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VISCOSITY MEASUREMENTS AT HIGH TEMPERATURE AND HIGH PRESSURE - A NOVEL TECHNIQUE

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1. Introduction

Most modelling of transport phenomena in materials processing from fluid phases suffers from the lack of reliable data for the transport properties under typical process conditions. Our group is involved in extensive numerical modelling efforts for the melt growth of mercury cadmium telluride. To-date the viscosity of this liquid material has only been estimated [1]. To increase the fidelity of our modelling, we set out to determine the kinematic viscosity of liquid $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ at various compositions in the range $0 < x < 0.2$ and at temperatures around and below the respective melting point. The phase diagram of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ [2] shows that for this range the melting point varies from 670°C for pure HgTe to 790°C at $x = 0.2$. The vapor pressure above the melt varies correspondingly from 15 atm to about 40 atm. Hence, the measurement of viscosities in this system requires a technique that allows for combinations of high temperatures and pressures. In addition, a closed isothermal system is required. Otherwise, due to the large disparity of the fugacities of the two binary constituents [2], rapid and uncontrolled compositional shifts in the liquid would occur during a measurement. The high pressure melt container must also be inert to molten $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ to avoid possible errors from contamination of the liquid.

Similar problems were faced earlier by Kakimoto and Hibiya who determined the viscosity of molten GaAs employing the oscillating cup method [3]. The accuracy of this method, however, tends to be limited by the temperature and load dependence of the torsional spring constant of the suspension fiber used. In addition, it is difficult to design a suspension system for the oscillating cup that ensures purely rotational motion.

In this paper, we describe a novel technique that largely circumvents the above experimental problems. The principle of this technique and its theory are presented in Section 2. The actual instrumentation is described in Section 3, together with viscosity measurements of room temperature liquids, which illustrate the precision and accuracy of the method. The planned extension of the technique to high temperatures and pressures is touched upon in Section 4.

2. Principle and theory of the technique

As sketched in Fig. 1, the viscometer cell consists of two cylindrical containers (radii r_1 and r_2) that are connected at the bottom by a capillary tube of radius r and length L . The liquid of interest is initially filled into the cylinders to unequal heights. The resulting pressure head forces the liquid to flow through the capillary until equal heights are attained. The mass transfer associated with this equilibration is recorded by differential weighing. This is done with an electrobalance which, advantageously, keeps the cell horizontally positioned at all times. The kinematic viscosity of the liquid can be obtained from the time-dependent weight shift between the two cylinders. Note that the cell used in this technique resembles a classic viscosity measuring arrangement devised by Ostwald[4].

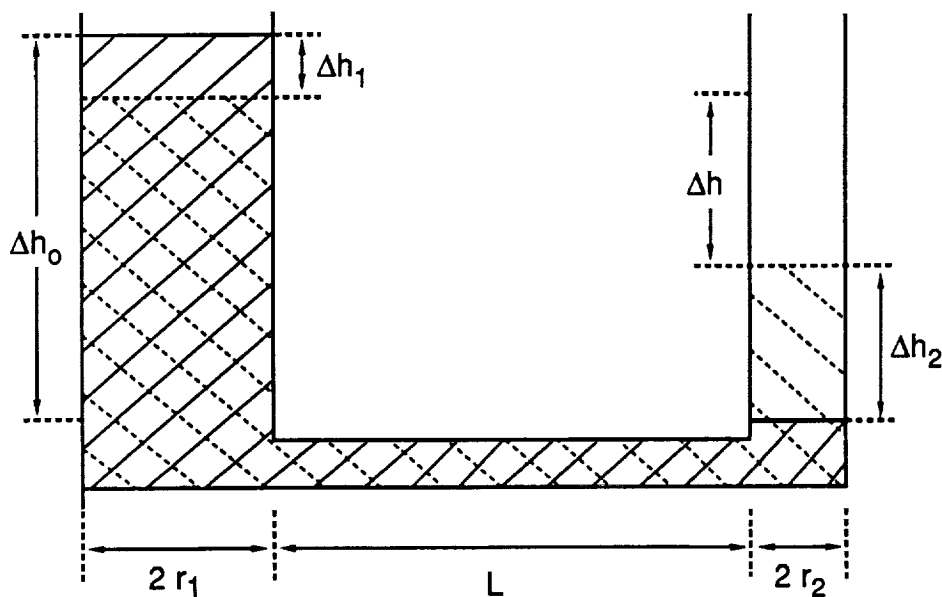


Figure 1. Schematic diagram of viscometer

The theory is based on the premise that the exchange of mass between the two reservoirs (see fig. 1) takes place by a time-dependent Poiseuille flow through the narrow capillary. The flow is driven by a pressure gradient $G(t)$ which is taken to be uniform in the capillary. The pressure gradient is given by

$$G(t) = \frac{\rho g \Delta h(t)}{L} , \quad (1)$$

where ρ is the constant density of the fluid, g is the gravitational acceleration and $\Delta h(t)$ is the liquid head.

For a unidirectional flow driven by a uniform time-dependent pressure gradient, the creeping flow assumption is valid provided that its Reynolds number is much smaller than unity at all times, i.e.

$$Re = \frac{V_{\max} L}{\nu} \ll 1 , \quad (2)$$

where $\nu = \eta/\rho$ the kinematic viscosity, with η the dynamic viscosity. The reference velocity V_{\max} arises in response to the initial pressure head ΔP_{\max} associated with the initial liquid head Δh_0 at t_0 , the time of the first differential (height) measurement. In a Poiseuille flow through the capillary

$$V_{\max} = \frac{r^2 \pi}{8 \eta L} \Delta P_{\max} = \frac{r^2 \pi \rho g \Delta h_0}{8 \eta L} . \quad (3)$$

Consequently, the limiting condition (2) becomes

$$Re = \frac{g \Delta h_0 r^2}{8 \nu^2} \ll 1 . \quad (4)$$

Provided that (4) is satisfied, the volume flow rate at time t can then be written as a modified form of Poiseuille's relation [5]

$$Q(t) = \frac{\pi r^4}{8 \eta L} \Delta P(t) . \quad (5)$$

where $\Delta P(t)$ is the time-dependent pressure difference between the two ends of the capillary.

The mass of liquid in container 1 is

$$M_1(t) = M_1(t_0) + \Delta M_1(t) , \quad (6)$$

with a similar expression for the mass in container 2. The mass difference between the two containers is then

$$\Delta M(t) = M_1(t) - M_2(t) = \Delta M_0 + 2\Delta M_1(t) , \quad (7)$$

where the $2\Delta M_1$ term follows from the fact that the total mass is constant ($\Delta M_1(t) = -\Delta M_2(t)$), and the difference in mass between the two containers at $t=t_0$ is

$$\Delta M_0 = M_1(t_0) - M_2(t_0) . \quad (8)$$

The liquid head $\Delta h(t)$ between containers 1 and 2 can be expressed as

$$\Delta h(t) = h_1(t) - h_2(t) = \Delta h_0 + \frac{(r_1^2 + r_2^2)}{r_2^2} \Delta h_1(t) , \quad (9)$$

where we have used the identity $r_1^2 \Delta h_1(t) = -r_2^2 \Delta h_2(t)$, which follows from the conservation of mass. The changes in liquid level Δh_1 and Δh_2 are as defined in Fig.1.

The rate of change of the mass difference between the two containers, using (5), is

$$\frac{d\Delta M(t)}{dt} = 2 \frac{d\Delta M_1(t)}{dt} = 2 \rho Q(t) = \frac{\pi r^4}{4 \nu L} \Delta P(t) . \quad (10)$$

The pressure difference $\Delta P(t)$ is

$$\Delta P(t) = \rho g \Delta h(t) = \frac{g(r_1^2 + r_2^2)}{\pi r_1^2 r_2^2} \Delta M(t) , \quad (11)$$

where we have used equations (6) and (7) together with the identities

$$\Delta M_0 = \frac{2\rho \pi r_1^2 r_2^2}{r_1^2 + r_2^2} \Delta h_0 , \quad (12)$$

and

$$\Delta M_1(t) = \rho \pi R_1^2 \Delta h_1(t) \quad . \quad (13)$$

The equation for rate of change of the mass difference $\Delta M(t)$ is obtained upon substitution of (11) into (10) and takes the form

$$\frac{d\Delta M(t)}{dt} = \frac{g r^4 (r_1^2 + r_2^2)}{8 \nu L r_1^2 r_2^2} \Delta M(t) \quad , \quad (14)$$

with $\Delta M(t_0) = \Delta M_0$. This has the solution

$$\Delta M(t) = \Delta M_0 \exp\left(-\frac{t}{\tau}\right) \quad , \quad (15)$$

where the characteristic time τ is

$$\tau = \frac{8 \nu L r_1^2 r_2^2}{r^4 g (r_1^2 + r_2^2)} \quad . \quad (16)$$

Fig.2 illustrates this exponential decay of the mass difference between the initially unequally filled containers.

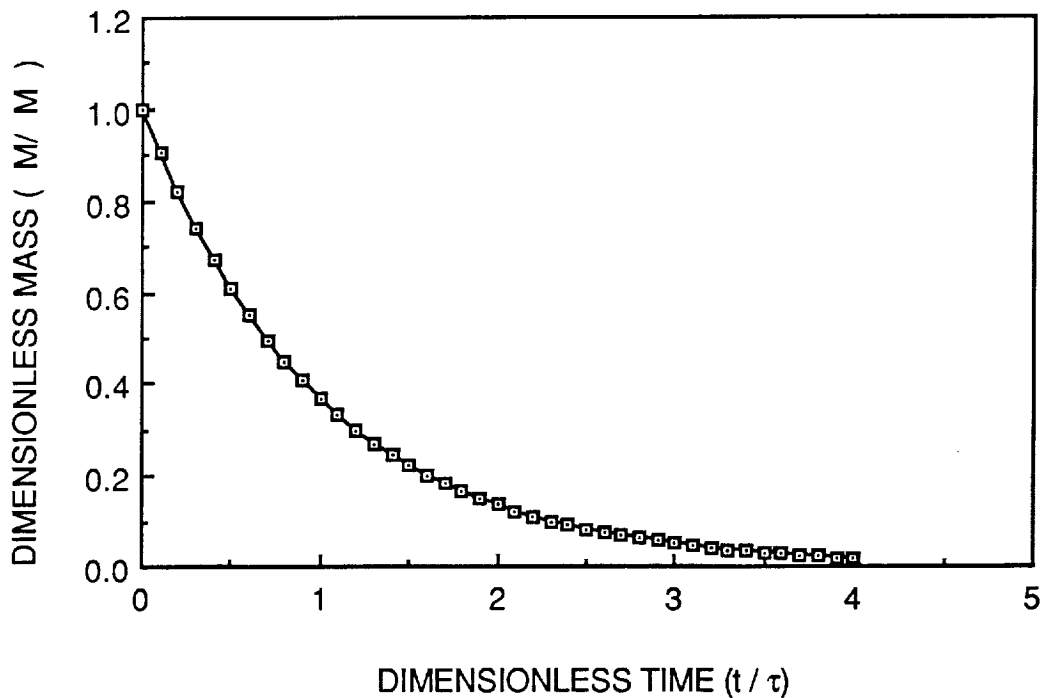


Figure 2. Normalized mass difference $\Delta M(t) / \Delta M_0$ versus normalized time t/τ

The kinematic viscosity can be obtained from equations (15) and (16) and is given by

$$v = - \frac{r^4 g (r_1^2 + r_2^2)}{8 L r_1^2 r_2^2} t / \ln (\Delta M / \Delta M_0) \quad (17)$$

For the special case that $r_1 = r_2 = R$, equation (17) simplifies to

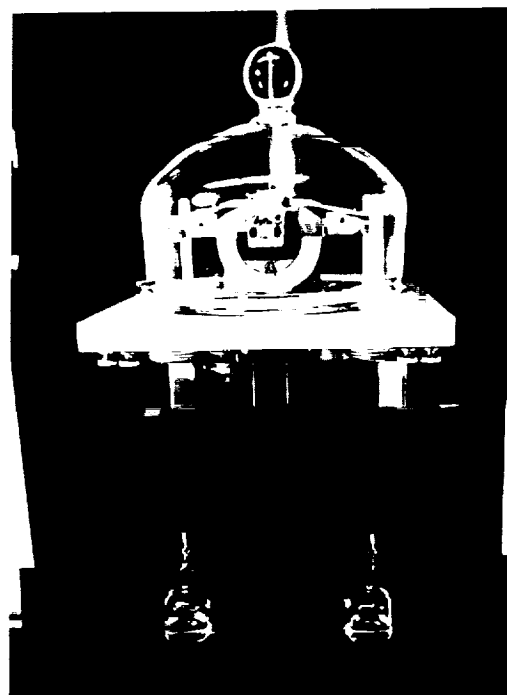
$$v = - \frac{r^4 g}{4LR^2} t / \ln (\Delta M / \Delta M_0) = - \beta t / \ln (\Delta M / \Delta M_0) \quad (18)$$

where the viscometer cell constant is $\beta = \frac{r^4 g}{4 L R^2}$ (19)

3. Apparatus and low temperature measurements

In order to determine the precision and accuracy of this method, we have performed viscosity measurements at 24 °C with water, at 25 °C with ethanol and carbon tetrachloride and at 22 °C with glacial acetic acid. The experimental arrangement used consisted of a viscometry cell suspended from an electrobalance (Cahn model 1000), see Fig. 3, the output of which was fed to a chart recorder. We used a glass cell with $R = 1.42$ cm, $L = 9.5$ cm, and $r = 0.0431$ cm. Besides the capillary connecting the bottom part of the cylinders, the cell was reinforced by a rod connecting their upper parts. Holes in the upper shoulders of the cylinders facilitated cleaning and filling.

Figure 3. Photograph of viscosity measurement cell suspended from electrobalance.



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The measurement procedure was as follows. After filling the horizontally positioned cell to a certain level, one of the hang-down wires from the balance was raised and the liquid was allowed to equilibrate to the new levels in the tilted cell. On rapid re-levelling *of the cell*, there is then a liquid head which drives mass transfer between the containers. The associated differential weight change ($\Delta M/\Delta M_0$), which is directly computed by the data processing system of the electrobalance, was then recorded versus time.

Figure 4 shows a chart recording obtained with CCl_4 . From this curve, values of $-\ln(\Delta M/\Delta M_0)$ and $-t/\ln(\Delta M/\Delta M_0)$ are calculated for increasing times after the first reading is taken. Note that t_0 can be taken at any point after the balance has stabilized after the re-levelling of the cell. The results shown in Table 1 illustrate that the mass transfer indeed follows an exponential function with high precision, as can be seen from the small variations in the values of the last column.

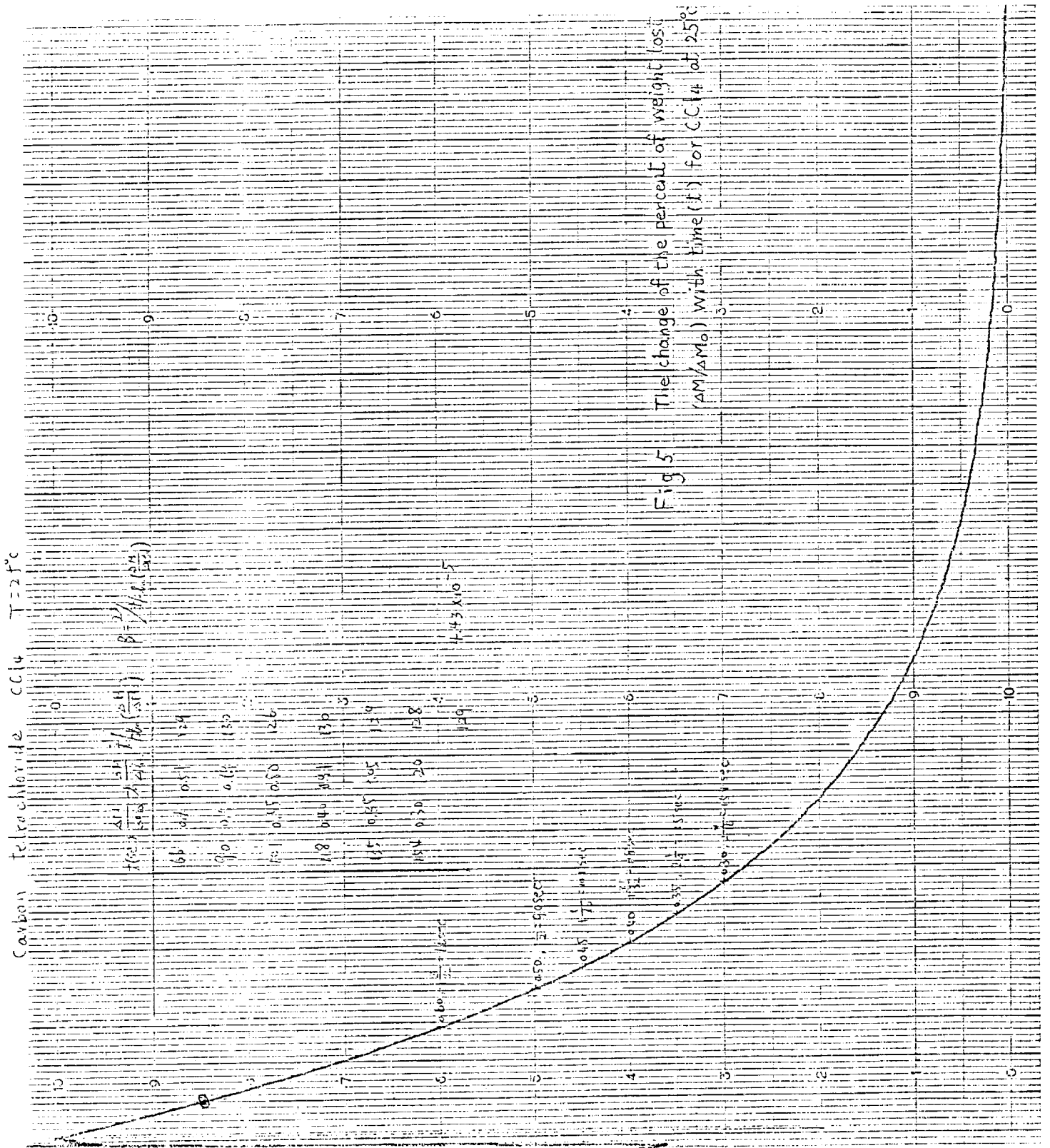
Table 1: Experimental values of $-\ln(\Delta M/\Delta M_0)$ and $-t/\ln(\Delta M/\Delta M_0)$ for CCl_4 at 25 °C

t (sec)	$\Delta M/\Delta M_0$	$-\ln(\Delta M/\Delta M_0)$	$-t/\ln(\Delta M/\Delta M_0)$
66	0.60	0.51	129
90	0.50	0.69	130
101	0.45	0.80	126
118	0.40	0.91	130
135	0.35	1.05	129
154	0.30	1.20	128

The reproducibility of the measurements from run to run falls within the fluctuations of the $-t/\ln(\Delta M/\Delta M_0)$ values obtained within a run. Table 2 displays the weight transfer results obtained from several runs for the four liquids investigated.

In order to evaluate these data for the kinematic viscosity, the cell constant β needs to be determined, see eq. (18). We have first evaluated eq.(19) for the geometrical dimensions used.

Figure 4. Chartrecording of weight transfer versus time obtained with CCl4 at 25°C.



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This resulted in $\beta^{\text{geom}} = 4.44 \times 10^{-5} \text{ cm}^2/\text{s}^2$. Note, however, that due to the fourth power dependence of β on the capillary radius an uncertainty of 1% in r translates into an error of 4% in β and, thus, in v . Considering all dimensions (r, L, R) entering the evaluation of eq. (19), we estimate the total uncertainty to be $\pm 5\%$. Hence, we have also determined the cell constant from eq. (18) and our data for water (Table 2), for which the dynamic viscosity is known with high accuracy [6]. Thus we obtained a $\beta^{\text{calib}} = 4.52 \times 10^{-5} \text{ cm}^2/\text{s}^2$.

Table 2: Experimental values of $-t / \ln (\Delta M / \Delta M_0)$ [sec] for four liquids

Water H ₂ O	Ethanol C ₂ H ₆ O	Carbon tetrachloride CCl ₄	Glacial acetic acid C ₂ H ₄ O ₂
202	313	129	324
201	310	130	320
199	313	126	319
202	316	130	322
204	310	129	318
207	313	128	322
204	306	132	324
201	310	130	323
207	308	131	319
204	310	132	322
207	311	132	318
204	309	129	319

In Table 3 we have listed the kinematic viscosities deduced from the weight transfer data of Table 2, using both cell constants. Percent deviations from the v -values (last column) computed from the published results for η and ρ (for which no accuracy statement could be found) are given in parentheses. The deviations for the upper three liquids shown in Table 3 are 2% or less. Thus, from the results for these three liquids we conclude that our technique is very accurate. However, our result for glacial acetic acid deviates by +28% from the value deduced from the

literature data. This may be due to a lack of purity of the acid we used. Glacialacetic acid is rather hygroscopic. Addition of water to the pure acid, which can occur by absorption in a moist atmosphere, changes the viscosity significantly [7].

Table 3: Comparison of experimental results for kinematic viscosities (in cm^2/s) obtained in this study and corresponding values computed from literature data for η and ρ .

Liquid	v from		η [6] 10^{-3}Nsm^{-2}	ρ [7] gcm^{-3}	v (calc.) cm^2s^{-1}
	β_{geom}	β_{calib}			
Water	0.00906		0.8985	0.9973	0.009221
H ₂ O (24°C)	(-1.8%)		(±0.1%)		
Ethanol	0.0138	0.00140	1.081	0.7852	0.01376
C ₂ H ₆ O (25°C)	(+0.3%)	(+1.7%)	(±0.5%)		
Carbon tetrachloride	0.00577	0.00587	0.9116	1.5867	0.005746
CCl ₄ (25°C)	(+0.4%)	(+2.1%)	(±0.5%)		
Glacial Acetic Acid	0.0143	0.0145	1.1004	1.0477	0.01050
C ₂ H ₄ O ₂ (22°C)	(+27%)	(+28%)	(±1.0%)		

4. Extension of technique to high pressures and temperatures

Encouraged by the favorable results obtained at atmospheric pressure and ambient temperature, we plan to employ this technique for studies on liquid mercury-cadmium-telluride. Note that the arrangement described above is well suited for operation at high temperatures and pressures since a cell, constructed of heavy wall silica tubing, can be hermetically sealed and hung on non-oxidizing wires into a high temperature furnace. Thus, the sensitive electrobalance can be well isolated thermally. In order to prevent a differential pressure build-up between the cylinders in the cell during mass transfer, the upper rod (Fig. 3) will be replaced by another capillary. A split tube furnace has been ordered, that will facilitate the mounting of the cell on the hang-down wires.

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