

DEPARTMENT OF
MINES AND TECHNICAL SURVEYS
MINES BRANCH

*THEORY AND EXPERIMENT IN
METHODS FOR THE PRECISION
MEASUREMENT OF VISCOSITY*

H. R. THRESH

PHYSICAL METALLURGY DIVISION

Reprinted from Transactions ASM 55(3), 790-818 (1962)

© Crown Copyrights reserved

Available by mail from the Queen's Printer, Ottawa,
and at the following Canadian Government bookshops:

OTTAWA

Daly Building, Corner Mackenzie and Rideau

TORONTO

Mackenzie Building, 36 Adelaide St. East

MONTREAL

Aeterna-Vie Building, 1182 St. Catherine St. West

or through your bookseller

A deposit copy of this publication is also available
for reference in public libraries across Canada

Price 25 cents Catalogue No. M38-8/9

Price subject to change without notice

ROGER DUHAMEL, F.R.S.C.

Queen's Printer and Controller of Stationery
Ottawa, Canada

1966

TABLES
CONTENTS

Mines Branch Reprint Series RS 9

No.	Page	Page
1.	Comparison of Time Periods Obtained from Oscillation	13
2.	Variation of Viscosity with Temperature	15
3.	Variation of Measured Height in Vertical Tubes with	17
	Variation of Contact Angles	17
	by	
	H. R. Thresh**	
7.	Oscillational Viscometers	17
8.	Theoretical Considerations	17
	Absolute Measurements by the Oscillational Method	17
2.	Variation of Viscosity with Temperature	17
	(a) Spherical Boundary Conditions	17
	(b) Cylindrical Boundary Conditions	17
	ABSTRACT	
	Methods of measuring viscosity are appraised	
	for their suitability to liquid metals at elevated tem-	
	peratures. Selected methods are examined for their	
	potential sources of error, and means are dis-	
	cussed for eliminating, minimizing or correcting	
	for error.	
4.	Pure Liquid	25
5.	Meniscus	25
6.	End Correction	25
	Calibration Methods	25
7.	Experimental Arrangements	25
	Five Different Types	25
8.	The Oscillating Viscometer	25
	Theoretical Aspects	25
9.	Experimental Arrangements	25
10.	References	25
	Figures 1-10	25

*Paper presented at ASM Symposium on Structure and Properties of Liquid Metals, ASM Metals Congress, New York, October 1962; publ. Trans. ASM 55(3), 790-818 (1962).
 **Senior Scientific Officer, Physical Metallurgy Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada.

CONTENTS

	<u>Page</u>
Abstract	i
Introduction	1
Definition of Viscosity	2
General Experimental Procedures	3
Oscillational Viscometers	7
Theoretical Considerations	8
Absolute Measurements by the Oscillational Method	9
(a) Spherical Boundary Conditions	9
(b) Cylindrical Boundary Conditions	17
Calibration Methods	26
Experimental Arrangements	29
Capillary Viscometers	34
Theoretical Considerations	35
1) Kinetic Energy Correction	35
2) End Correction	36
Calibration Methods	37
Experimental Arrangements	37
Rotational Viscometers	42
Theoretical Aspects	42
Experimental Arrangements	43
References	45-49
Figures 1-10	50-59

TABLES

<u>No.</u>		<u>Page</u>
1.	Comparison of Time Periods Obtained from Oscillation Viscometer	13
2.	Variation of Time Period with Liquids of Varying Density	21
3.	Variation of Meniscus Height in Various Liquids with Variation in Contact Angle	25

FIGURES

1.	Variation of Logarithmic Decrement, Time Period and Temperature with Time Through Melting and Freezing Cycles	50
2.	Variation of Logarithmic Decrements with Temperature, Showing Abnormal Effects near the Freezing Point	51
3.	The Variation of Logarithmic Decrement with Temperature for Pure Liquid Tin, Showing the Influence of Contamination .	52
4.	Effect of Oxide Contamination on Liquid Pure Aluminum . . .	53
5.	Variation of Error, Arising in Viscosity Data due to Meniscus Effects, with Vessel Dimensions	54
6.	Calibration Curve for an Oscillating Cylindrical Crucible, Showing the Variation of the Kinematic Viscosity (η/ρ) with δ/ρ	55
7.	Logarithmic Decrement Varying with Temperature, for Five Different Samples of Pure Zinc	56
8.	The Oscillating Viscometer Employing a Cylindrical Vessel, as Used at the Mines Branch	57
9.	Capillary Viscometer	58
10.	Capillary Viscometer Employing a Closed System	59

INTRODUCTION

To the layman, the nature of liquids is readily characterized by whether a liquid is wetting or non-adhering, light or heavy, "thick" or "thin". These are, of course, extremes of state where the obvious is apparent. However, twofold variation in many liquid properties will often pass unobserved.

In spite of many outstanding contributions, the theory of the liquid state has, so far, defied advancement to the point where liquid properties such as viscosity may be predicted from interactions at the atomic level. A large amount of viscosity data exists for many of the common organic and inorganic liquids, but these do not lend themselves to studies relating atomic species and viscous flow. In this respect, the relatively simple structure of liquid metals appears most suitable.

Established physico-chemical methods in the field of viscometry are capable of yielding precision data for ordinary liquids. The extension of these techniques to liquid metals at elevated temperatures introduces special difficulties which, in general, have severely limited the accuracy of the results obtained. Much of the present confusion and disagreement arising in this field originates from the misapplication of theory and the use of unsuitable procedures in experimental work.

Consequently, on the basis of several years of experimentation at the Mines Branch, a critical appraisal of theory and method has been attempted to place in a correct perspective the major problems associated with accuracy and reproducibility of viscosity measurement.

DEFINITION OF VISCOSITY

From the hydrodynamic standpoint, the motion of an ideal fluid recognizes no internal constraint. In this sense, all fluids are imperfect -- it was postulated by Newton⁽¹⁾ that resistance to flow within a fluid was proportional to the velocity. Extension of this simple hypothesis to the laminar nature of flow within liquids, where the sliding of one portion of a fluid over another or over a solid interface is considered, leads to the well known proposition that:

"the shearing force F exerted by the fluid per unit area of a plane, parallel to the velocity v , is proportional to the velocity gradient $\frac{dv}{dx}$ measured normal to the plane."

In mathematical terms, this is:

$$F = \eta \frac{dv}{dx}.$$

The constant of proportionality, η , is known as the viscosity coefficient. Unit values of F and $\frac{dv}{dx}$ give the CGS unit of viscosity as $\text{g cm}^{-1} \text{sec}^{-1}$ (known as the poise). This simple hypothesis is the basis of virtually all viscometry; indeed, the numerous methods of experiment, some of which are to be considered here, rely on this definition. One reservation is pertinent to Newton's law: if the velocity gradients induced by motion are of such magnitude that a critical point is reached, laminar flow gives way to a turbulent state whereby the definition of viscosity is no longer true. This aspect will not receive detailed consideration in this paper, but should be borne in mind when reviewing the experimental methods behind some published results.

GENERAL EXPERIMENTAL PROCEDURES

Many suspicions held by some early workers, regarding the validity and reproducibility of liquid metal viscometry, were gradually dispelled as the approach to experiment became more precise. For a large number of liquids, where the viscosity is confined to the fractional poise range, an exponential relationship is found to exist between the viscosity and the temperature of experiment. Liquid metals might be expected to behave in a similar manner, owing to their relatively simple atomic structure. In general this is found to be true. However, a number of irregularities have been observed which bear no general comparison with other fluids. Subsequent interpretation of these observations has tended to obscure, and indeed contradict, some established ideas of metallic liquids. Before proceeding to discuss some aspects of viscosity, it is relevant that these controversial observations be mentioned, especially as their origin may well arise from unfavourable experimental procedures.

A few investigators^(2, 3, 4) have obtained results which show a marked rise in viscosity as the freezing point is approached. This trend is claimed to be indicative of a structural re-arrangement of the liquid prior to solidification. McLaughlin and Ubbelohde⁽⁵⁾, in developing a cluster theory to explain large pre-freezing deviations of viscosity for large complex molecules such as the polyphenyls, indicated that the data of Yao and Kondic⁽²⁾ substantiated their theoretical arguments. Again, Yao⁽⁴⁾ has claimed to have measured similar effects, shown in Figures 1 and 2, which are more pronounced on the heating cycle than on the cooling cycle. From this observation, he suggests that reference viscosity data, usually implied at the freezing point, should now be quoted at 50 centigrade degrees of superheat.

As will be explained in detail later, it is believed that many of these conclusions are not justified, in that they arise from insufficiently accurate techniques, misinterpretation of data, and an unsound theoretical background. A common error has been the use of a calibrational method

taking as the viscosity standard a liquid metal whose viscosity is not adequately known. It is not surprising, under these circumstances, that good agreement is reached between authors when both have used the same data for standardization, but this does not confirm the validity of such results, neither does it prevent incorrect conclusions. In view of these irregularities, the need for greater accuracy in experiments is very apparent.

Experimentally, the magnitude of viscous constraints within a liquid can only be measured in a dynamic system, where a solid interface is essential in creating a controlled velocity gradient. Of the many methods available, the following cases are considered worthy of attention in the liquid metal field:

- 1) Fixed interface, such as the bore of a narrow tube: capillary method, where energy is supplied to the liquid through an auxiliary medium, usually by gas pressure or its own hydrostatic pressure.
- 2) Moving interface of constant velocity: rotational method, where energy is transferred to the interface throughout the experimental cycle.
- 3) Moving interface of variable velocity: oscillational method, where the momentum gained by the interface through an initial transfer of energy is gradually dissipated by the liquid damping.

Many of the experimental difficulties of viscometry are common to the above-mentioned methods, and these will be reviewed before proceeding to more specialized details.

It is important to consider whether a given metallic liquid will be inert, will undergo contamination by solution of a second element (either from the sample container or from the gaseous media above the sample), or will form a separate stable phase, which in general will float on the surface

of the liquid. Where the latter exists, the solubility of the foreign element in the liquid is usually small. In practice, there should be no contaminants present. However, even the best technique may only hold these effects to a minimum level.

A foreign layer floating on the surface assumes a varying degree of importance, depending on the method. If the moving interface is immersed within the liquid, giving rise to an exterior connecting link emerging through the free surface, as in some arrangements of the torsional and rotational methods, interference with the suspended system does arise where such contaminating layers are present⁽⁶⁾. On the other hand, the open crucible used with the oscillating method is not subject to the same consideration, provided the film does not become coherent to the extent of behaving like an additional surface. Hopkins and Toye⁽⁷⁾ claimed to have used a powdered carbon layer upon molten zinc without increasing the liquid damping.

The influence of constitutional changes by direct solution is more difficult to estimate. In general, small additions of a solute to the pure liquid have been considered to influence the viscosity to a degree not detectable within the accuracy of a good technique. The work of Toye and Jones⁽⁸⁾ would appear to modify this view to the extent that if smaller additions of solute rapidly introduce an invariant point such as a eutectic, the viscosity may change extensively.

All liquid metals demonstrate a high chemical affinity for many of the electronegative elements, especially oxygen. Good vacuum techniques should be employed in the design of liquid metal viscometers intended for serious work. Simple gas purging methods are definitely not adequate in dealing with the problem of desorption during the melting cycle. Where the oxide is thermodynamically very stable, the equilibrium partial pressure of oxygen at which the oxide becomes unstable requires the use of extreme vacuum techniques to reduce the residual oxygen pressure of the system to a safe level. For liquid aluminum⁽⁶⁾ it was never found possible to obtain a completely oxide-free surface on a vacuum-melted ingot.

Liquid metals possessing appreciable vapour pressures necessitate a gas atmosphere. Hydrogen or the inert gases are usually employed for this purpose. Fractional contaminants such as oxygen and oxygen-bearing compound gases must be removed by the usual methods⁽⁹⁾. Some measure of the protection enjoyed in a given apparatus can be judged from the appearance of the frozen sample.

As previously mentioned, viscosity is very temperature dependent. The viscosity of liquid zinc is 0.0377 poise at 432°C compared with 0.0293 poise at 510°C. Thus, whatever design the hot zone takes, thermal gradient verification will be necessary to determine the amount of control and length of zone possible. The most accurate form of temperature control is obtained by the thermostatically controlled liquid bath. The use of silicone fluids and binary salt mixtures as heat transfer media permits a control of better than 0.5 centigrade degree up to 500°C. However, the use of such baths depends on the method selected and on other design features of the apparatus.

The convenience and flexibility of electric heating are not without their difficulty. Toroidally-wound heaters require individual control of the power applied to separate portions of the resistor, to manipulate the thermal gradient over a range of temperature. A non-inductive winding must be considered for the torsion method, to prevent magnetic effect supplementing the liquid decrement. Low-resistance heaters employing high current are always associated with magnetic damping problems. Up to 1000°C a careful technique should realize a relative control, during measurement, of better than 0.25 centigrade degree and the absolute temperature should be known to within 2 centigrade degrees.

Finally, the questions of density and metal purity deserve attention. Many viscosity formulae involve the liquid density. This means that in measuring the viscosity to an accuracy of 1% by the oscillating cylinder method, the liquid density should be known to better than 0.2%, taking into account the errors that arise in other variables. Accurate density values

are often not available for pure metals in the literature, and the uncritical acceptance of inaccurate density values has been a source of error in viscosity determinations in the past.

The problem of metal purity has virtually disappeared, in that 99.999% weight per cent material can now be obtained for a large number of metals. Many measurements prior to the last war were carried out on 99.5% material, and even in recent times supposedly pure metal data have been reported without quoting the purity levels.

OSCILLATIONAL VISCOMETERS

In the high-temperature field of viscosity the oscillational method is probably the most important. Its extensive use, compared with other methods, arises from the simplicity of the general features of the apparatus, facilitating the use of vacuum techniques for reducing contamination problems to the lowest level. Depending on the variations of this method selected, it is possible to operate experimentally with a bulk sample of the order of 30 cc. Consequently, a thermal zone, which ideally should be free from temperature gradients, may be restricted to a height of some 7.5 cm and a diameter of 5 cm, which is an attractive design feature.

Historically, oscillational viscometers found their origins in the early work of such investigators as Meyer⁽¹⁰⁾ and Maxwell⁽¹¹⁾, and accompanied the development of capillary viscometry of this era. However, it was soon apparent that the theory of the torsional apparatus was complex, severely curtailing its further development. Of the many early attempts to analyze the theoretical considerations involved, that of Verschaffelt⁽¹²⁾ represents a most significant contribution to advancing the theory. Founded on Verschaffelt's work⁽¹²⁾, the careful and precise experiments of Andrade and his co-workers^(13, 14) clearly demonstrated the ability of the oscillational viscometer to realize results accurate to 1% for the case of a spherical container.

To overcome the practical disadvantage of spherical vessels in loading the solid samples, Hopkins and Toye⁽⁷⁾ analyzed the case of a torsional cylindrical crucible possessing a free liquid surface. The loss of one degree of symmetry, compared with a sphere, was found to increase the complexity of the solution whereby the final working formulae became tedious and cumbersome. Recently, Roscoe⁽¹⁵⁾ has made significant improvements in the theoretical analyses of the above authors. By employing the theory of complex variables a more direct solution has been derived, free from fractional errors originating from approximations made to produce a working formula.

Theoretical Considerations

Irrespective of the type of pendulum employed, the approach to the theory of the method remains identical. If a given symmetrical torsion system of moment of inertia I is permitted to oscillate about the vertical axis of suspension, the resultant motion will be simple harmonic, provided the maximum value of the angular displacement α in time t is not excessive. However, if a damping restraint is applied to this system in the form of viscous forces developed within a moving liquid, the usual differential equation governing harmonic motion will become:

$$I \frac{d^2 \alpha}{dt^2} + L \frac{d\alpha}{dt} + G\alpha = 0, \quad \dots 1)$$

where G is the restoring couple acting on the system. The damping influence must be rational to the extent of modifying the motion so that it remains harmonic. Inasmuch as the viscosity of liquid metals lies within a relatively narrow range, namely 0.005 poise to 0.1 poise, all liquid metals possess a sufficiently restricted viscosity to fulfill this criterion. Experimentally, this should receive attention and should be verified where a good technique is required.

A solution given by the differential equation 1) for the case of an oscillating body may be expressed as

$$\alpha = Ae^{-\delta \frac{t}{T}} \cos 2\pi \frac{t}{T}, \quad \dots \quad 2)$$

where T is the time of one complete oscillation and δ is the logarithmic decrement, expressing the decay of the motion.

At this point, the four measurable quantities I , G , δ and T are related to the density ρ and viscosity η , by a procedure which involves the elimination of the variables α and t . The damping factor in equation 1) may be shown to be of the form $L \frac{d\alpha}{dt}$, by considering the couple exerted on the suspended system due to the viscous forces in the liquid. Hence, the value of the complex quantity L depends on the geometrical shape of the pendulum, which may either be immersed in or contain the liquid. A further value of L can be extracted from the equation governing the restoring force of the suspension system. Equating the real and complex parts of these two values permits the viscosity η to be derived by a method of successive approximations. In reviewing the experimental application of the torsional method it is possible to consider the relevant material in two parts. First, the above ideas related to practical viscometry give an absolute approach. Secondly, the simpler approach of utilizing liquids of known fluid properties to establish apparatus parameters permits a calibrational method.

Absolute Measurements by the Oscillational Method

(a) Spherical Boundary Conditions

A full treatment of this method applied to a sphere of radius R oscillating in a fluid, which experimentally may be considered infinite, has been given by Verschaffelt⁽¹²⁾. Viscous forces in the liquid were attributed to hypothetical spherical shells of liquid moving with the same time period T and decrement δ as the rigid pendulum. However, the maximum angular

displacement and relative movement of each shell were not regarded as constant, whereby the zone of influence due to the moving liquid terminates at a practical distance from the surface of the sphere.

Placing the relevant quantities in Verschaffelt's final expression, the following relation is obtained:

$$(2 + p)\eta + R\left(\frac{\rho\pi}{T}\right)^{\frac{1}{2}}\eta^{\frac{1}{2}} - \frac{3I\Delta}{4R^3T}\left(\frac{T^2}{T_0^2} + 1\right) = 0 \quad \dots\dots 3)$$

$$\text{where } \Delta = \frac{\delta}{2\pi}, \quad p = \frac{gR + 1}{(gR + 1)^2 + h^2R^2},$$

$$\text{the quantity } g = \left(\frac{\rho\pi}{\eta T}\right)^{\frac{1}{2}}\left(1 - \frac{1}{2}\Delta + \frac{1}{8}\Delta^2 + \dots\dots\right), \quad \dots\dots 4)$$

$$\text{and } h = \left(\frac{\rho\pi}{\eta T}\right)^{\frac{1}{2}}\left(1 + \frac{1}{2}\Delta + \frac{1}{8}\Delta^2 + \dots\dots\right). \quad \dots\dots 5)$$

The time period, T_0 , is usually defined as the period of oscillation in the absence of liquid damping. However, T_0 measured under these conditions does not experience the buoyancy or load effects of the liquid sample on the suspension system, which exist during the measurement of T . Thus it is, in fact, the time period of the torsional system produced by a hypothetical liquid of the same density as the liquid sample under experiment but void of internal friction properties.

Because of the appreciable magnitude of the densities of liquid metals, the use of the calculated T becomes increasingly important, as indicated by Andrade and Dobbs⁽¹⁴⁾. The solution of the above equation in $\eta^{\frac{1}{2}}$ is not direct, due to the pseudo-quadratic form introduced by the quantity p , which in fact contains η . However, as p is always of the order of 1% of the term $2 + p$ for liquids, an approximate value of η may be used to calculate p , permitting the equation to be solved for $\eta^{\frac{1}{2}}$. This value is

used to recalculate p until the initial value of η agrees with the final value to the required accuracy.

Experimentally, the verification of Verschaffelt's⁽¹²⁾ analysis was confined, except for one determination for water at room temperature, to the viscosity of liquid gases. This was unfortunate in that the cryogenic problems encountered gave rise to large temperature variations and evaporation difficulties, which curtailed the accuracy of the final results.

The work of Verschaffelt attracted little interest in the liquid metal field until the measurements on the viscosity of the alkali metals were initiated by Andrade^(13, 14) and his co-workers. In his original analysis Verschaffelt outlined the conjugate case of a spherical pendulum oscillating in a fluid, i. e., a spherical vessel filled with liquid permitted to oscillate in a damped harmonic form. By considering the Navier-Stokes⁽¹⁶⁾ hydrodynamic equations, Andrade and Chiong⁽¹³⁾ derive the same expression as Verschaffelt⁽¹²⁾. This solution takes the same form as 3), except for some changes of sign, which leads to:

$$\eta = \frac{a^2 R^2 \pi \rho}{4(2-q)^2 T} \left\{ 1 - (1 - \mu)^{\frac{1}{2}} \right\}^2, \quad \dots 6)$$

$$\text{where } \mu = \frac{3(2-q)I\delta}{2\pi a^2 R^5 \rho} \left(\frac{T^2}{T_o^2} + 1 \right), \quad \dots 7)$$

$$a = 1 - \frac{1}{2}\Delta + \frac{1}{8}\Delta^2,$$

$$\text{and } q = \frac{gR - 1}{(gR - 1)^2 + h^2 R^2}.$$

where the solution of η is expressed in the solved quadratic form. The ability of the formula to yield absolute viscosity data was demonstrated by the application of this method to a simple but unique spherical viscometer employing spheres of several sizes for the test fluid, water.

By measuring each of the parameters I , δ , R , T and T_0 to an error of less than 0.1%, viscosity data over the range 2°C to 65°C gave excellent agreement with figures from the International Critical Tables. The degree of uncertainty was reported at less than 1%. It may be noted, however, that T_0 was found by direct observation of the empty oscillating sphere. A simple calculation shows that for a liquid such as water, the error introduced is small.

Chiong⁽¹⁷⁾, employing the same apparatus, extended this technique to the viscosity of sodium and potassium over the range 60°C to 360°C, maintaining the same degree of care and precision.

Andrade and Dobbs⁽¹⁴⁾ returned to this work on the alkali metals, completing determinations on liquid rubidium, cesium and lithium. These experiments realized a further improvement in accuracy where the T_0 condition was satisfied. The origin of equation 6) lies in equating the real parts of two expressions for the damping factor L . If the imaginary parts of L are equated, an alternative expression is obtained from which η may still be obtained. This is given in an approximate form as

$$\eta^{\frac{1}{2}} = \frac{3I(T^2 - T_0^2)}{4T_0^2 R^4 (\pi T \rho)^{\frac{1}{2}}}, \quad \dots\dots 8)$$

which is sufficiently accurate for the calculation of T_0 .

The factor $T - T_0$ for liquid metals is of the order of 0.1, being the difference of two quantities which are measured to within 0.1%. The resulting possible error of 10% does not permit the calculation of η to a reasonable degree of accuracy. However, noting that $T + T_0 \approx 2T$, to a first approximation

$$T_0 = \frac{T}{1 + \frac{2R^4}{3I} \sqrt{\pi \rho \eta T}} \quad \dots\dots 9)$$

It is found, by calculation, that these approximations are justified, as the errors introduced into T_0 are lower than the experimental accuracy of T . Values of η must be selected to within a few per cent, and, in practice, these may be estimated from the experimental logarithmic decrements.

The significance of using the calculated T_0 in preference to T_0 observed, can be adequately shown by figures taken from the work of Thresh⁽⁶⁾, using an oscillating solid sphere surrounded by liquid. In Table 1, the large difference between T_0 observed and T_0 calculated is very apparent. Further, the magnitude of this difference increases when the buoyancy force originates from liquids of higher densities. These remarks are particularly pertinent where a bifilar suspension is used to support the pendulum, but evidence does exist that this type of behaviour can occur to some degree for the case of a single suspension wire.

TABLE 1
Comparison of Time Periods Obtained from
Oscillation Viscometer

	T	T_0 (calculated)	T_0 (observed)
Liquid tin	11.322	11.248	9.556
Liquid cadmium	12.770	12.692	9.556
Liquid lead	13.755	13.657	10.835
Liquid bismuth	13.446	13.373	10.835

In this series of papers, the success of establishing the torsional method has depended on giving the original analysis adequate experimental treatments. Among these may be mentioned the operation of the viscometer in high vacuum to remove frictional effects of a gas atmosphere; prevention of contamination by enclosing the metal in a sealed container; verification of the harmonic nature of the damped oscillations; and the removal of the $(\tan \theta) - \theta$ correction by employing a curved scale, in place of a flat scale,

in measuring the liquid decrement. Recently, measurements have been extended by Culpin⁽¹⁸⁾ to indium, tin, magnesium and calcium, using the same basic technique. Liquid bromine was selected to confirm the operation of the apparatus. Excellent agreement may be observed with early work on bromine, using absolute capillary viscometers.

Due to the work of Roscoe⁽¹⁵⁾, further unique improvements have recently been realized in the working formula for the hollow sphere. By re-arranging the final equations of Andrade and Chiong⁽¹³⁾, the expression for the damping L is retained in the complex form and expressed as a converging series. In extracting the real and imaginary parts of L in this form, it is necessary to consider the fractional terms of the series. A solution by successive approximations is still retained but appears to be of somewhat simpler algebraic form. This is given as:

$$\eta = \frac{\left(\frac{3I\Delta}{2R^4 Z}\right)^2}{\pi\rho T}, \quad \dots 10)$$

$$\text{where } Z = a_0 - \frac{2}{p} + \frac{a_2}{2p^2}; \quad p = \left(\frac{\pi\rho}{\eta T}\right)^{\frac{1}{2}} R; \quad \dots 11)$$

$$a_0 = 1 - \frac{1}{2}\Delta - \frac{3}{8}\Delta^2; \quad a_2 = 1 + \frac{1}{2}\Delta + \frac{1}{8}\Delta^2.$$

The important feature of this equation lies in the absence of T_0 , eliminating the special methods required for its derivation during computation of η . As before, an assumed value of η gives p , hence z , from which a corrected value of η is derived. It is found that only a few iterations for the loop $\eta \rightarrow p \rightarrow Z \rightarrow \eta$ are required to give the final accuracy.

Roscoe and Bainbridge⁽¹⁹⁾ verified this formula by a precision measurement on the viscosity of water at 20°C. The accuracy in the value 1.0025 centipoises was estimated as better than 0.1%, confirming the

figure 1.0019 centipoises obtained by Swindells, Coe and Godfrey⁽²⁰⁾, employing a precision capillary viscometer.

Although this relatively new method offers many advantages to liquid metals, probably the most important limitation with regard to the high-temperature field has been in the fabrication of spherical vessels from suitable refractory materials.

Returning to Verschaffelt's⁽¹²⁾ original approach, this has found little application in the liquid metal field. Polyak and Sergeev⁽²¹⁾ designed an apparatus based on Verschaffelt's formula. Measurements were carried out on aluminum and aluminum alloys which appear to be very high for metals of low density. Most of the inertia of the apparatus comprised that part of the torsion system hanging in the furnace zone, creating a degree of temperature dependence on the moment of inertia.

Serious objections may be put forward regarding inadequate protection of the liquid from contamination. The use of fluxes to prevent or dissolve surface films on the melt cannot be considered a great improvement. The uncertainties created by contaminating surface films, particularly in the case where the torsion pendulum passes through the liquid surface in the form of a small connecting shaft, have been realized from early experiments in this field. In this method, the main experimental variable is always found to be the decrement, δ . Errors introduced into δ by surface films may be reproducible or inconsistent, giving large errors in the final value of η , which to a first approximation varies as $\delta^{\frac{1}{2}}$. In re-examining this problem, Thresh⁽⁶⁾ constructed a torsional viscometer employing a spherical solid pendulum fabricated from standard ball bearings. The essential parts were totally enclosed to permit the operation of the viscometer under high vacuum. Thus, metals of low vapour pressure were melted in the absence of a reactive gas atmosphere or accumulated gases arising from desorption at the container walls during heating. The criterion established for the acceptability of the data obtained was that the liquid sample should possess a clean surface.

This fact was assessed from the solid sample removed from the apparatus at the end of the viscosity determinations.

Part of this work was devoted to relative measurements of the damping, δ , on liquids regarded as free of oxide contamination, followed by experiments on liquids known to be contaminated. In the case of pure tin, a stainless steel bob protected by a thin coating of colloidal graphite was used to determine the liquid damping. Decrement recordings under high vacuum were obtained from liquid tin retaining an appreciable layer of oxide upon the surface by melting under an argon atmosphere of 99.9% purity. A second determination on metal liquified under high vacuum revealed only a small trace of oxide to be present. Figure 3 clearly illustrates that, in the case of liquid tin, the contaminating layer induces an appreciable degree of scatter about the smooth decrement curve of the liquid with a clean surface.

Similar experiments with aluminum were made, using a graphite sphere. The results shown in Figure 4 were, in fact, the difference between melting high-purity aluminum from stock material for the first trial in the viscometer and reprocessing the same ingot after a surface cleaning by scratch brushing. The stock ingot indicated the presence of a thin film of surface oxide, which appeared complete except for the collapsed area of the piped region down the centre. This oxide film was just sufficiently thick to suppress the high reflectivity of the clean metal surface observed in the ingot pipe. The subsequently remelted aluminum indicated the presence of a cleaner surface condition. While not perfect, only isolated areas of oxide could then be observed. At this stage, attempts to improve upon this situation by further remelting proved futile. The values of the decrement obtained demonstrate, again, how the presence of an oxide film can introduce scatter into the final data. An additional feature may be observed, presumably due to the tenacious character of the aluminum oxide film, in that the viscosity of the contaminated liquid is appreciably higher than that given by the cleaner melt. This difference is approximately 8%, signifying how a much thicker film could give rise to completely false data.

(b) Cylindrical Boundary Conditions

The outstanding advantage of the cylinder over the sphere from the practical standpoint has long been recognized. Exploitation of this feature has always been severely curtailed by the complexity of the mathematical aspects of the problem.

One of the first attempts to analyze the case of a hollow cylinder filled with liquid oscillating on a torsion wire was made by Meyer⁽¹⁰⁾. Although a solution was obtained for the condition where the height of the liquid was small compared with the diameter, it is apparent that the final calculations involve a large degree of computation. In a simplified form, the relation can be expressed as:

$$\eta = \frac{1}{\rho T} \left[\frac{216}{R^4 \sqrt{\frac{1}{2}(\pi - \delta)^3 + KHR^3}} \right], \quad \dots\dots 12)$$

where $K = \Sigma f(\eta, \rho, H, T)$.

Mutzel⁽²²⁾ utilized the analysis to measure the viscosity of some aqueous solutions. From his final results, complete verification of this method could not be claimed.

Further theoretical considerations were given to this problem many years later by Okaya and Hasegawa⁽²³⁾, and Okaya⁽²⁴⁾. In considering the oscillations of a closed cylindrical vessel containing a liquid, a concise working formula was not found possible. A somewhat indirect method of checking was employed, in that the measured decrement was compared with that derived from the analysis, using a viscosity value obtained from the literature. Marginal agreement was found, this being of the order of a few per cent.

A further treatment of this problem was attempted by Shvidkovski and others⁽²⁵⁾, seeking the means to determine the viscosity of liquid steels. The basic hydrodynamic equations were considered in conjunction with the

Newtonian viscosity influencing the damping on the walls of the container. These were compared with the relation governing the action of a damped harmonic system. However, the criterion of bringing the working solution into a manageable form compelled the use of approximations, where

$$\eta = \rho \delta T^3 A \left(\frac{B}{\sigma^2} \right), \quad \dots\dots 13)$$

such that

$$A = \left[\frac{I}{2MR T^2 (\pi)^{\frac{1}{2}}} \right]$$

and

$$B = \left[1 + \frac{T_o^2}{T^2} - \frac{2\delta_o T_o}{\delta T} \right]^2;$$

where

$$\sigma = 1 - \frac{\delta}{4\pi} + \left(\frac{T\eta}{\pi\rho} \right) \frac{1}{2R} + \frac{2}{HR} \sum \frac{1}{J_n^2}, \text{ and}$$

j_1, j_2 are the positive roots of $J_1(Z) = 0$; M the mass of liquid within the vessel.

The mathematical assumptions employed stipulate that the value of T must be small, i. e., experimentally not greater than four seconds. This, in turn, brings about greater maximum velocities within the shearing liquid, leaving some doubt as to whether a damped harmonic system is maintained. Further, their final working equation is subject to the T_o requirement and no alternative procedure is available for the calculation of this figure. The calibre of the experimental work utilizing this equation is such that this method cannot be verified as being absolute.

A most significant contribution to the evaluation of absolute viscometry by this method was put forward by Hopkins and Toye⁽⁷⁾. Proceeding in a manner similar to that of Andrade and Chiong⁽¹³⁾, the Navier-Stokes⁽¹⁶⁾ equations are considered again to establish the equation of motion of a particle of liquid in the moving fluid layer. The damping

factor L experienced by the crucible, as derived by the above authors, is more conveniently expressed as that given recently by Roscoe⁽¹⁵⁾,

$$\text{where } L = 2\pi \left\{ bR^3 H \frac{J_2(ibR)}{iJ_2(ibR)} + 2b^4 R^7 \sum_{n=1}^{\infty} \frac{\tan h \left[(j_n^2 + b^2 R^2)^{\frac{1}{2}} \frac{H}{R} \right]}{j_n^2 (j_n^2 + b^2 R^2)^{\frac{3}{2}}} \right\} \dots 14)$$

Hence, R is the radius of the crucible, H is the height of fluid contained in the vessel. $J_1(ibR)$ and $J_2(ibR)$ define Bessel functions, of the first type of orders one and two, and j_1, \dots, j_n are given by the positive roots of $J_1(ibR) = 0$. The notation used by Hopkins and Toye denotes

$$m = ib; a = R \text{ and } c = H,$$

where b is still given by equations 4) and 5).

The two factors comprising the quantity L arise from the damping on the crucible wall and bottom surface. The greater the ratio $\frac{H}{R}$, the larger is the contribution of the first factor to L .

From the above form, Hopkins and Toye⁽⁷⁾ proceed to extract the real parts of both factors by adopting a series of approximations; the most serious difficulty arises in defining the quantity μ from the complex number \underline{m} , where the real and imaginary parts of \underline{m} are considered to be of equal value. This is identical to neglecting the series term in equations 4) and 5), whereby equations 4) and 5) assume the same value.

The final working solution is given as

$$\left[2\pi ca^2 - K(\mu) \right] \eta - \pi ca^2 \sqrt{\eta} \cdot \mu \cdot \phi(\mu) \eta^{\frac{1}{2}} + \frac{16}{2T} \left(\frac{T^2}{T_0^2} + 1 \right) = 0. \quad \dots 15)$$

The last term has been reduced by a factor of two to keep the usual definition of δ consistent with the time period of one oscillation T , where $\beta = \frac{\delta}{T}$. In equation 15), the quantity $K(\mu)$ arises from the term governing the liquid damping on the bottom surface. Here, the hyperbolic function can be taken as unity without introducing significant error, and the real part of the denominator can be extracted independently of the radius, a , permitting its tabulation as a function of μ . Similarly, the damping from the wall of the vessel can be computed as $\phi(\mu)$. These two functions, $\frac{K(\mu)}{a^3}$ and $\phi(\mu)$, are reported by Thomas⁽⁸⁾ in an appendix to a recent paper by Toye and Jones⁽⁸⁾. Again, the form of equation 15) is not completely quadratic in $\eta^{\frac{1}{2}}$, because of the extra term in $\eta^{\frac{1}{2}}$ occurring in the middle factor. Hence, an assumed value of η permits an initial value of μ to be computed. $K(\mu)$ and $\phi(\mu)$ are now observed, from which $\eta^{\frac{1}{2}}$ may be found. This procedure is repeated until η is obtained to the required accuracy.

This analysis is readily extended to the case of a closed cylinder full of a given liquid. Such a cylinder can be regarded as two open cylinders, one inverted upon the other, where the height is now $\frac{H}{2}$. This, in fact, requires the real part of L to be multiplied by a factor of 2. Algebraically, the term $K(\mu)$ is increased twofold in equation 15).

The unique improvements realized by Roscoe⁽¹⁵⁾ for the case of the oscillating spherical vessel were extended, in the same paper, to the hollow cylindrical vessel. By considering equation 14), it was still found possible to express both factors comprising L in the form of a converging power series of bR . Two equations result from this approach, the most important being

$$\eta = \frac{\left(\frac{I \delta}{\pi R^3 H Z} \right)^2}{\pi \rho T} \quad \dots\dots 16)$$

$$\text{where } Z = \left(\left(1 + \frac{1}{4} \frac{R}{H} \right) a_o - \left(\frac{3}{2} + \frac{4R}{\pi H} \right) \frac{1}{p} + \left(\frac{3}{8} + \frac{9}{4} \frac{R}{H} \right) \frac{a_2}{2p} \right)$$

and p , a_o and a_2 take the same values given for the sphere. For a given crucible, the ratio $\frac{R}{H}$ can be regarded as constant, simplifying the form of Z . This equation, though solved by successive approximations, may be observed not to contain T_o . This feature alone can be considered a major improvement from the experimental standpoint. The T_o condition, outlined in the case of the sphere, is still applicable to the cylindrical vessel. Ideally, the restoring force of a single torsion wire is dependent only on its length, diameter, inertia and rigidity, and not on the suspended mass. Though the rigidity is known to be temperature sensitive, the results of Hopkins and Toyé⁽⁷⁾ indicate that the suspended mass of liquid influences the time period. For example, the following table lists their variation of time period with liquids of varying density:

TABLE 2
Variation of Time Period with Liquids of Varying Density
 (Hopkins and Toyé)

Crucible Content	Density (g/cm ³)	Time Period (sec)
Empty	-	19.81
Water	0.997	19.86
Zinc	6.494	20.26

By calculation, the ratio $\frac{T}{T_o^c}$ is found to be of the order of 1.005,

T_o observed and T_o calculated being denoted by T_o^o and T_o^c . This figure is based on determinations recently made at the Mines Branch⁽²⁶⁾, employing a closed cylindrical crucible as the oscillating vessel. Data obtained on pure zinc, using Roscoe's⁽¹⁵⁾ analysis, permit the measured value of T to be compared with a calculated value of T_o using Roscoe's equation 20. In the case of zinc, from Table 2, $\frac{T}{T_o^o} = 1.023$, which is some 1.8% above the calculated value (1.005). Calculation shows that by increasing the quantity $\frac{T}{T_o}$ from 1.005 to 1.023 in the formula presented by Hopkins and Toye⁽⁷⁾, the viscosity is increased by some 3.5%. In fact, these observations suggest that adopting $\frac{T}{T_o}$ as unity would introduce less error than employing T_o^o . Roscoe's new approach provides the means for overcoming this type of appreciable error, though in theory an expression to derive T_o^c is possible by equating the imaginary parts of L in Hopkins and Toye's original paper. At this point, it is relevant to briefly mention these affects related to the bifilar suspension wire. As in the case of a solid sphere, the presence of liquid metals introduces large and unrealistic differences between T_o^o and T_o^c . Quoting from recent work by Thresh⁽²⁶⁾ on zinc, these quantities are found to be 15.164 seconds and 12.946 seconds, respectively.

Before leaving these various procedures for computing viscosity data for the cylindrical crucible, some mention of the ability of one method to yield comparative data with another is very relevant. For example, is it possible to compare the results yielded by the Andrade and Chiong⁽¹³⁾ approach with those of Roscoe⁽¹⁵⁾, for the spherical vessel for a given set of data? Fortunately, Andrade and Chiong have quoted a full set of data, which is more than adequate for verification purposes. On recalculating the viscosity of water, where T_o^c has been found and utilized instead of T_o^o , and removing a small fractional error in η , agreement to better than 1 part in 1000 is

obtained between the respective methods. Similarly, data on zinc have been employed to compare the formula of Hopkins and Toye⁽⁷⁾ to the working solution of Roscoe, with the proviso that T_o^c can be computed from Roscoe's equation 20. The degree of concordance is still observed to be commendable at 1 part in 200. It is interesting to observe this agreement, as Hopkins and Toye's formula was never verified against a reliable liquid standard.

Where experimental techniques involve a free liquid surface, further uncertainties are introduced in the derivation of the viscosity. Theory demands that the surface be and remain horizontally planar during the fluid motion. In practice, several possibilities may exist. If one considers the relatively large free surface area associated with a liquid in the open crucible, some form of meniscus effect may be expected to prevail where the liquid touches the crucible wall. Depending on the degree of contamination present on the liquid surface, a non-wetting behaviour will tend to persist. In crucibles of appreciable size ($R \approx 2.5$ cm), this effect will still extend to the centre of the vessel, giving a convex surface. This creates a measure of uncertainty in the value of H , which is usually computed from the mass of the initial charge and the density at the experimental temperature. Consequently, where the value of the contact angle between the liquid metal and the vessel, measured within the liquid, is greater than 90° , the computed height of liquid, H_c , will always be greater than the height of liquid, H_m , in contact with the wall of the crucible. Subsequent viscosity values based on H_c will be somewhat lower than values derived from H_m . Recently, Armbruster, Azon and Bastien⁽²⁷⁾ have examined some experimental aspects of this error by conducting duplicate viscosity measurements with the open cylindrical vessel at given experimental conditions for two values of H . This phenomenon was expressed as a fractional quantity, h , by which H_c was modified in the final calculation of η . Figure 5 shows how the fallacious shift in the viscosity varies as the ratio H_c/R of the liquid is increased.

From this graph, the correction factor h may be derived, modifying Schvidkovski's⁽²⁵⁾ original expression as follows:

$$\eta = \frac{\rho}{\pi} \left[\frac{I}{MR(1 + \frac{h}{H})} \right]^2 \frac{\delta - \left(\frac{T}{T_0}\right) \delta_0}{T \sigma^2} \dots\dots\dots 17)$$

where $\sigma = A - \frac{3\delta}{4\pi} \left[1 - \frac{1}{4} \left(\frac{\delta}{2\pi} \right) \right] + \frac{2nR}{H+h} \left[B - C \frac{\delta}{2\pi} \left\{ 1 - \frac{3}{64} \left(\frac{\delta}{2\pi} \right) \right\} \right]$,

such that A, B, and C are fractional coefficients and n the number of horizontal surfaces undergoing viscous damping.

The extent of the meniscus correction would be expected to follow, to a first approximation, the height to which the liquid rises under the curved free surface. Some estimate of the meniscus height or depression may be obtained from tables derived by Porter⁽²⁸⁾ from the work of Bashforth and Adams⁽²⁹⁾ and Rayleigh⁽³⁰⁾. In Table 3 some approximate values are calculated showing the variation of the meniscus height for various liquids with respect to the contact angle for a crucible of radius 1.5 cm.

TABLE 3
Variation of Meniscus Height in Various Liquids
with Variation in Contact Angle

Capillary Constant $\left(\sqrt{\frac{2\gamma}{\rho g}}\right)$	Benzene	Carbon Tetrachloride	Water	Mercury
Contact Angle	6.72	3.43	14.88	6.97
0°	4.1	2.8	5.9	4.1
20°	3.2	2.2	4.7	3.2
40°	2.3	1.6	3.4	2.4

Thus, for a given contact angle and tube diameter, the height of the meniscus is essentially controlled by the capillary constant, which in turn depends on the ratio of the surface tension, γ , to the density, ρ , of the fluid. This indicates that, for certain metals such as aluminum where $\frac{\gamma}{\rho} = 217$, the meniscus rise under certain conditions could be appreciable.

Some correlation between Table 3 and Figure 5 may be observed, in that water gives the highest meniscus rise and the largest positive deviation in the viscosity of the four liquids. However, the experimental observations on benzene and carbon tetrachloride appear to be much smaller than anticipated. Practically, the contact angle remains the elusive variable. Particularly for liquid metals, the contact angle varies for different container materials, and depends on the surrounding chemical conditions and the presence of foreign material on the liquid surface. It is highly probable, however, that in most liquid metal viscosity work, where this correction should have been applied, a sufficient degree of contamination has been present to suppress the meniscus to the point where the correction is insignificant.

Associated with the above considerations, the possibility of capillary rise effects exists, at least in theory. The computations of Richards and Carver⁽³¹⁾ clearly show that for crucible diameters of the order of 3 cm for water, the capillary rise is about 0.01 cm. For the ratio $H/R = 3$, this increase would introduce an error of greater than one part in a hundred in η .

Probably the simplest procedure to define the value of H in a more precise manner lies in the use of a closed cylindrical vessel. Previous objections from the theoretical aspect now appear to have been removed, leaving only the problem of the precision engineering of ceramic vessels where materials such as graphite cannot be used.

Calibration Methods

A large part of the viscosity data assembled in the liquid metal field has been measured by calibrational procedures applied to the torsion method. This trend has arisen from the fact that the relatively simple experimental approach is counterbalanced by severe theoretical complexities. The concept of calibration appears to have been applied in three ways:

1. Calibration of arbitrary shaped pendulums with organic liquids to derive a completely empirical relationship.
2. Calibration of approximate or simplified formulae originating from some form of theoretical first principles.
3. Calibration of a working equation, which is exact in its first principles and subsequent derivation.

These three ways are now considered in some detail, together with relevant types and shapes of torsion pendulums:

1. This approach would appear rather unsatisfactory in that all geometrical factors relating to the pendulum are disregarded and a measure of postulation is employed to recognize the significant experimental variables. Stott⁽³²⁾ attempted to find the viscosity of liquid tin by proceeding

in this way, using a thin bevelled disc of alumina as the pendulum. He assumed that the quantities δ , η , T , and I were relevant and applied the theory of dimensions to deduce possible relationships. Although his calibration curve was regular and continuous, agreement with other published data on tin was not found. On the other hand, recent experiments by Cavalier⁽³³⁾ have realized a measure of success by calibrating a small open crucible with a series of selected organic liquids of known physical properties. Although the properties of these liquids are known accurately, the density and viscosity of liquid metals are such that little or no overlap can be found on the calibration curve. As is seen from Figure 6, Cavalier found that the simple relationship

$$\eta = \frac{\rho \alpha_1}{1 - \frac{\delta}{\rho}} \quad \dots\dots\dots 18)$$

was possible, where only one calibration constant, α_1 , had to be derived. Some degree of uncertainty is noted on the calibration curve to which meniscus effects and changing contact angles due to slight evaporation must have contributed. Perhaps the greatest difficulty in such simplified procedures lies in detecting unforeseen variations, especially those due to temperature (since most calibration is carried out at room temperature), and in predicting the effect of these on the accuracy of the results.

2. A large amount of experimental effort has centred around the approach of calibration, using simple formulae. Particularly in Germany this technique has been favoured by Yao⁽⁴⁾, Koeniger and Sahm⁽³⁴⁾, Roeder and Morawietz⁽³⁵⁾, and Gebhardt⁽³⁶⁾ and his co-workers Theilmann and Wimmer⁽³⁷⁾.

Whatever criticism is levelled at calibrational methods, especially with regard to their approximate nature, further injustice is often realized by a relaxation in the approach to the experiment, it being widely assumed that the calibration with a known liquid will compensate for all errors of theory or technique. In the first place, the formula adopted for experiment

should possess a hydrodynamic background. The more fundamental this is, the greater is the complexity of the working solution. For example, Meyer's^(10, 37) solution for the hollow cylinder will involve finding three calibration constants, whereas Gebhardt's⁽³⁶⁾ formula, based on Knappwost's⁽³⁸⁾ considerations, requires only one. Several liquids should be used to calibrate at room temperature, due regard being given to purity. If three constants are involved, seven or eight measurements of δ with liquids of known η and ρ are not excessive. The method of least squares should be used to fit the experimental constants to the data relating the physical properties of the liquids. The question has been raised as to whether it is hydrodynamically correct to calibrate a system for use with liquid metals by employing liquids possessing appreciably different properties and structure. Stott⁽³²⁾ came to the conclusion that this technique is not valid. This issue is further obscured by the lack of confidence in many of the accepted values of η and ρ existing for liquid metals today. Further, it is common practice to calibrate using organic or inorganic fluids in combination with liquid metal data. Unfortunately, one cannot place the accuracy of liquid metal data, quoted in the International Critical Tables, on the same level as the data for other fluids which have been subjected to very rigorous and extensive experimentation and in fact have become well established. A number of investigators, among them Yao and Kondic⁽²⁾, Fisher and Phillips⁽³⁹⁾, Gebhardt et al.⁽³⁶⁾, have calibrated with pure metals such as tin or zinc, using Sauerwald's⁽⁴⁰⁾ data; they have proceeded to measure the damping of these liquids over a temperature range and they claim to have derived pertinent viscosity data for such metals. It is not surprising, therefore, that many sets of data show agreement with the rather restricted values of Sauerwald. The most suitable approach appears to lie in testing the calibration with a fluid at room temperature, followed by tests on mercury to verify the application of the technique to other liquid metals. At the present time, mercury can be regarded as the most reliable liquid metal standard where viscosity and density are concerned.

In conclusion, whatever formula is used and the acceptability of its absolute error recognized, the experimental procedure should be adequate to the extent that the apparatus should yield reproducible results on a given liquid.

3. Though many of the comments related to the above section are still pertinent, a fundamentally correct formula is eminently desirable where calibration is anticipated. Hopkins and Toye⁽⁷⁾, in their absolute measurements on pure zinc, demonstrated that agreement could be achieved between the absolute results and the data derived from calibrating the same crucible. For this purpose, their final equation becomes

$$\delta \left(\frac{T^2}{T_o^2} + 1 \right) = A\eta T + B(\rho\eta T)^{\frac{1}{2}} + C \left[\frac{(\eta T)^3}{\rho} \right]^{\frac{1}{2}}, \quad \dots 19)$$

where A, B, and C are found by observing δ and T on given liquids. Subsequent data, when inserted in this equation, give rise to a cubic equation in $\frac{1}{\eta^2}$.

Experimental Arrangements

Many liquid metal measurements have been reported using some variation of the oscillational method. A recent review by Bockris, White and MacKenzie⁽⁵⁶⁾ has listed in detail the geometry of apparatus layout. Consequently, the present discussion is limited to design and correction factors.

The choice of the parameters I, T and f(R, H), where f(R, H) denotes inner vessel dimensions, should result from consideration of the working viscosity formula together with the equation governing the time period of the suspension system. If the $\frac{\text{inertia}}{\text{mass}}$ ratio of a torsion system is held constant for a given crucible, the increase of I will suppress the corresponding value of δ . Thus a balance must be struck between the damping

due to the fluid and the inertia of the suspension system. δ must be large enough to permit accurate measurement, but not so large as to suppress the number of oscillations taking place during recording. The magnitude of T can be adjusted by manipulating the dimensions of the torsion wire. The final choice of wire diameter depends on the largest mass, including sample, which the system will experience. This factor is important because of the necessary correction for internal friction in the wire, which is found to be dependent on the wire diameter. Hence, δ should be of the order of 0.01 to 0.07, being measured over at least 50 oscillations with the motion harmonically damped. With I about $2,000 \text{ g/cm}^2$, the total inertia will not be subjected to excessive corrections arising from dimensional changes in that portion of the system within the thermal zone. To maintain reasonable accuracy in measurement, the minimum value of T appears to be about 8 seconds. Values of the order of 2 seconds have been used^(4, 21, 25), but these appear questionable because of the maximum shear velocities in the liquid approaching the onset of aperiodic motion.

Observations leading to the calculation of δ involve obtaining the extremities of a consecutive number of amplitudes of motion. The usual lamp and scale technique gives considerable error during actual measurement, where the position of an image momentarily at rest must be assessed by eye. If the mirror-to-scale distance is increased to improve the accuracy of visual observation and reduce the $(\tan \phi) - \phi$ correction for a flat scale, the number of observations now possible is curtailed. Recording photographically, together with an engine-engraved curved scale⁽¹³⁾, appears to be the most convenient method. Telescopic techniques are comparable with regard to accuracy but need longer time periods, i. e. $T \geq 20$ seconds, to reduce excessive eye fatigue. The evaluation of I is usually carried out by designing the suspension unit to include a known inertia, which in some arrangements can be varied. Andrade and Chiong⁽¹³⁾ successfully employed two identical cylindrical inertial masses, which could be positioned along radial arms by the use of special gauges. Inertia rings^(12, 19, 26), though less flexible, do not

call for delicate adjustment. Roscoe⁽¹⁹⁾ has demonstrated that only one ring is necessary in place of the usual three. Here, two decrements are obtained on a given liquid at a fixed temperature, one with and one without the inertia ring. From the relevant viscosity equation, the value of the unknown inertia is calculated.

Metal shot has been used by Hopkins and Toye⁽⁷⁾ where the change of T with a known increase of I is related to the time period equation of the suspension. In bifilar torsion wires this method is not valid, as all changes in inertia must be made with the mass constant.

The recorded logarithmic decrement arises from the total frictional effects exerted on the suspension system. From design aspects, the primary damping due to the liquid should comprise the largest portion of the total decrement. Extraneous frictional effects are found to arise from the following causes:

- 1) internal friction in the torsion wire,
- 2) damping due to the gas surrounding the oscillating system, and
- 3) damping caused by magnetic effects arising from induction in the furnace windings.

Standardization of a given apparatus should always include a quantitative measure of auxiliary friction corrections. It is never possible to eliminate these effects, even by superior design, and the exact value of 1) and 3) cannot be separated from that of the liquid damping. In the past there has been a tendency to accept the wire decrement value, irrespective of its magnitude, rather than to suppress it to the smallest level possible. Andrade and Dobbs⁽¹⁴⁾ lowered the residual decrement of 0.004-in. diameter tungsten wire to the order of 600×10^{-6} by heat treatment under the protection of hydrogen. A value of 200×10^{-6} , amounting to correction of less than 2% in η , was obtained by Thresh⁽⁶⁾, using a filament which had been vacuum heat treated under tension. At this order of magnitude the dependence of the wire decrement on the time period cannot give rise to

measurable uncertainty, inasmuch as this correction decrement is always found whether the crucible is empty or is carrying a solid sample; thus, there may be some further slight correction for the change of state.

In general, the frictional effects of gas are determined by oscillating the empty crucible in the relevant gas atmosphere. Ideally, this correction is required without a contribution from the inner walls of the container, and this condition can be approached by using a crucible full of solid charge. Roscoe⁽¹⁵⁾ derived theoretically an expression which permits the gas resistance over the outside of the crucible to be calculated. As this is essentially a gas viscosity effect, the density of the protective gas is important. Therefore, hydrogen and helium are to be preferred to nitrogen or argon. In contrast to liquids, the viscosity of gases increases with increasing temperature; thus, a survey is necessary to find the variation of the gas resistance over the range of experimental temperatures.

The frictional effects of gas (Correction 2) can always be avoided by the use of vacuum techniques. From experiment, it is found that a vacuum of the order 5×10^{-5} mm Hg must be attained before the residual decrement can be regarded as free from the influence of the gas atmosphere. Liquid metals possessing an appreciable vapour pressure can be handled readily in a sealed vessel⁽¹⁴⁾ if practical conditions permit. Where refractory materials are essential for the container, an enclosed crucible can be used with advantage to reduce the evaporation surface. By incorporating a small expansion chamber for the liquid, which in turn is connected to the apparatus atmosphere by a small evacuation hole (0.030 in. diameter), evaporation of the metal is restricted to the level where damping measurements under short periods of vacuum are permissible^(18, 26)

Residual damping due to furnace currents must be verified at some temperature below the melting point for a given metal. Preliminary tests with the crucible empty are useful to discover whether this correction exists over the temperature range envisaged. By the use of a non-inductive

heater design, this correction can usually be avoided at temperatures up to 700°C. Carbon resistor furnaces for high-temperature work are prone to this problem, due to the use of high currents. The experiments of Culpin⁽¹⁸⁾ outline the measurement of current damping in detail.

The basic design of torsional viscometers is simple. As an example of present-day technique, the apparatus currently in use at the Mines Branch is shown in Figure 8. The complete apparatus operates under a vacuum of 5×10^{-6} mm Hg, serviced by pumps at the base of the unit. The suspension system design is such that the top portion of the apparatus may be elevated along the vertical axis of oscillation, permitting a sample to be changed at the mouth of the furnace zone with the least amount of disturbance to the suspension wires.

Some measure of the reproducibility of the apparatus is shown in Figure 7. This logarithmic decrement-temperature plot was derived from five zinc samples of different extraction with a purity of better than 99.99%.

Three silica-encapsulated iron-constantan thermocouples straddle the thermal zone where the maximum temperature variation is within 1 degree centigrade. Besides pre-calibration against liquid metal freezing standards, a further check is provided by using an incremental stepwise heating cycle through the melting point of a given pure metal. After an equilibration period of four hours just below the melting point, the charge is raised through an interval of one degree. The first sign of the molten state is an immediate change of time period, and this is the most exact means of detecting the change of inertia (due to liquation) in a dynamic system. Hence, by raising the furnace temperature one degree every four hours until the change of state is detected, the melting point of the liquid, as determined by the calibrated thermocouple, can be confirmed to within one degree. In this connection, it is of interest to refer back to Figure 1. Here, Yao⁽⁴⁾ interprets the decrement values of the lower curve together with

corresponding values of temperature from the top curve. Hence, all values to the right of line a are associated with the liquid state. Examination of the time period variation shows distinctly that the end of melting lies at approximately 42 minutes, i. e., the intersection of line b. Thus, from the decrement aspect, the melting point should also have been taken as the point where line b intersects the decrement cusp and not where line a intersects the apex. This would mean that the abnormal deviation observed in this region is not a genuine liquid metal phenomenon.

This behaviour demonstrates that, where the system is undergoing heating, particularly if a change of state occurs, the thermocouple and its environment can be expected to reveal hysteresis effects. In the ideal case, with very slow heating, the lines a and b of Figure 1 should become superimposed.

CAPILLARY VISCOMETERS

In strong contrast to the oscillational method, capillary viscometry, originating from Poiseuille's law⁽⁴¹⁾, has been well established for at least a century. An extensive volume of experimental work exists on numerous liquids at about room temperature. This background would have appeared to favour the use of this technique for such metals as tin, lead, and zinc. However, little interest has centred around this approach in the liquid metal field and it has virtually fallen into disuse. This is somewhat regrettable in that the technique has been developed to yield results of about the same accuracy as with oscillational viscometry. Recent experiments on water⁽²⁰⁾ have yielded agreement within 0.1%. Thus, in theory, low-temperature liquid metal viscometry is possible by two methods capable of measuring data with agreement to 1 or 2%.

Theoretical Considerations

When a given liquid is permitted to flow through a capillary tube of radius r and length l such that a known volume V passes in a time t under a pressure difference P , the physical properties η and ρ are related to the experimental parameters by

$$\eta = \frac{\pi r^4 P t}{8 V l} \quad \dots 20)$$

This relationship, due to Poiseuille⁽⁴¹⁾, is subject to one limitation. Flow through the tube must be Newtonian, thus excluding extraneous phenomena -- e. g. turbulence, under which the postulated law of viscous flow is void.

Where the fundamental considerations are limited to a tube of finite length, two major corrections arise modifying equation 20).

1) Kinetic Energy Correction

Equation 20) implies that energy applied by the pressure P is completely accounted for in overcoming the viscous forces arising from the shearing layers of fluid. In practice, the liquid entering the capillary must be accelerated to the velocity of the main flow stream at the expense of part of the static pressure. This conversion to kinetic energy was expressed mathematically by Hagenbach⁽⁴²⁾ and Couette⁽⁴³⁾, who modified equation 20) to

$$\eta = \frac{\pi r^4 P t}{8 V l} - \frac{m V \rho}{8 \pi l t}, \quad \dots 21)$$

where m is a constant, to which various workers have given the value 1.00 to 1.17. This correction is dependent on the density ρ . Thus, at increasing rates of flow, its influence will be more significant for liquid metals than for, say, organic liquids. Though various theoretical values exist for m , evidence exists to show that it varies for different tubes. By a graphical method of Knibbs⁽⁴⁴⁾, it is possible to estimate whether m is constant for

a given tube and to determine its value. Equation 21) may be manipulated and written as

$$Pt = a + \frac{b}{t}, \quad \dots\dots 22)$$

where a and b are known constants. Thus, by measuring the corresponding values of t which arise when P is varied at a given temperature, Pt can be related to 1/t for a specific tube. A straight line denotes the constancy of m, whose magnitude follows from the value of the gradient.

2) End Correction

This correction is not readily apparent from the theory and has only been recognized in experiments. Its origin is found in the extra work required to bring about a re-arrangement of the velocity distribution at the entry and exit points. This entails a converging of streamlines to flow within the tube, followed by a divergence on emerging at the other end. In magnitude it is found to be proportional to r and can be expressed as a hypothetical increase in the length, $l + nr$.

The corrected expression for the viscosity now becomes

$$\eta = \frac{\pi r^4 Pt}{8V(1 + nr)} - \frac{mV\rho}{8\pi t(1 + nr)} \quad \dots\dots\dots 23)$$

Again, the measurement of n has been the centre of much interest. Values quoted lie between zero and unity. One of the most reliable figures appears to be given by Bond⁽⁴⁵⁾ at $n = 0.57$. Experimentally, n may be determined by using two tubes of different lengths, l_1 and l_2 , where $r_1 \approx r_2$ and m_1 and m_2 have been measured on the same liquid. By considering a given flow rate for both tubes, $n_1 r_1 - n_2 r_2$ may be neglected, leaving an expression involving only $m_1 - m_2$. For a 10-cm-long tube of internal radius 0.025 cm and $n = 0.5$, the error due to this cause can be limited to considerably less than 0.5%.

Calibration Methods

The recognition of the property of viscosity as an important means of quality control within industrial fields has created a demand for assessing the viscous behaviour of fluids in a simple relative manner, as opposed to the more involved absolute approach. A large literature background exists on this topic, and calibrated capillary tubes are readily available for ordinary liquids. With such tubes, the values of V , r and l , are fixed, and equation 23) becomes:

$$\eta = APt - \frac{B\rho}{t} \quad \dots 24)$$

Thus, the constants A and B are the object of calibration in the use of this relationship. Although some procedures over narrow ranges of viscosity can neglect the kinetic energy corrections, this is not so for liquid metals. To verify the constancy of m in equation 23), the variable pressure, P , in the absolute method is attained by the use of an external pressure head of a suitable gas. In relative viscometers an alternative is permissible because m is taken into the term B : the hydrostatic head can be relied upon solely to create flow in the tube. The former technique gives the advantage of greater flexibility for one instrument, but the magnitude of the viscosity of liquid metals lies in such a restricted range that the static head method will suffice. If the static head is not measured by special means, its proportionality is taken to depend on ρ and equation 24) becomes:

$$\eta = \rho \left(At - \frac{B}{t} \right) \quad \dots 25)$$

Experimental Arrangements

Of the early investigators in this field, the classic work of Sauerwald and his co-workers^(40, 46, 47) demonstrates a notable attempt at correlating theory and measurement. The general layout of his vertical

capillary is shown in Figure 9. Two contacts are used to define the volume of liquid flowing in a measured time. One problem inherent in measuring this volume depends on the design of the upper capillary. The usual method of observing the passage of a meniscus past two fiducial marks requires the measuring bulb to be tapered at the entry and exit portions of the capillary. Although direct observation of the liquid is still possible for low-temperature liquid metals as with ordinary liquids, the curved part of the volume bulb surface gives rise to a changing contact angle and to capillary effects as the liquid traverses this region. Ewing, Grand and Miller⁽⁴⁸⁾ observed that static head values for liquid sodium and potassium contained within a 3-cc bulb could not be measured in such an apparatus, because of continued fluctuations of the meniscus through surface tension. The use of contacts in a region where this measuring bulb is of constant cross-section avoids this feature at the expense of losing sensitivity in the determination of the time of flow. Further, a clean liquid surface is essential if tailing of the liquid on the contacts is to be avoided. Even in a well cleaned system, detailed consideration must be given to contact geometry and vibration, in relation to the rising convex liquid surface.

Sauerwald⁽⁴⁷⁾ and Lewis⁽⁴⁹⁾ attempted to limit contamination by employing hydrogen as a gas atmosphere. However, one difficulty of the method arises from the fact that a purging stream of gas cannot be maintained over the liquid surfaces with ease. Also, the reduction of any reaction products formed during melting demands appreciably higher temperatures, and introduces the problem of sweeping away the water vapour formed.

In the ideal case a thoroughly outgassed vacuum system is essential in this technique where any possible blockage in the fine capillary must be completely avoided. With respect to the capillary, in general only glass or silica materials will be available. This restricts the application of the apparatus to liquids which do not react with these. Because the viscosity depends on the fourth power of the radius, bore inaccuracies present one of the severest problems in capillary methods. This situation has

become easier in recent years, due to the appearance of precision bore capillary tubing in some grades of glass. Thus, in selecting a capillary suitable for liquid metal work, stock material can be used where the maximum error in the radius will be about 1%. Microscopical examination can be used to decide on the initial selection with respect to uniformity of bore and imperfections of the inner surface. Subsequent measurements using gravimetric and electrical resistance methods⁽⁶⁰⁾ will give the mean radius to the order of 1 part in a 1000.

Silica capillaries display a much larger tolerance margin and call for careful selection from batch material. Construction of the apparatus must be carried out with meticulous care to maintain the definition of the length, l . A gradual change of diameter from the capillary to the volume bulb will mean an uncertainty in the end point of the length. Alternatively, attaching the bulb below the upper end of the capillary introduces the possibility of severe distortion of the capillary channel.

The driving pressure is measured by the usual manometric techniques. In practice, the constant external gas pressure applied to one liquid surface must be corrected for the hydrostatic head created through the existence of two liquid-free surfaces at different heights. As these heights vary during the experiment, the mean value of the effective pressure must be found. Derivations of this mean value have been considered by Simeon⁽⁵⁰⁾, Bingham, Schesinger and Coleman⁽⁵¹⁾ and Lidstone⁽⁵²⁾. Where the measuring and receiving vessels are of circular cross-section, the mean effective pressure, P , is given by

$$P = \frac{(h_2 \mp h_1) \rho g}{\log_e \frac{H \mp h_1}{H \mp h_2}}, \quad \dots\dots 26)$$

where H is the applied pressure, and the initial and final hydrostatic heads of liquid metal are h_1 and h_2 , respectively.

If the kinetic energy must be taken into consideration, equation 26) is not adequate, and, according to Herschel and Bulkley⁽⁵³⁾, the mean effective pressure can be stated as:

$$P = \rho g \left(H + \frac{1}{4} C H^2 \right), \quad \dots\dots\dots 27)$$

where

$$H = \frac{h_1 - h_2}{\log \left(\frac{y_1}{y_2} \right) + y_1 - y_2}$$

$$y_1 = (1 + C h_1)^{\frac{1}{2}} - 1, \quad y_2 = (1 + C h_2)^{\frac{1}{2}} - 1,$$

and

$$C = \frac{m g \rho^2 R^4}{16 \eta^2 l}$$

Lewis⁽⁴⁹⁾, using a viscometer similar to Sauerwald's⁽⁴⁷⁾ design, examined the above corrections with respect to tin. By considering values of h_1 , and h_2 pertinent to his own apparatus, the difference between equations 26) and 27) remains negligible down to $H = 9$ cm, provided $K \leq 0.5$. For mercury and tin, this maximum value of K was found to be 0.18 and 0.02 respectively. Thus, the use of equation 26), instead of equation 27), in equation 21) was verified.

Investigators such as Spells⁽⁵⁴⁾ and Ewing, Grand and Miller⁽⁴⁸⁾ have utilized calibration techniques on liquid gallium, sodium and potassium. Spells demonstrated in a unique manner how a calibrated horizontal silica capillary was ideal for viscosity measurement on very small volumes of liquid. A fixed quantity of liquid was permitted to flow from a measuring bulb under its own hydrostatic pressure, through the capillary to a similar receiving bulb. The gallium was retained under vacuum throughout the experiments, to avoid the highly tenacious films formed with reactive gases. Even though temperatures reached over 1000°C, fluid re-setting and time

observations were done manually. Because the liquid was flowing under its own head, by keeping the volume constant, or calibrating to allow for its expansion and employing similarly shaped volume bulbs, calibration was made according to equation 25).

Preliminary calibrations with benzene gave a few results that were some 4% below the results obtained by calibrating with mercury. This was attributed to the marked difference in physical properties between the two standards.

Ewing, Grand and Miller⁽⁴⁸⁾ designed a modified Ostwald capillary viscometer to handle reactive metals such as sodium and potassium. This apparatus appeared very flexible in that the charge could be distilled into the apparatus, which had been previously outgassed, and the whole apparatus then transferred to the constant temperature bath for the flow measurements. At this stage the unit operated as a closed system under the pressure of purified nitrogen. An arrangement similar to that of Maas and Boomer⁽⁵⁵⁾ was used to manipulate the liquid to the correct height. An expansion bulb permitted an excess pressure to be generated at the lower liquid surface. Equalization of the pressure throughout the apparatus commenced the flow cycle. The schematic layout of this well designed apparatus is shown in Figure 10. Some details of the pressure head measurement are worthy of mention. Even though the densities of sodium and potassium were similar to that of water, the calibrating liquid, a method for assessing the mean effective head was followed by noting the values of the hydrostatic head required to hold the liquid meniscus at several fixed levels in the upper measuring bulb. Further measurement of the time required to reach these levels under free flow allowed the mean head to be derived by a graphical method. It can be seen from equation 26) that in this case, i. e. $H = 0$, the mean effective head is not the average of the initial and final hydrostatic heads. Excellent agreement was noted for sodium when compared with Chiong's⁽¹⁷⁾ data from the oscillating sphere, but there was some conflict in the data for potassium.

Thus it appears that the capillary method still has a contribution to make in the low-temperature liquid metal field, since the order of accuracy is comparable to that of the oscillational method.

ROTATIONAL VISCOMETERS

The rotation of a curved interface, in the form of a sphere, disc or cylinder, has attracted little attention in the liquid metal field. What interest there has been has centred around the case of a revolving cylinder. Theoretical considerations leading to a viscosity equation are quite simple, but experimental difficulties arise when the ideal case of an infinite surface is related to a cylinder of practical length. In comparison with the oscillation method, the main advantage attributed to rotational viscometers is that they are suitable for a wide range of fluids.

Theoretical Aspects

Consider an infinitely long cylinder of radius a revolving about its axis in a viscous fluid with a constant angular velocity Ω . Then, the total couple G exerted by the fluid of viscosity η on the surface of a fixed coaxial cylinder of radius b and length h is given by

$$G = 4\pi\eta h\Omega\left(\frac{1}{a^2} - \frac{1}{b^2}\right). \quad \dots\dots 28)$$

The experimental interpretation of this simple relation is one of relative motion. This means that either cylindrical surface may be permitted to rotate, although the measurement of the couple at the fixed radius calls for differing procedures.

Experimental Arrangements

Where the inner cylinder rotates, one arrangement permits the application of a known torque from masses falling under the action of gravity. When a steady state is reached, the rate of rotation is measured. Saito and Matsukawa⁽⁵⁷⁾ have used an apparatus embodying this design for liquid aluminum. These authors report the interference of oxide layers on the surface of the melt. The investigations of Rait⁽⁵⁸⁾ suggest that the friction effects found limit the use of this method to slags and glasses.

In general, the measurement of the torque is achieved by suspending the fixed cylinder on a torsion wire and observing the angular displacement θ .

Thus $G = K\theta$ 29)

By suitable choice of the torsion wire, and by variation of $a - b$, a large viscosity range can be accommodated.

One severe limitation from the practical application of equation 28) lies in the end correction, where finite cylinders must be considered.

As no suitable end correction has been developed mathematically, elimination can be approached in two ways:

- (1) use of mechanical devices such as guard rings;
- (2) use of differential methods by varying the height of liquid.

Considerable importance has been attached to the use of guard rings, which were originally adopted by Couette⁽⁴³⁾. Essentially, these are comprised of fixed cylinders positioned coaxially above and below the stationary cylinder. The rotating shell of liquid is now prevented from influencing the top and bottom portions of the suspended cylinder. This approach has not been applied to liquid metal viscometry, doubtless because of the experimental problems involved. It is of interest to observe that one of the few absolute

viscosity determinations reported for this technique verifying equation 28) employed guard rings. The work of Bearden⁽⁵⁹⁾ on the viscosity of air used a motor-driven inner cylinder surrounded by a suspended outer cylinder, protected by guard rings. The agreement with data obtained by a capillary method was excellent.

With regard to the differential methods, from equations 28) and 29) it follows that

$$\eta = \frac{K\theta}{\Omega} .$$

Jones and Bartlett⁽³⁾ calibrated a rotating outer cylinder viscometer with water and rape oil and found that θ was directly proportional to the angular velocity at a given temperature. Contrary to this observation, Yao and Kondic⁽²⁾ abandoned this approach on finding θ non-linear with respect to angular velocity.

Jones and Bartlett⁽³⁾ now consider the end effects as an apparent lengthening of the inner cylinder, and the components of the top and bottom end effects are assessed by measuring θ at different liquid heights, keeping Ω constant. Under certain dimensional conditions the end effects were independent of the liquid medium. This type of apparatus, employing a liquid zone some 16 cm high and 12 cm in diameter, presents a severe problem where thermal gradients are considered.

As yet, the rotational method has made little contribution to liquid metal viscometry. No doubt this neglect originates from the complex nature of the design and assembly anticipated in this approach.

REFERENCES

1. R. Newton - "Principia" - (1713).
2. T. Yao and V. Kondic - "The Viscosity of Molten Tin, Lead, Zinc, Aluminium, and Some of Their Alloys" - J. Inst. Met. 81, 17-24 (1952).
3. W. Jones and W. Bartlett - "The Viscosity of Aluminium and Binary Aluminium Alloys" - J. Inst. Met. 81, 145-152 (1952).
4. T. Yao - "The Viscosity of Liquid Metals" - Giesserei Tech. Wiss. Beihefte 16, 837-851 (1956).
5. E. McLaughlin and A. Ubbelohde - "Pre-Freezing Phenomena in Molten Metals" - Trans. Faraday Soc. 56, 989-993 (1960).
6. H. R. Thresh - "The Viscosity of Pure Liquid Metals and Lead-Rich Magnesium Alloys" - Ph.D. Thesis, Univ. Birmingham (1957).
7. M. R. Hopkins and T. C. Toye - "Determination of the Viscosity of Molten Metals" - Proc. Phys. Soc. B63, 773-782 (1950).
8. T. C. Toye and E. R. Jones - "Physical Properties of Certain Liquid Binary Alloys of Tin and Zinc" - Proc. Phys. Soc. 71, 88-99 (1958).
9. A. Seybolt and J. Burke - "Procedures in Experimental Metallurgy" - Chapman and Hall, London (1953).
10. O. Meyer - "A Method for Deriving the Viscosity of Liquids" - Wied. Ann. 43, 1-14 (1891).
11. J. C. Maxwell - "Bakerian Lecture" - Phil. Trans. 156, 249 (1866).
12. J. E. Verschaffelt - "The Viscosity of Liquefied Gases: I. The Rotational Oscillation of a Sphere in a Viscous Liquid" - Commun. Phys. Lab., Univ. Leiden, 148b, 17-39 (1915).
13. E. N. da C. Andrade and Y. S. Chiong - "Determination of Viscosity by the Oscillation of a Vessel Enclosing a Fluid" - Proc. Phys. Soc. 48, 247-260 (1936).
14. E. N. da C. Andrade and E. R. Dobbs - "The Viscosities of Liquid Lithium, Rubidium and Cesium" - Proc. Roy. Soc. A211, 12-30 (1952).

15. R. Roscoe - "Viscosity Determination by the Oscillating Vessel Method: I. Theoretical Considerations" - Proc. Phys. Soc. 72, 576-584 (1958).
16. S. Navier - Mem. Acad. Sci. 6 (1823).
17. Y. S. Chiong - "The Viscosities of Liquid Sodium and Potassium" - Proc. Roy. Soc. A157, 264-277 (1936).
18. M. F. Culpin - "The Viscosity of Liquid Indium and Liquid Tin" - Proc. Phys. Soc. B70, 1069-1078 (1957).
19. R. Roscoe and W. Bainbridge - "Viscosity Determination by the Oscillating Vessel Method: II. The Viscosity of Water at 20°C" - Proc. Phys. Soc. 72, 585-595 (1958).
20. J. F. Swindells, J. R. Coe, Jr. and T. B. Godfrey - "Absolute Viscosity of Water at 20°C" - J. Res. Nat. Bur. Standards 48, 1-31 (1952).
21. E. V. Polyak and S. V. Sergeev - "Determination of the Viscosity of Molten Aluminium and Its Alloys" - Compt. Rend. Acad. Sci. USSR 30, 137 (1941).
22. K. Mutzel - "On the Viscosity of Liquids" - Wied. Ann. 43, 15-42 (1891).
23. T. Okaya and M. Hasegawa - "On the Motion of Liquid in a Hollow Cylinder Caused by the Torsional Vibration" - Jap. Journ. Phys. 11, 13-22 (1936).
24. T. Okaya - "On a Method of Determination of the Coefficient of Viscosity of a Liquid by the Torsional Vibration" - Proc. Phys. Math. Soc. Japan 18, 268-279 (1936).
25. E. G. Shvidkovski and others - "Uchenye Zapiski" - M. V. Lomonosov Univ. Fizika 74, 145-166 (1944).
26. H. R. Thresh - "An Absolute Determination of the Viscosity of Liquid Metals by Oscillating a Cylindrical Vessel" - Physical Metallurgy Division Internal Report PM-R-60-9, Mines Branch, Department of Mines and Technical Surveys, Ottawa (1960).
27. J. C. Armbruster, P. Azon and P. Bastien - "On an Absolute Viscosity Method" - Compt. Rend. Acad. Sci. (Paris) 250, 2816-2818 (1960).
28. A. Porter - "Volume of the Meniscus at the Surface of a Liquid" - Phil. Mag. 17, 511-517 (1934).

29. F. Bashforth and J. C. Adams - "An Attempt to Test the Theory of Capillary Action" - Cambridge Univ. Press, London (1883).
30. J. Rayleigh - "On the Theory of the Capillary Tube" - Proc. Roy. Soc. A92, 184-195 (1915).
31. T. Richards and E. Carver - "A Critical Study of the Capillary-Rise Method of Determining Surface Tension with Data for Water and Organic Liquids" - J. Amer. Chem. Soc. 43, 827-847 (1921).
32. V. Stott - "The Measurement of the Viscosity of a Molten Metal by Means of an Oscillating Disc" - Proc. Phys. Soc. 45, 530-544 (1933).
33. A. Cavalier - "Measurements of the Viscosity of Under-cooled Molten Metals" - National Physical Laboratory, Symposium No. 9, 2 (1958).
34. A. Koeniger and P. Sahn - "Viscosity and Flowability in the System Zinc-Aluminium with Special Consideration of the Zinc-Aluminium Pressure Cast Alloy GD-ZnAl₄" - Giesserei Tech. Wiss. Beihefte 30, 1673-1678 (1960).
35. A. Roeder and W. Morawietz - "Viscosity and Density Measurements in Liquid Potassium Amalgams" - Z. Metallkunde 47, 734-741 (1956).
36. E. Gebhardt and others - "Properties of Metallic Melts" - Z. Metallkunde 42, 111-117 (1951); 43, 106-108 (1952); 44, 379-382 (1953); 45, 83-85 (1954); 46, 90-94 (1955); 47, 684-688 (1956).
37. H. Theilmann and A. Wimmer - "On the Viscosity of Liquid Pig Iron" - Stahl und Eisen 47, 389-399 (1927).
38. A. Knappwost - "A Simple Method for Measuring Viscosity at High Temperatures" - Z. Metallkunde 39, 314-318 (1948).
39. H. Fisher and A. Phillips - "Viscosity and Density of Liquid Lead-Tin and Antimony-Cadmium Alloys" - Trans. AIME 200, 1060-1070 (1954).
40. F. Sauerwald and K. Topler - "Further Measurements on the Viscosity of Bismuth-Tin Alloys and Copper-Tin Alloys" - Z. anorg. Chem. 157, 117-137 (1926).
41. J. Poiseuille - Compt. Rend. Acad. Sci. 11, 961 and 1041 (1840).
42. E. Hagenbach - Pogg. Ann. 109, 385-426 (1860).

43. M. Couette - "Studies on the Viscosity of Liquids" - Ann. Chim. Phys. (Series 6) 21, 433-510 (1890).
44. G. Knibbs - J. Roy. Soc. of N.S.W. 29, 97-103 (1895); 30, 190 (1895).
45. W. N. Bond - "Viscosity Determinations by Means of Orifices and Short Tubes" - Proc. Phys. Soc. 34, 139-144 (1922).
46. F. Sauerwald - "A Method for the Measurement of the Viscosity of Lead-Bismuth Alloys" - Z. anorg. Chem. 135, 255-264 (1924).
47. A. Bienias and F. Sauerwald - "On the Viscosity of Copper, Antimony, Lead, and Copper-Antimony, Copper-Tin, Lead-Bismuth Systems" - Z. anorg. Chem. 161, 51-75 (1927).
48. C. T. Ewing, J. A. Grand and R. R. Miller - "Viscosity of the Sodium-Potassium System" - J. Am. Chem. Soc. 73, 1168-1171 (1951).
49. A. J. Lewis - "The Absolute Measurement of the Viscosity of Liquid Tin" - Proc. Phys. Soc. 48, 102-110 (1936).
50. F. Simeon - "The Viscosity of Calcium Chloride Solutions" - Phil. Mag. 27, 95-100 (1914).
51. E. C. Bingham, H. I. Schlesinger and A. B. Coleman - "Some Sources of Error in Viscosity Measurement" - J. Am. Chem. Soc. 38, 27-41 (1916).
52. F. M. Lidstone - "The Measurement of the Absolute Viscosity" - Phil. Mag. 43, 354-357 (1922).
53. W. H. Herschel and R. Bulkley - "Calibration of the Buret Consistometer" - Ind. Eng. Chem. 19, 134-139 (1927).
54. K. E. Spells - "The Determination of the Viscosity of Liquid Gallium Over an Extended Range of Temperature" - Proc. Phys. Soc. 48, 299-311 (1936).
55. O. Maas and E. Boomer - "Vapour Densities at Low Pressures and Over an Extended Temperature Range: I" - J. Am. Chem. Soc. 44, 1709-1728 (1922).
56. J. Bockris, J. White and J. MacKenzie - "Physicochemical Measurements at High Temperatures" - Butterworths Publications, London (1959).

57. D. Saito and T. Matsukawa - "Viscosity of Alloys at High Temperatures" - Mem. Coll. Eng. Kyoto 2, 49-114 (1932).
58. J. Rait - "The Viscosity of Slags and Glasses" - Trans. Brit. Cer. Soc. 40, 157-204 (1941).
59. J. Bearden - "A Precision Determination of the Viscosity of Air" - Phys. Rev. 56, 1023-1040 (1939).
60. G. Barr - "Monograph of Viscometry" - Oxford University Press (1931).

IRT:(FES)KW

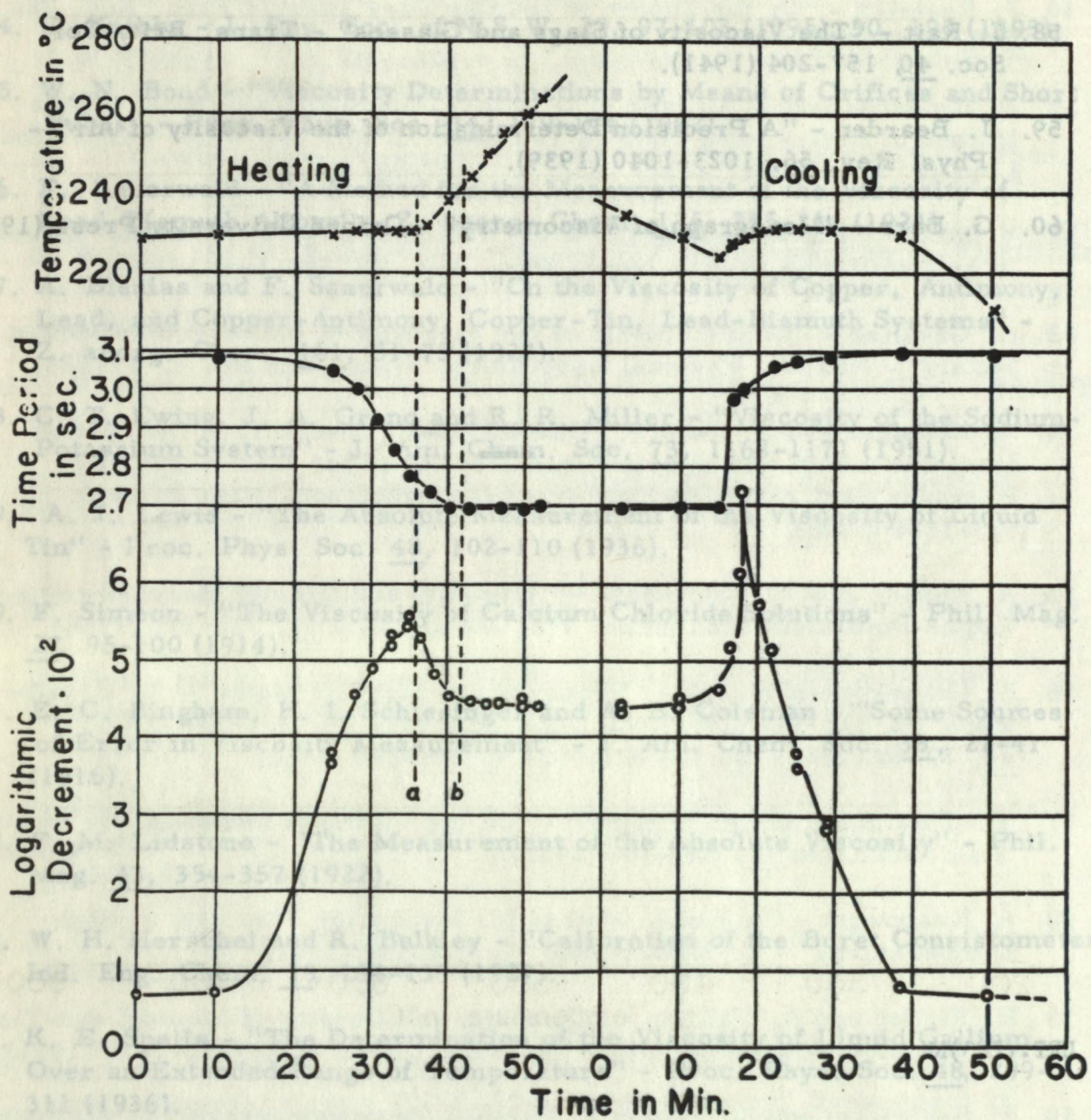


Figure 1. Variation of Logarithmic Decrement, Time Period and Temperature with Time Through Melting and Freezing Cycles. (After Yao⁽²⁾)

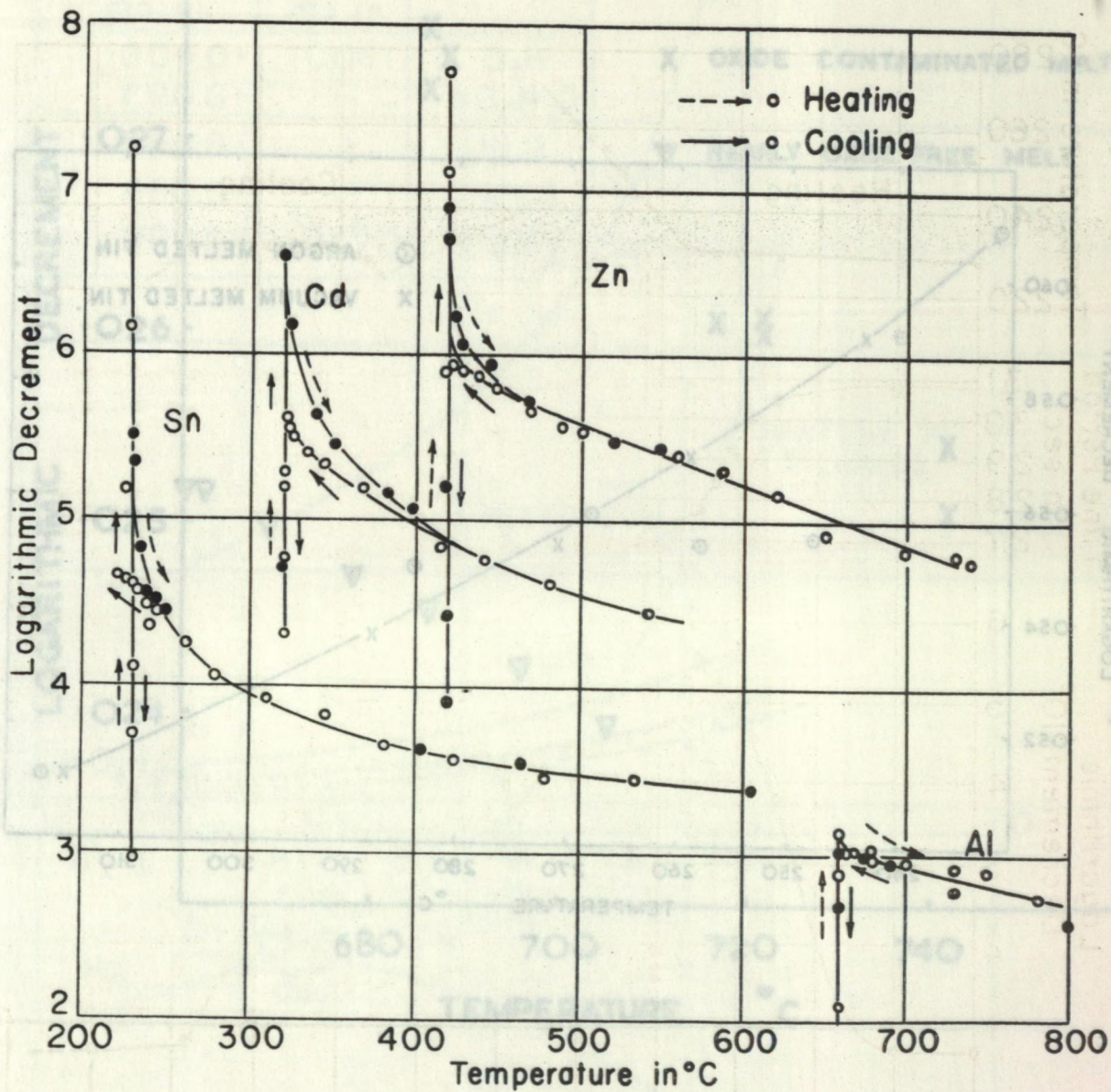


Figure 2. Variation of Logarithmic Decrements with Temperature, Showing Abnormal Effects near the Freezing Point. (After Yao⁽⁴⁾)

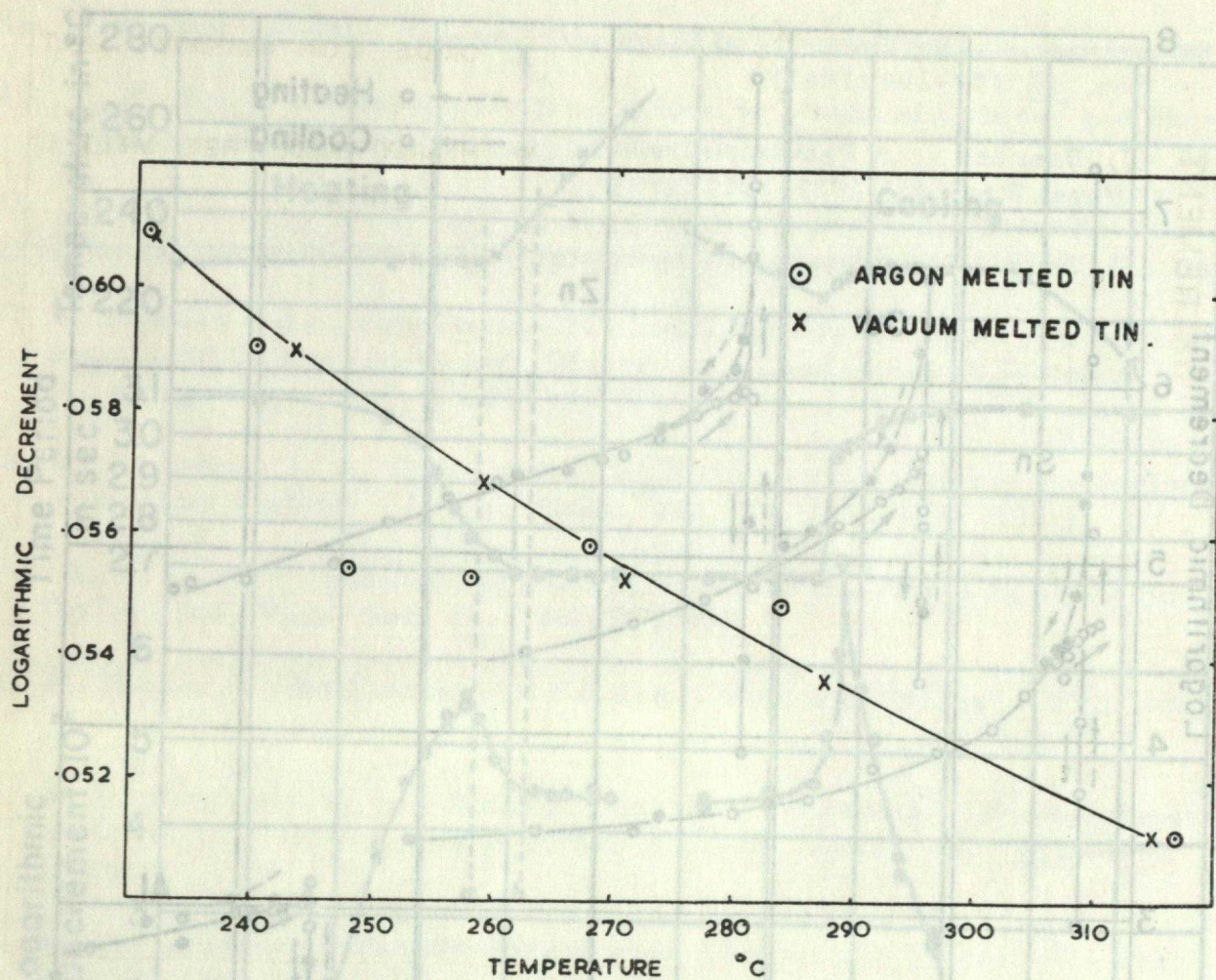


Figure 3. The Variation of Logarithmic Decrement with Temperature for Pure Liquid Tin, Showing the Influence of Contamination.

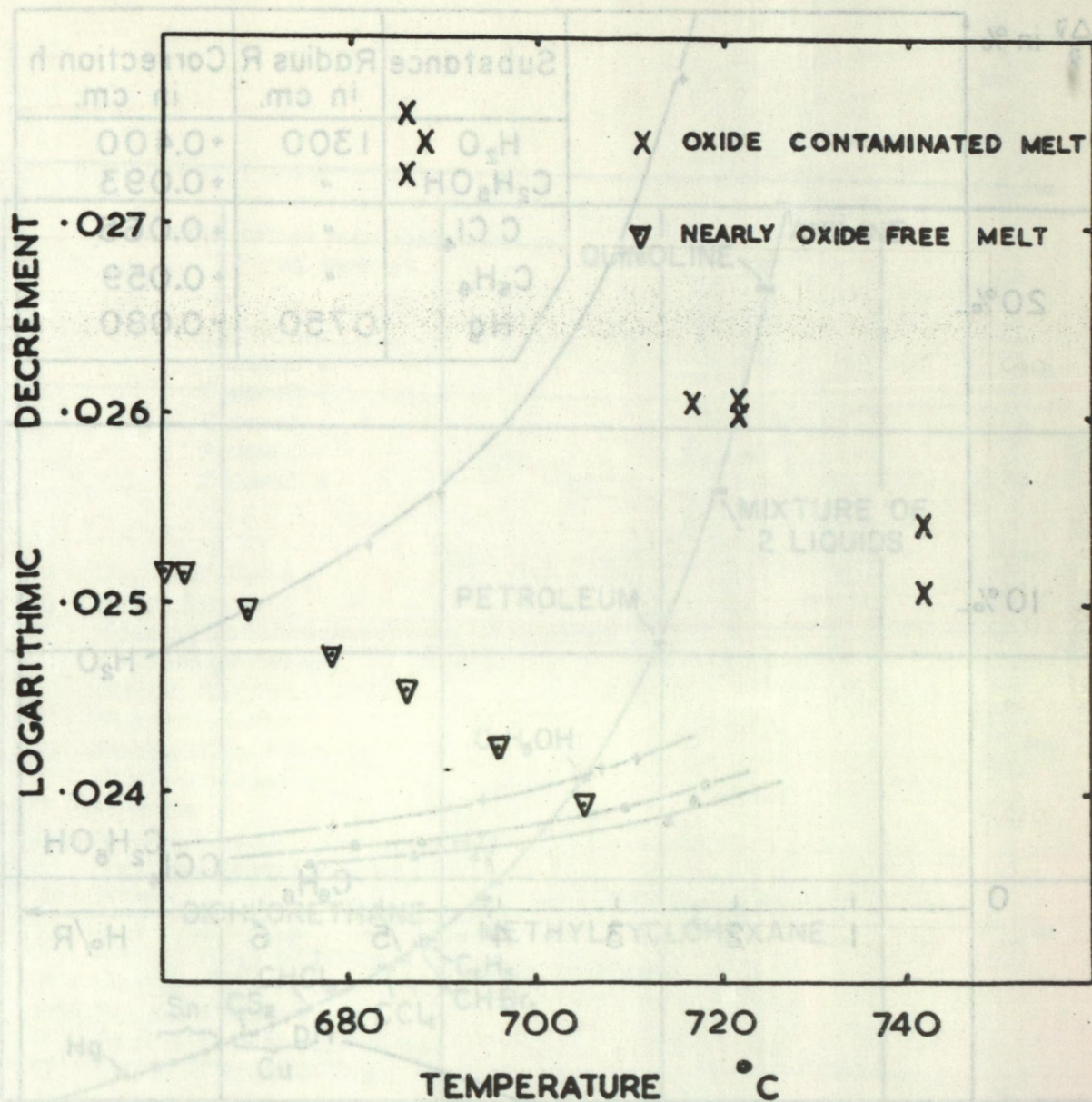


Figure 4. Effect of Oxide Contamination on Liquid Pure Aluminum.

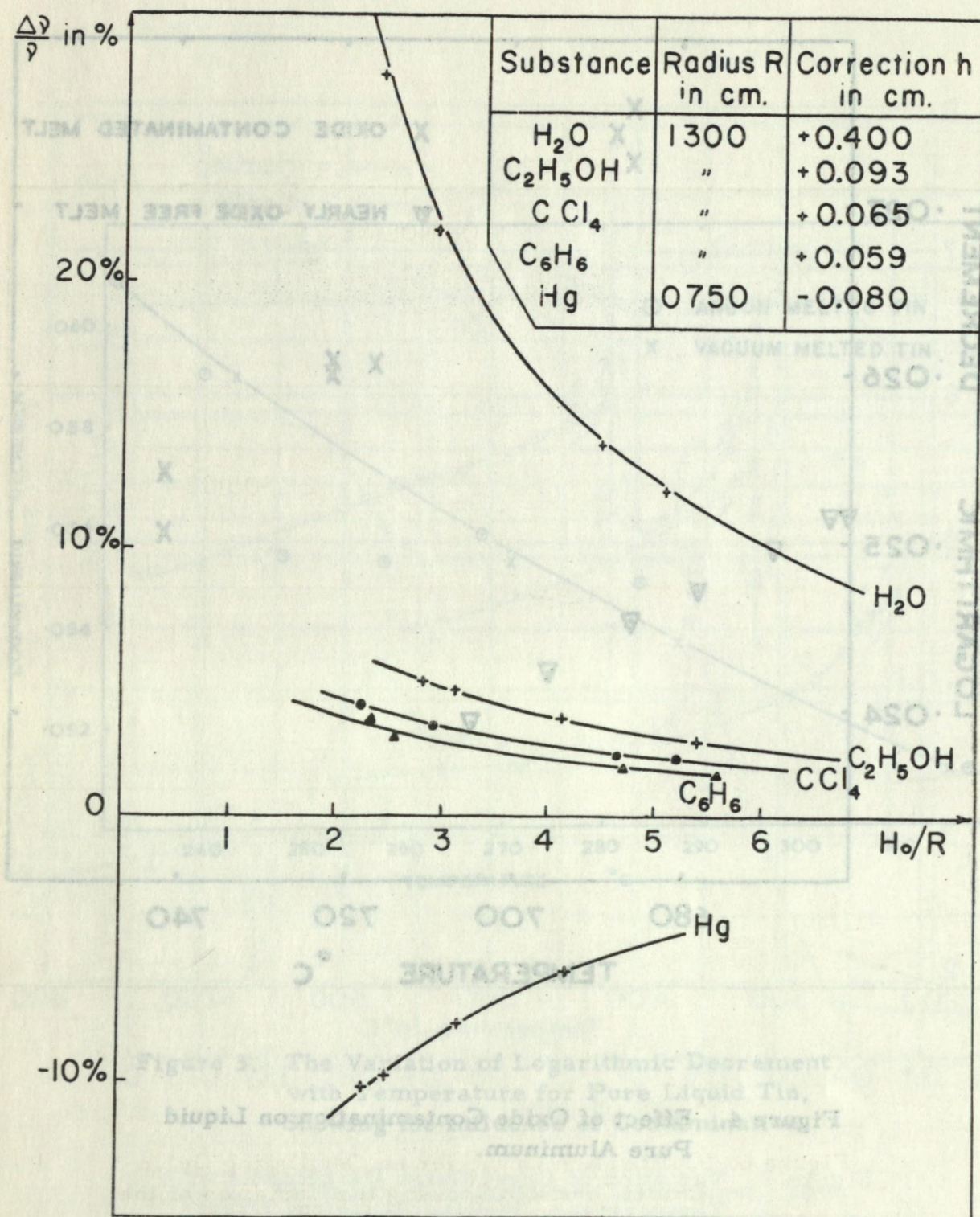


Figure 5. Variation of Error, Arising in Viscosity Data due to Meniscus Effects, with Vessel Dimensions. (After Armbruster, Azon and Bastien⁽²⁷⁾)

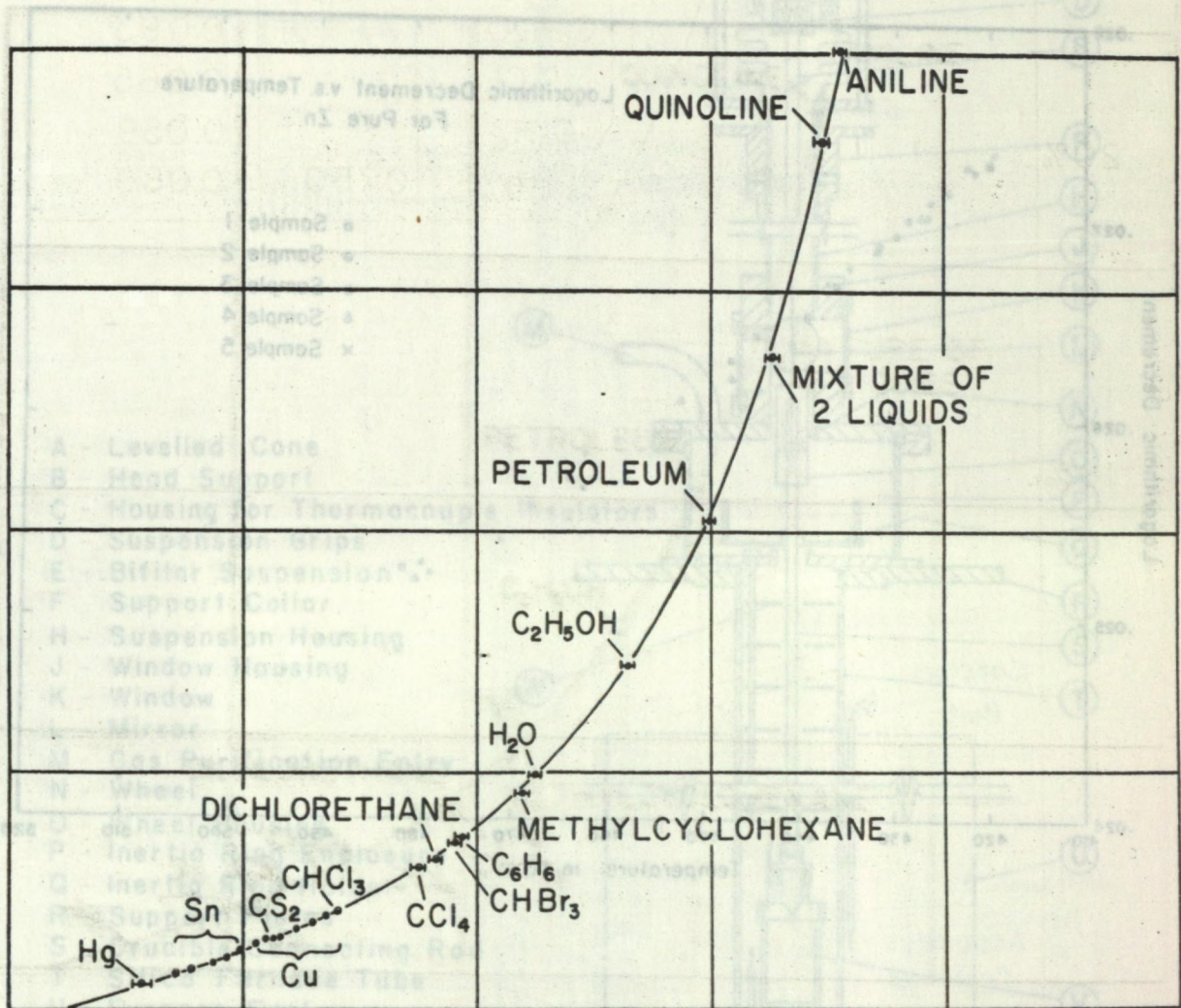


Figure 6. Calibration Curve for an Oscillating Cylindrical Crucible, Showing the Variation of the Kinematic Viscosity (η/ρ) with δ/ρ . (After Cavalier⁽³³⁾)

Figure 8. The Oscillating Viscosimeter Employing a Cylindrical Vessel, as Used at the Mines Branch.

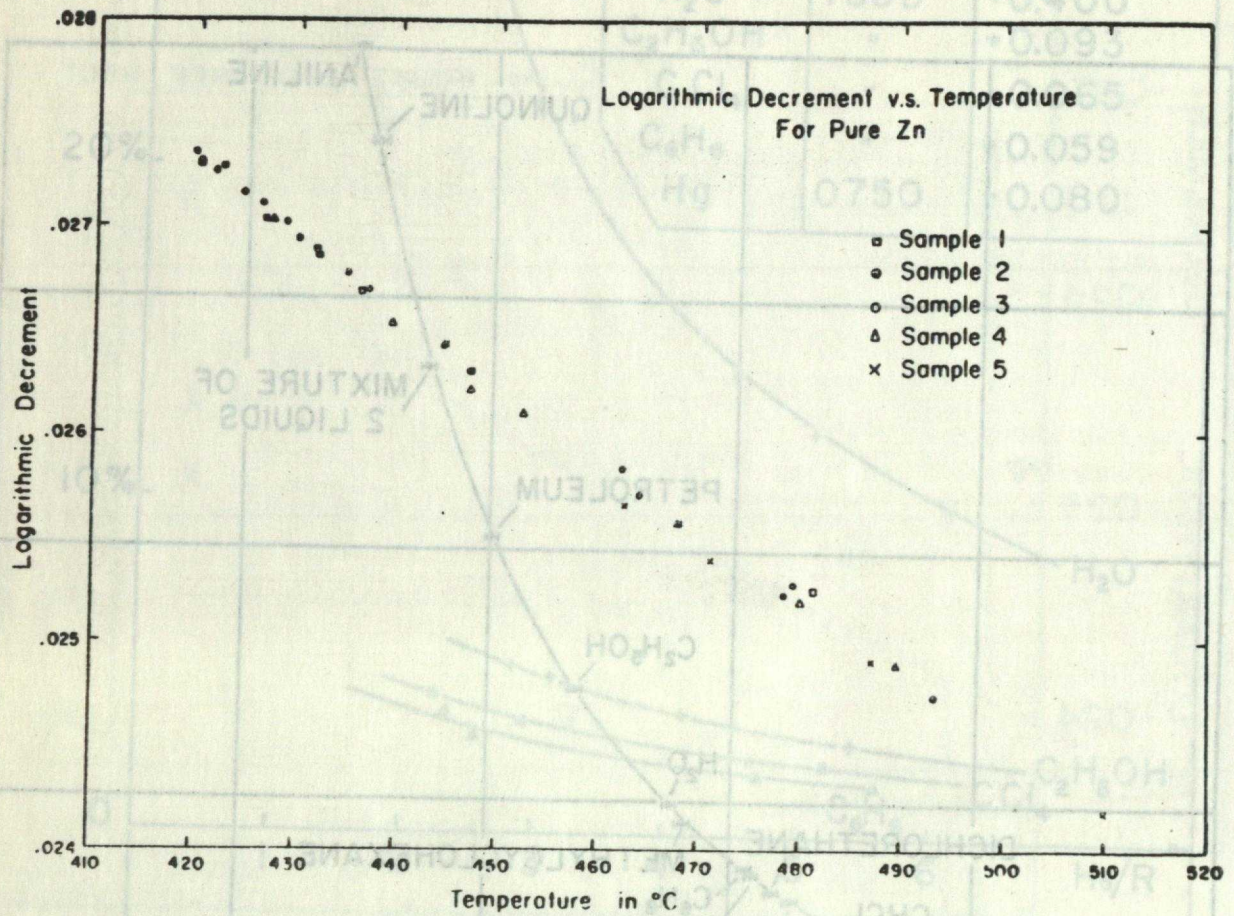


Figure 7. Logarithmic Decrement Varying with Temperature, for Five Different Samples of Pure Zinc.

Figure 6. Calibration Curve for the Variation of the Rotational Cradle, Showing the Variation of the Rheometric Viscosity (η) with ϕ . (After Cavalieri, 1933)

Figure 5. Variation of Error, Arising in Viscosity Data due to Meniscus Effects, with Vessel Dimensions. (After Armbruster, Azon and Bastian, 1927)

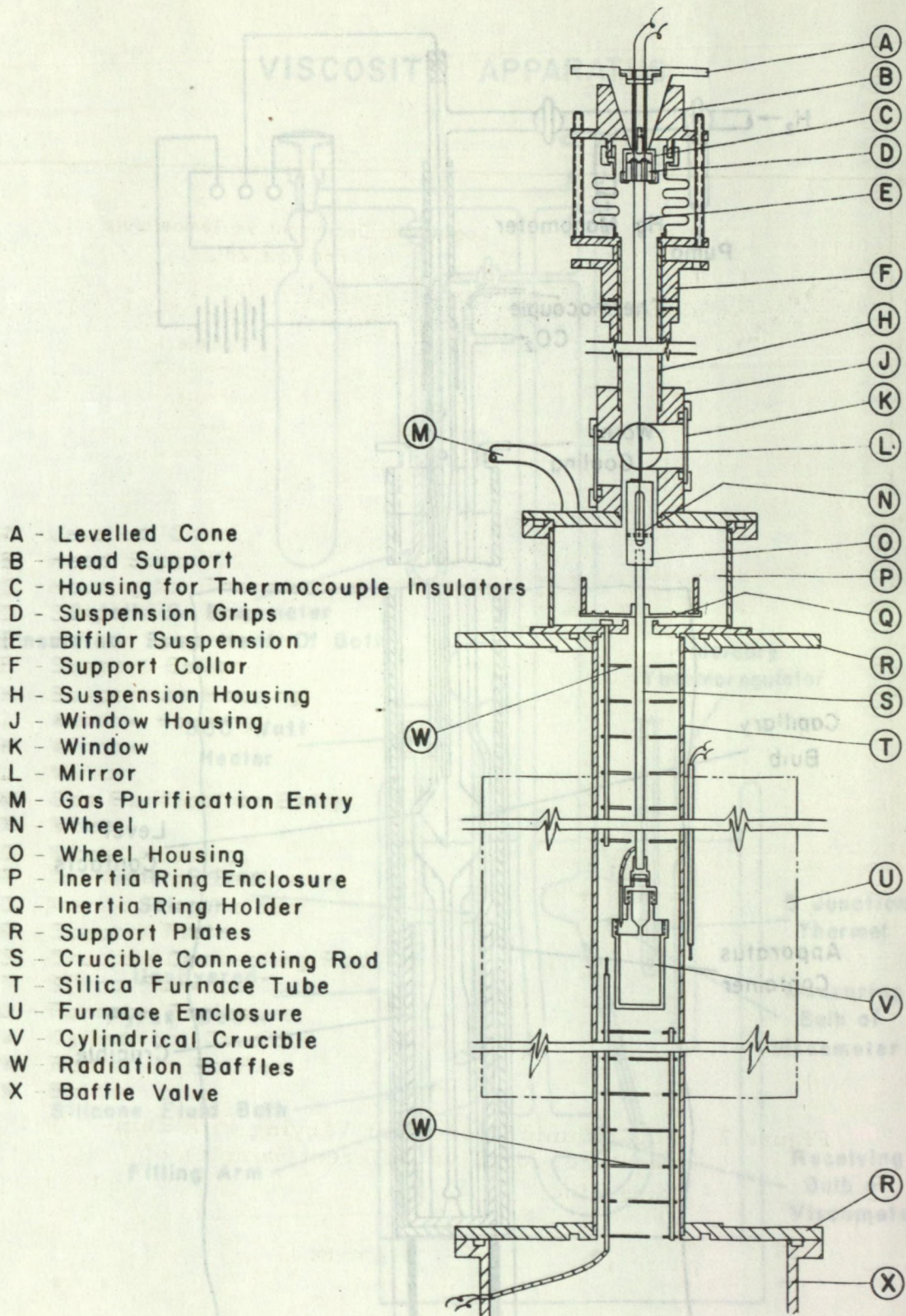


Figure 8. The Oscillating Viscometer Employing a Cylindrical Vessel, as Used at the Mines Branch.

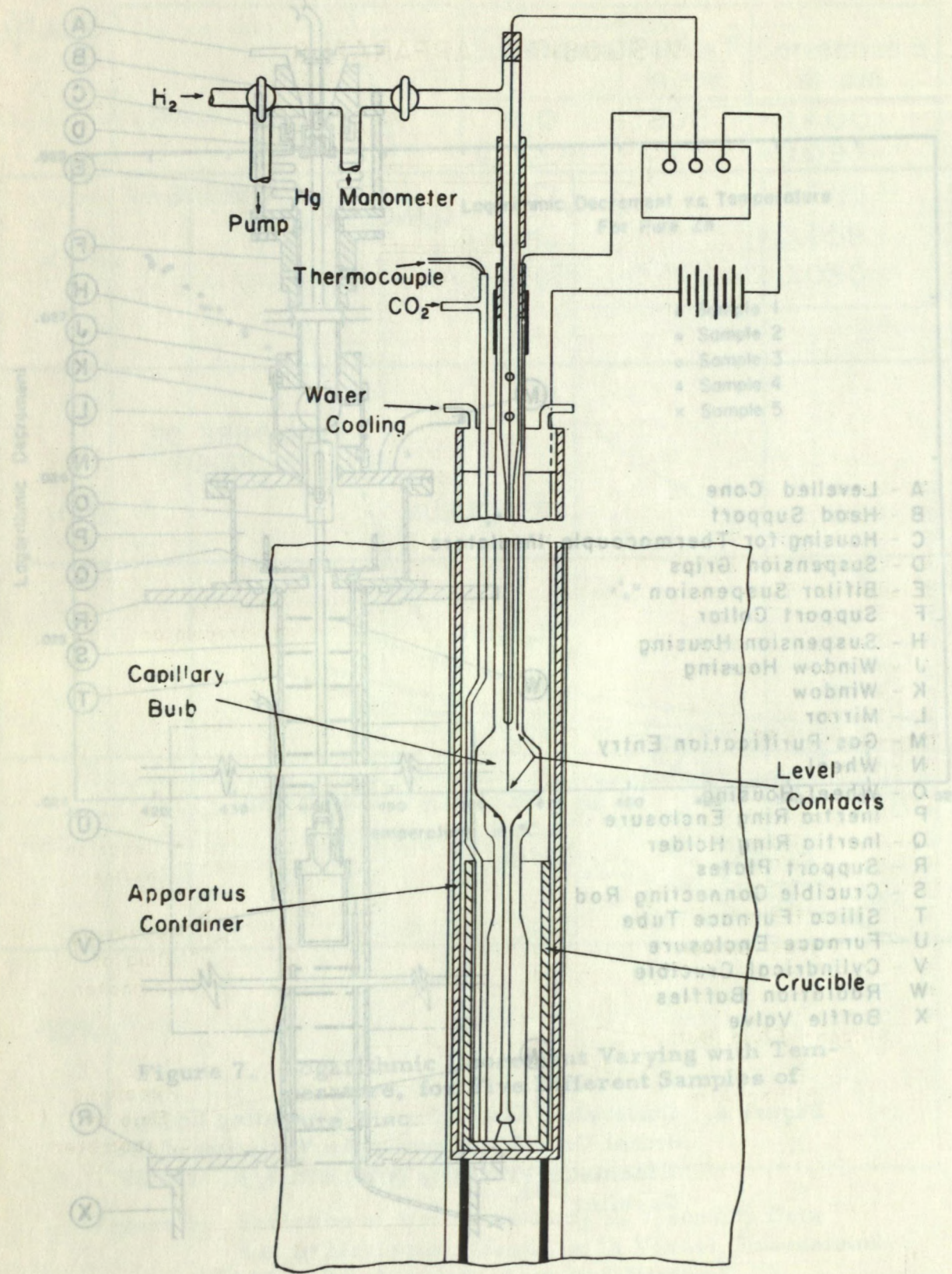


Figure 9. Capillary Viscometer (after Sauerwald and others (40, 46, 47)).

VISCOSITY APPARATUS

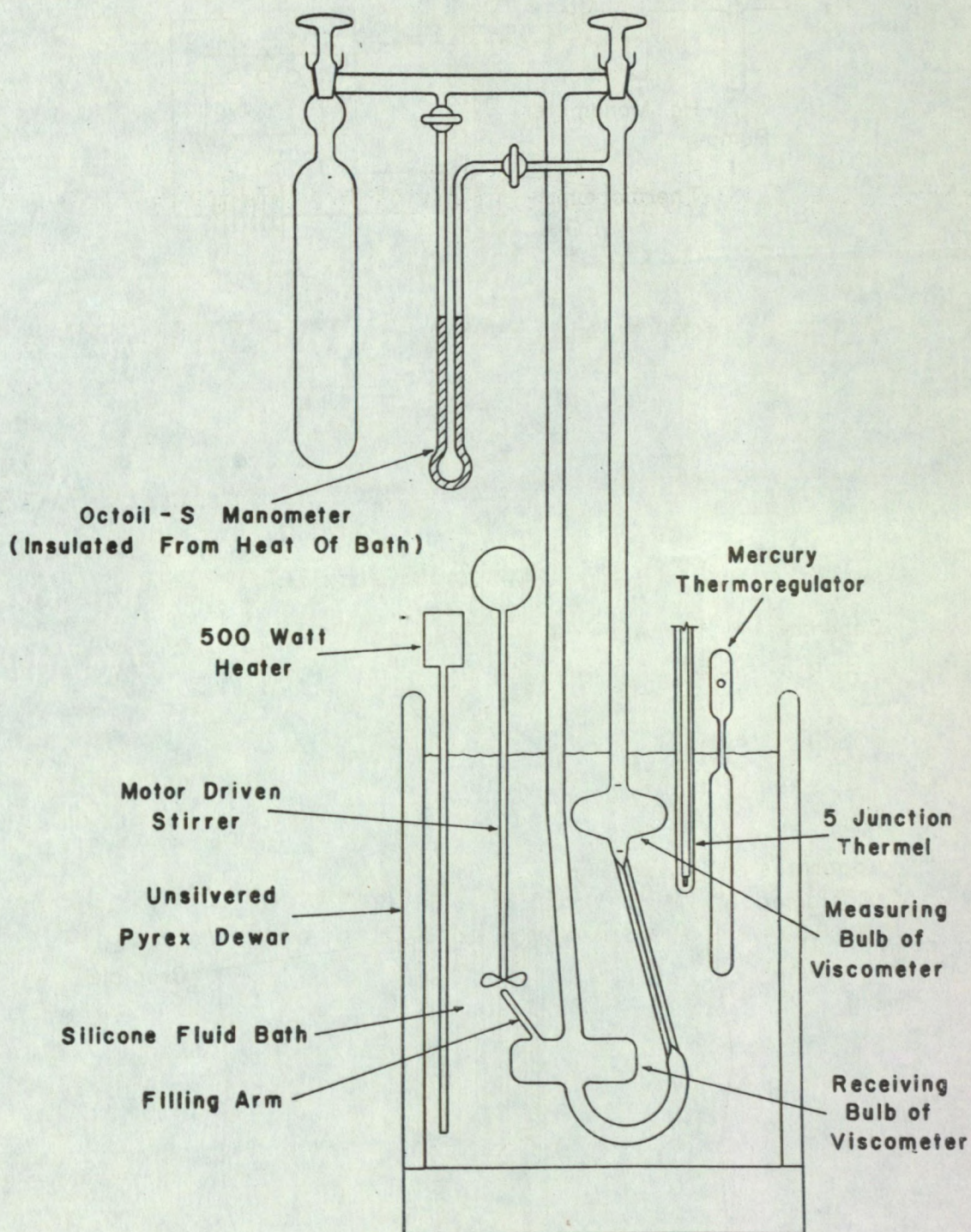


Figure 10. Capillary Viscometer Employing a Closed System.
(After Ewing, Grand and Miller⁽⁴⁸⁾)