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A High-Temperature Viscometer for Molten Materials[1]

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An oscillating-cup viscometer for the measurement of the viscosity of molten materials from room temperature to 1400 K was developed. The instrument is described in detail and the working equations are presented. The operational behavior was tested with water at room temperature. Preliminary measurements show that the new viscometer is capable of measuring the viscosity of water at room temperature to within 0.2%. As the primary objective of this work is the establishment of standard reference data for high-temperature viscosity measurements in molten salts, molten metals, and molten semiconductors, references of earlier viscosity measurements of molten KNO_3 are given.

KEY WORDS: high temperature; molten salts; oscillating-cup viscometer; viscosity.

1. INTRODUCTION

The measurement of viscosity of high-temperature melts has proven to be a difficult task because of the high temperatures involved and the necessity to account for a variety of phenomena that generally do not occur at low temperatures [1]. To measure the viscosity of these materials oscillating-body viscometers seem to be the most appropriate.

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Any type of oscillating-body viscometer consists of an axially symmetric body suspended from an elastic stand, where it can induce torsional oscillations. The viscosity of the fluid is obtained from the measured decrement of the oscillations. Once an oscillation is induced, the damping of the fluid will cause a logarithmic decrement in the amplitude of oscillation and an increase in the period of oscillation. These parameters depend on the viscosity and density of the fluid. The only measurements that are necessary, besides pressure and temperature, are mass and time, which can be obtained with a high accuracy. This is an absolute method, so it is not necessary to make any calibrations with fluids of known viscosity.

The success of this type of instrument can be illustrated by the different classes of fluids for which it has been used. They include gases at high and low pressures [2], water and aqueous solutions [3–6], organic liquids including hydrocarbons [7, 8], and molten materials, including molten salts [9, 10], metals [11, 12], and molten semiconductors [13].

In an overall program to obtain accurate measurements of the viscosity of molten materials to contribute to the establishment of standard reference data, we are interested in the measurement of the viscosity of molten salts, molten metals, and molten semiconductors. The first stage is the determination of data for molten salts. For this kind of material there are still a few data that can be used as reference data. Since the 1960s many workers have provided results with a good accuracy for the viscosity of high-temperature melts. However, there are still large discrepancies between laboratories, amounting to 50% for molten NaCl at 1100 K [1].

For potassium nitrate the situation is better. The results of Murgulescu and Zuca [14], Janz and Saegusa [15], Protsenko and Razumouskaya [16], Wellman et al. [17], Timidei et al. [18], Dumas et al. [19], Zuca [20], Ohta et al [21], Janz et al. [22], Yokoo et al. [23], and Abe et al. [10] agree within $\pm 4\%$. These results were obtained by different techniques, including oscillating-body viscometers and capillary viscometers. Although the discrepancies are smaller, there are still nonnegligible differences among these sets of data.

The use of oscillating-body viscometers was limited due to the complexity of the mathematical treatment of the equations for the motion of the body. However, Kestin and Newell [24] and Beckwitt and Newell [25] provided solutions for this, triggering their intensive utilization since 1970.

In Section 2 we give an outline of the working equations for the method that are applicable to our viscometer. In the succeeding sections we describe the instrument designed and constructed in our laboratory and present some preliminary tests.

2. WORKING EQUATIONS

The viscosity calculation is obtained from the imaginary part of a rigorous solution for oscillating-body viscometers, derived by Kestin and Newell [24]. The equation is

$$(s+\Delta_0)^2 + l + D(s) = 0 \tag{1}$$

where $D(s)$ is a characteristic function and s is the complex frequency of oscillation, given by

$$s = T_0/T(-\Delta \pm i) \tag{2}$$

Δ and Δ_0 are the logarithmic decrements of oscillation with and without fluid in units of 2π, i.e, $\Delta = \delta/2\pi$ and $\Delta_0 = \delta_0/2\pi$, and T and T_0 are the periods of oscillation of the oscillating-body with fluid and in vacuum, respectively.

The characteristic function can be an exact solution [24] or an approximate solution derived by Beckwitt and Newell [25]. The latter is

$$D(s) = s^2 \frac{I'}{I}\left(\frac{4}{s^{1/2}\zeta_0} - \frac{6}{s\zeta_0^2} + \frac{3}{2s^{3/2}\zeta_0^3} + \frac{3}{2s^2\zeta_0^4} + \frac{1}{s^{1/2}z_0} - \frac{16}{\pi s\zeta_0 z_0} - \frac{9}{s^{3/2}\zeta_0 z_0} - \frac{8}{s^2\zeta_0 z_0} - \frac{\exp[-2s^{1/2}z_0]}{2s^{1/2}z_0}\right) \tag{3}$$

where $\zeta_0 = R/(\eta T_0/2\pi\rho)^{1/2}$ and $z_0 = h/(\eta T_0/2\pi\rho)^{1/2}$ are dimensionless quantities for the inner radius of the cup, R, and the height of the fluid in the cup, h; I is the moment of inertia of the suspension system alone; I' is the moment of inertia of the fluid; η is the viscosity; and ρ is the density of the fluid. $\delta' = (\eta T_0/2\pi\rho)^{1/2}$ is the boundary layer thickness for the oscillatory motion of the fluid.

Equation (3) is applicable when $\zeta_0 \gg 1$ and $z_0 \gg 1$. From this general solution the following working equations were derived for the oscillating-cup viscometer [26]:

$$(\pi\rho hR^4/(2I))[A(\Delta p + q)\, x^{-1} - B\,\Delta x^{-2} - Cpx^{-3} - Dx^{-4}] = 1/\theta^2 - 1 + (\Delta - \Delta_0/\theta)^2 \tag{4}$$

and

$$(\pi\rho hR^4/(2I))[A(p - \Delta q)\, x^{-1} - Bx^{-2} + Cqx^{-3}] = 2(\Delta - \Delta_0/\theta) \tag{5}$$

where

$$A = 4 + (R/h)$$

$$B = 6 + (16/\pi)(R/h)$$

$$C = 1.5 + 9(R/h)$$

$$D = 1.5 - (8/\pi)(R/h)$$

$$\theta = T_0/T$$

$$p = 1/(2(\Delta + (I + \Delta^2)^{1/2}))^{1/2}$$

$$q = 1/(2p)$$

$$x = R(2\pi\rho/(\eta T))^{1/2}$$

Equations (4) and (5) are used to calculate the viscosity from the period ratio and the logarithmic decrement, respectively. Equation (5) is preferred due to large uncertainties in the term $1/\theta^2 - 1$ in Eq. (4), which is nearly zero. Equation (5) is solved for the viscosity, giving

$$\eta = 2\pi\rho R^2/(Tx^2) \tag{6}$$

The error of this solution is smaller than 0.1% when $R/h < 1$ and $x > 10$ [26]. In Eq. (3) the fluid equations used are the linearized Navier–Stokes equations for an incompressible fluid and are strictly applicable when the motion of the fluid is unidimensional, which we assume to be the case for the present instrument. Also, no effect of the vapor pressure of the vapor above the liquid was considered, assuming that its effect on the overall torque induced in the mechanical system was negligible. Equation (6) was solved to obtain the viscosity of the liquid by an iterative method using a simple computer program in BASIC language.

3. EXPERIMENTAL APPARATUS

The oscillating-cup viscometer is composed of four fundamental systems: an oscillating system (including the suspension system and oscillation initiator), a heating system, a vacuum system, and a system for the detection of oscillations. In this section we describe these systems of the viscometer designed and constructed in our laboratory.

The oscillating system is composed of a Pt92/W8 wire with a 0.5 mm diameter and a length of 603 mm. This material was chosen due to its low

internal friction and stable elastic behavior [27]. This wire is silver-soldered to a special device that permits the suspension of the wire and the manual initiation of oscillations. The other end of the wire is silver-soldered to a mirror holder and an inertial disk screwed to a molybdenum suspension rod. This rod, with a diameter of 6 mm, is 585 mm long and serves to separate the torsion wire from the high temperatures in the furnace. Screwed to the rod is a molybdenum cup of 17.18 mm inner diameter. The cup was machined with a precision of ± 0.005 mm and holds the fluid. Figure 1 shows a schematic diagram of the viscometer, and Fig. 2 the design and major dimensions of the molybdenum cup.

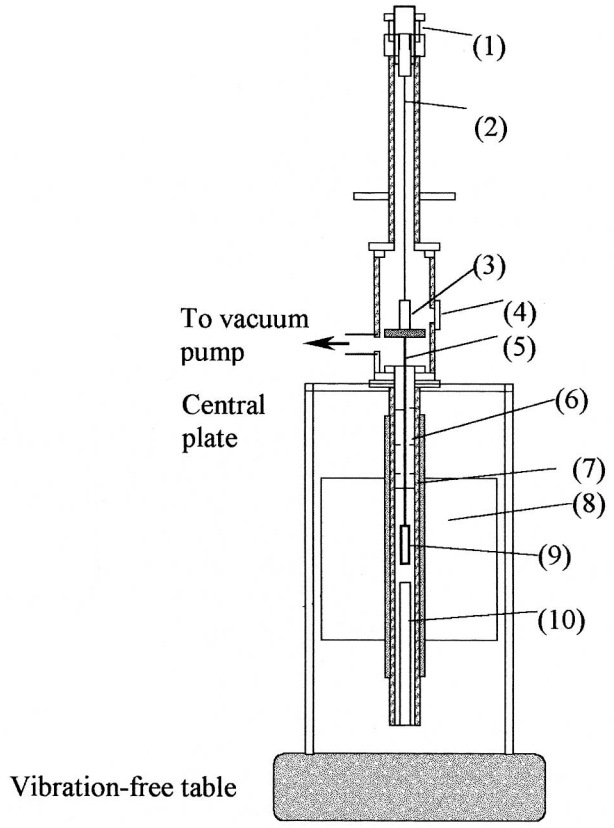

Fig. 1. High-temperature oscillating-cup viscometer. (1) Oscillating initiator; (2) Pt92/W8 wire; (3) mirror and inertial disk; (4) window for laser beam; (5) molybdenum rod; (6) tube with radiation shields; (7) ceramic and steel tubes; (8) furnace; (9) molybdenum cylindrical cup; (10) thermocouple assembly.

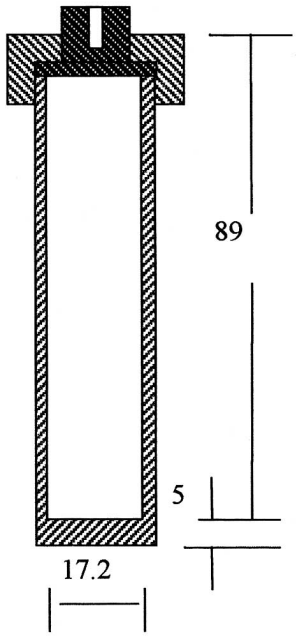

Fig. 2. Cylindrical molybdenum cup, with dimensions in millimeters.

To achieve high temperatures we used a vertical tubular furnace (Termolab), composed of a ceramic tube open at both ends, 700 mm high, and with an internal diameter of 60 mm. A PID controller is coupled to this furnace (Eurotherm Model 902 P), allowing a temperature stabilization within 1 K. Inside this tube is a stainless steel tube that is vacuum-tight. This tube is attached to the upper parts of the instrument, at room temperature, with adequate flanges. In all flanges are viton O-rings to seal the instrument. The tube of the furnace and the rest of the instrument are supported by a central plate, which is about 300 mm above the furnace. This plate was leveled in the plane with the aid of a water-level system.

To avoid the conduction of heat to the upper parts, namely, to the torsion wire, we have another tube inside the first one supporting radiation shields. The temperature is measured with a Type N thermocouple, calibrated up to the silver point, with an accuracy of 0.1 to 0.5 K. This thermocouple is held in the axial direction just beneath the bottom of the cup.

Figure 3 shows the measuring system. This system is composed of a He–Ne laser light source (Melles Griot; 632.8 nm, 1 mW of output power), photodetectors (Melles Griot), a time interval counter (Stanford Research

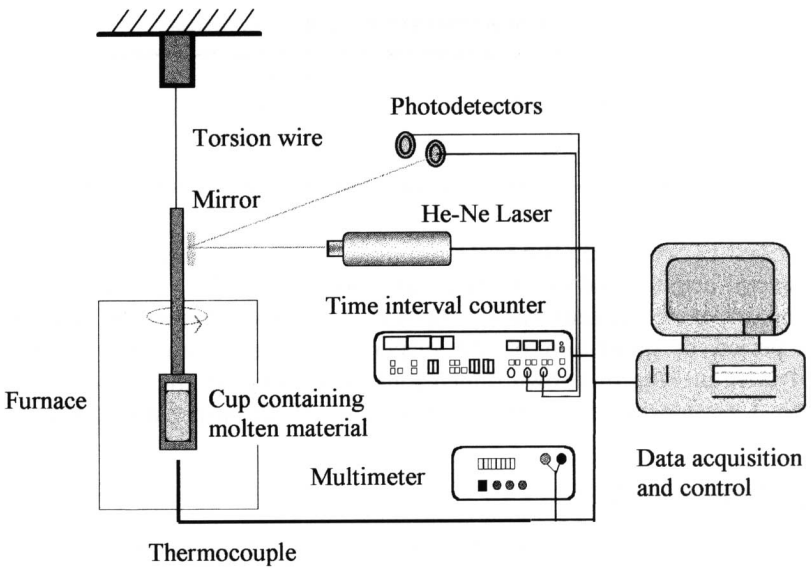

Fig. 3. Schematic diagram of the measuring system.

Systems Model SR620) capable of a resolution of 25 ps, and a computer to control and process the data. The laser is directed to the mirror in the suspension system, and its beam divergence is only 1.35 mrad. The mirror is a highly polished planar steel surface coated with aluminium, forming a reflecting surface for the optical detection system. The period and logarithmic decrement of the oscillations were obtained by measuring the time intervals of the reflected light from the mirror to two photodiodes located about 2 m from the mirror and 15 cm apart and coupled to the accurate time interval counter. The period is determined from successive passing of the light reflected from the mirror to a photodetector placed at the center of oscillation. The logarithmic decrement is also obtained optically by measuring successive time intervals of the light passing trough the two detectors. The precision of the measurement of the decrement and period was estimated to be 0.9 and 0.02%, respectively. The logarithmic decrement was calculated by Kestin's equation [28], which eliminates the necessity of any length measurements.

4. PRELIMINARY TESTS

4.1. Characteristics of the Suspension System

The characteristics of the suspension system were determined at room temperature. The decrement and period of oscillation were obtained as

Table I. Characteristics of the Suspension System

R(mm)	8.590 ± 0.005
$10^7 I(\text{kg} \cdot \text{m}^2)$	600 ± 4
T_0(s)	1.6622 ± 0.0004
$10^{-3}\delta_0$	1.46 ± 0.07

described in Section 3. The inner radius of the cup was carefully measured at several heights, and the average value was taken. The moment of inertia of the suspension system was determined in the usual manner by measuring the period of oscillation of the suspension system with and without a molybdenum ring of known dimensions and placed on the top of the cup. Table I summarizes the main characteristics of the suspension system.

4.2. Viscosity of Water

To test the performance of the instrument, we measured the viscosity of water at 19.8°C. The viscosity of water can be calculated from Eq. (6) since the boundary layer thickness δ' is 0.5 mm, and therefore, $\zeta_0 = 17.2 \gg 1$ and $z_0 = 129.0 \gg 1$, for water at 20 C. Similar values will be found for molten salts. The period and decrement of oscillation were measured with the cup partially filled with water and the values obtained were $T = 1.6690 \pm 0.0004$ s and $\delta = (5.84 \pm 0.05) \times 10^{-3}$. The density of water was taken from the literature [29] to be 998.2474 $\text{kg} \cdot \text{m}^{-3}$ at 19.8°C. The viscosity was then calculated from Eq. (6), and a value of $\eta = 1.005$ mPa · s was obtained. This result is only 0.2% lower than the recommended values of 1.002 mPa · s at 20°C [30] and 1.007 mPa · s at 19.8°C [31]. This agreement demonstrates the satisfactory performance of the instrument.

Table II. Analysis of the Uncertainty in the Determination of Viscosity

Parameter	s_i	s_i (%)	Contribution to s_η (%)
δ	$5\text{x}10^{-5}$	0.9	2.8
T_0	400 μs	0.02	≈ 0
T	500 μs	0.03	0.03
I_0	$4\text{x}10^{-7}$ kg · m^2	0.7	1.3
R	5 μm	0.06	0.17
m	$5\text{x}10^{-6}$ kg	0.03	0.03
Total—s_η			3.09

To evaluate the experimental accuracy, the root mean square deviations for the different variables were determined and are presented in Table II. The actual overall accuracy is estimated to be about 3%. The main sources of error are the logarithmic decrement of the oscillation δ and the moment of inertia of the system I_0. The accuracy can be improved by a better determination of δ (to within 0.2 to 0.3%), and of I_0 (to within 0.3 to 0.4%), and we anticipate reporting new results for the viscosity of molten potassium nitrate in the near-future.

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