R_o^3} = \left( \frac{1-\lambda^2}{2} \right)^3 \int_{\tau_i}^{\tau_o} \dot{\gamma}\, \tau^2 \left\{ \frac{1}{\sqrt{1 + \left( \frac{2\lambda\tau_o}{\tau[1-\lambda^2]} \right)^2} + 4 + 3\sqrt{1 + \left( \frac{2\lambda\tau_o}{\tau[1-\lambda^2]} \right)^2} + \left( \frac{2\tau_o\lambda}{\tau[1-\lambda^2]} \right)^2} \right\} d\tau \quad (12a)$$

Considering the integrand of this integral equation, we note that $\dot{\gamma}$ is an odd function of $\tau$, $\tau^2$ is an even function of $\tau$, and each term in the { } brackets is an even function of $\tau$. Therefore the integrand is an odd function of $\tau$. From this it follows that the integral will be an even function of $\tau$ (*5*). Thus Equation (12$a$) may be written as

$$-\frac{Q\,\tau_o^3}{\pi R_o^3} = \left( \frac{1-\lambda^2}{2} \right)^3 \int_{|\tau_i|}^{|\tau_o|} \dot{\gamma}\, \tau^2 \left\{ \frac{1}{\sqrt{1 + \left( \frac{2\lambda\tau_o}{\tau[1-\lambda^2]} \right)^5} + 4 + 3\sqrt{1 + \left( \frac{2\lambda\tau_o}{\tau[1-\lambda^2]} \right)^2} + \left( \frac{2\tau_o\lambda}{\tau[1-\lambda^2]} \right)^2} \right\} d\tau \quad (13a)$$

Equation (13$a$) leads us to the interesting and important conclusion that in deriving Equations (24) and (28) the power law approximation must be applied only over the range $|\tau_i|$ to $|\tau_o|$, and not over the larger range of zero to $|\tau_i|$ covered by any given run. The significance of this result becomes apparent when one compares the magnitude of $\tau_i$ and $\tau_o$. From Equation (11$a$) one finds that

$$\tau_i/\tau_o = \frac{\kappa - \lambda^2/\kappa}{1-\lambda^2} \quad (14a)$$

Generally the position of $\lambda$ depends upon the fluid and $\Delta P/L$, but a good first approximation may be obtained by using the value of $\lambda$ obtained for a Newtonian fluid (*6*):

$$\lambda^2 = \frac{1-\kappa^2}{2\ln(1/\kappa)} \quad (15a)$$

Combining Equations (14$a$) and (15$a$) one can calculate the ratios of $\tau_i/\tau_o$ at various values of $\kappa$ (see Table 1). Table 1 clearly shows that as $\kappa = R_i/R_o \rightarrow 1.0$, $\tau_i/\tau_o \rightarrow -1.0$. Thus for any given fluid the accuracy of Equations (24) and (28) improve as $R_i \rightarrow R_o$.

Considering the data of Swift et al. in light of the previous discussion, one discerns that, for the annulus considered to generate the data shown in Figure 2, the power law assumption was applied over a range of shear stresses which we can estimate to be $|0.929\tau_i|$ to $|\tau_i|$. Similarly the range over which the power law approximation was made in order to analyze the data for Figure 4 is estimated to be $|0.788\tau_i|$ to $|\tau_i|$. By observing the capillary viscometer data shown in Figures 2 and 4 one sees that the power law approximation over these short shear stress ranges is quite good, and therefore we can expect the close agreement between the annular and capillary viscometers as is shown.

TABLE 1. $\tau_i/\tau_o$ VS. $\kappa$ FOR NEWTONIAN FLUIDS IN AN ANNULUS

| $\kappa$ | 0.9 | 0.8 | 0.7 | 0.6 | 0.5 | 0.4 |
|---|---|---|---|---|---|---|
| $\tau_i/\tau_o$ | −1.036 | −1.079 | −1.135 | −1.191 | −1.268 | −1.378 |

The comments concerning the annular rheometer should also apply to the falling cylinder rheometer since it is essentially an annular flow system with a moving boundary.

From the above discussion one may conclude that the method proposed by Swift et al. using the equations developed for the Couette, annular, and falling cylinder rheometers to obtain shear stress—shear rate data is an approximate one in which the accuracy of the results improve as $R_i \rightarrow R_o$.


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## NOTATION

$f_i$ = functionality symbol
$L$ = length over which $\Delta P$ is measured
$m$ = power law constant
$m'$ = function of torque, $T$, defined by Equation (2a)
$m''$ = function of shear stress defined by Equation (1a)
$n$ = power law constant
$n'$ = function of torque, $T$, defined by Equation (2a)
$n''$ = function of shear stress defined by Equation (1a)
$\Delta P$ = pressure drop
$Q$ = volumetric flow rate
$Q_1$ = volumetric flow rate when $\tau_w = 1.0$
$r$ = radial position
$R$ = capillary radius
$R_i$ = radius of inner cylinder
$R_o$ = radius of outer cylinder
$T$ = torque
$v_t$ = terminal velocity of falling cylinder

**Greek Letters**

$\dot{\gamma}$ = shear rate
$\lambda$ = dimensionless radius of zero shear
$\rho$ = fluid density
$\sigma$ = density of falling body
$\tau$ = shear stress
$\Omega_o$ = angular velocity at outer wall

**Subscripts**

$i$ = inner wall
$o$ = outer wall
$R$ = wall of capillary

## LITERATURE CITED


1. Lescarboura, J. A., F. J. Eichstadt, and G. W. Swift, *AIChE J.*, 13, 169 (1967).
2. Wilkinson, W. L., "Non-Newtonian Fluids," pp. 55, 134. Pergamon Press, New York (1960).
3. Metzner, A. B., and J. C. Reed, *AIChE J.*, 1, 434 (1955).
4. Hersey, M. D., *J. Rheol.*, 3, 196 (1932).
5. Hildebrand, F. B., "Advanced Calculus for Applications," p. 218, Prentice-Hall, Englewood Cliffs, N. J. (1962).
6. Bird, R. B., W. E. Stewart, and E. N. Lightfoot, "Transport Phenomena," p. 52, Wiley, New York (1960).


# Mass and Heat Transfer from Rigid Spheres


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Keey and Glen (*11*) have presented a critical analysis of results of investigations of mass transfer from rigid spheres. They consider the assumption that an exponential expression of the form

$$N_{Sh} = A + B\, N_{Re}^{m}\, N_{Sc}^{n} \qquad (1)$$

can be fitted to experimental data and point out that this equation is inadequate because the exponents $m$ and $n$ are not constants. This paper considers the variation of the exponents $m$ and $n$ with the Reynolds and Schmidt or Prandtl numbers as indicated by experimental heat and mass transfer data.

The constant $A$ has been theoretically treated (*13*) and experimentally verified to equal 2.

## REYNOLDS NUMBER RESPONSE

Figure 1 shows the Nusselt number as a function of Reynolds number at a constant Prandtl number of 0.73. Figure 2 shows the Sherwood number as a function of Reynolds number at a constant Schmidt number of 0.6 and Figure 3 shows the Sherwood number as a function of Reynolds number at a constant Schmidt number of 2,220.

Garner, Jenson, and Keey (*7*) have described the transitions in flow patterns that occur around spheres as a function of Reynolds number. At Reynolds numbers between 1 and 17 the flow is approximately symmetrical. At a Reynolds number of about 17 separation occurs and a weak toroidal vortex is formed near the rear stagnation point. As the Reynolds number increases, the vortex gains strength and the separation ring advances toward the equator, until at about a Reynolds number of 450 the separation angle is 104 deg. (*6*). The wake then becomes unstable and oscillates about the axis of motion and this continues above a Reynolds number of 1,000. The angle of separation remains at 104 deg. but the frequency of oscillation of the wake increased with Reynolds number. These two transition points are shown on the figures. Data

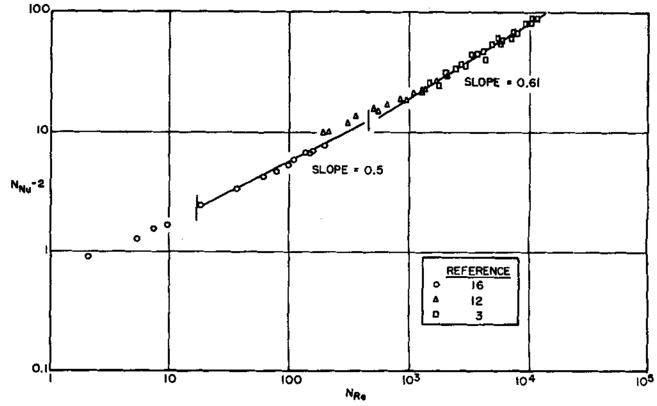


Fig. 1. Heat transfer data at $N_{Pr} = 0.73$.