H. T. Hall

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Viscosity ② of Metallic Mercury ③ (and Its Saturated Vapor) over Its Entire Liquid Range, *i.e.*, from Its Melting ① Point (234.3°K.) to Its Critical Point (1733°K.), and an Estimate of Its Critical Viscosity[1]

by A. V. Grosse

The Research Institute of Temple University, Philadelphia, Pennsylvania *(Received August 6, 1964)*

The viscosities of both liquid metallic mercury and its saturated vapor have been determined experimentally up to about 900°K. Using Andrade's equation, correlating viscosity, temperature, and specific volume, and from the known specific volumes of mercury up to the critical temperature, the viscosity of mercury and its saturated vapor are extrapolated to the critical point (1733°K.). Advantage is also taken of the experimental straight-line relations for the mean viscosity, *i.e.*, $^1/_2(\eta_{\text{liq}} + \eta_{\text{satd vap}})$, *vs.* temperature in the critical region. The critical viscosity of mercury is estimated to equal 0.4_1 cp.

Since some liquid metals can be heated up to very high temperatures, being elementary substances,[2] and methods of containing them up to temperatures of over 4500°K. have been developed,[3] it becomes of increasing interest to be able to estimate their more important physical properties at as high a temperature as possible.

Of all the 80 elementary metals known, mercury is the only one whose critical temperature has been determined experimentally and whose liquid densities or specific volumes are known up to the critical point.[2]

The so-called transport properties of fluids, *i.e.*, viscosity, diffusion, and thermal conductivity, are interrelated. Statistical mechanics gives mathematical expressions for these properties, in terms of molecular parameters and intermolecular forces, for the dilute gases with reasonable accuracy. The theory of the same properties for condensed fluids is much more complicated.[4] Particularly in recent years, a number of papers by physicists and chemical physicists[5-13] have appeared attacking this problem, especially for the simplest case, namely, monatomic liquids having a spherically symmetrical field of force, such as the liquid noble gases.

However, agreement between theory and experiment and lack of precise experimental data, even in the simplest case of liquid argon, leave much to be desired.

In the case of liquid *metals*, the relationships are further complicated by the metallic bonding forces in contrast to the much more readily understood van der Waals forces of homopolar substances. This complication is indicated, for example, by the fact that the thermal conductivity of a normal liquid (such as liquid argon, krypton, or xenon) *decreases* with temperature; in the case of liquid metals some behave normally—for example sodium and potassium—and others, *in contrast*, have thermal conductivities increasing with temperature, exemplified by lithium and mercury.

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(1) This work supported by the U. S. Atomic Energy Commission under Contract No. AT(30-1)-2082.

(2) A. V. Grosse, *J. Inorg. Nucl. Chem.*, **22**, 23 (1961).

(3) A. V. Grosse, *Science*, **140**, 781 (1963).

(4) See J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," John Wiley and Sons, Inc., New York, N. Y., 1954.

(5) P. Gray and S. A. Rice, *J. Chem. Phys.*, **40**, 3671 (1964).

(6) B. A. Lowry, S. A. Rice, and P. Gray, *ibid.*, **40**, 3673 (1964).

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(9) J. Naghizadeh and S. A. Rice, *ibid.*, **36**, 2710 (1962).

(10) E. Helfand and S. A. Rice, *ibid.*, **32**, 1642 (1960).

(11) H. Reiss, H. L. Frisch, E. Helfand, and J. L. Lebowitz, *ibid.*, **32**, 119 (1960).

(12) G. Ciui-Castognoli and F. P. Ricci, *ibid.*, **32**, 19 (1960).

(13) H. Mori, *Phys. Rev.*, **112**, 1829 (1958).

The thermal conductivity of liquid metals is directly related to electrical conductivity by the Wiedemann–Franz law. We are particularly interested to estimate electrical conductivities of liquid metals, at as high temperatures as possible, since they can now be heated to high temperatures by simple ohmic resistance, because the "pinch" effect can be readily overcome in a centrifugally rotating electrical furnace.[14] Attempts to develop the transport theory for electron–phonon interactions in metals are being made.[15]

In view of the present state of theory we are forced to rely on experiments and on empirical methods, which will be developed herewith.

In our previous papers on the viscosity of liquid metals[16,17] we used the *first* Andrade equation, namely

$$\eta = ae^{H_\eta/RT} \qquad (1)$$

to describe the change with temperature over a comparatively narrow temperature range (of about 500°K.). In his often-cited paper of 1934 on the theory of liquid viscosity, Andrade[18] emphasized that for a wider temperature range, the change in density or specific volume of the liquid should be taken into account and developed his *second* equation, *i.e.*

$$\eta v^{1/3} = Ae^{c/vT} \qquad (2)$$

where A and c are constants of a particular liquid, η (in poises) is its viscosity, and v (in cm.^{3}/g.) is its specific volume at the temperature, T, in °K. In its logarithmic form, *i.e.*, plotting log $(\eta v^{1/3})$ *vs.* $1/vT$, this equation is a straight line. Andrade applied his equation to mercury also and obtained the following values for his constants[18]

$$A = 2467 \times 10^{-6}; \ c = 21.0 \qquad (3)$$

All of the viscosity data on mercury up to 1960 are conveniently tabulated and critically evaluated in the mercury volume of the Gmelin handbook.[19] The data of Erk[20] cover the range from the melting point to ~500°K., while Chalilov[21] extended his measurements to 900°K. and also determined the viscosity of saturated mercury vapor.

Table I contains the pertinent data on viscosity[19]; also given are the experimental specific volumes of mercury from the melting point to the critical point, smoothed out according to our best present estimates (see ref. 2). The values of Andrade's variables, *i.e.*, $\eta v^{1/3}$ and $1/vT$, are also given in Table I.

They are plotted in Fig. 1; one can readily see that Andrade's straight-line relationship holds for the whole experimental range. The equation of this line is

$$\log (\eta v^{1/3}) = \log (2318 \times 10^{-6}) + 0.43429 \times 22.76/vT \qquad (4)$$

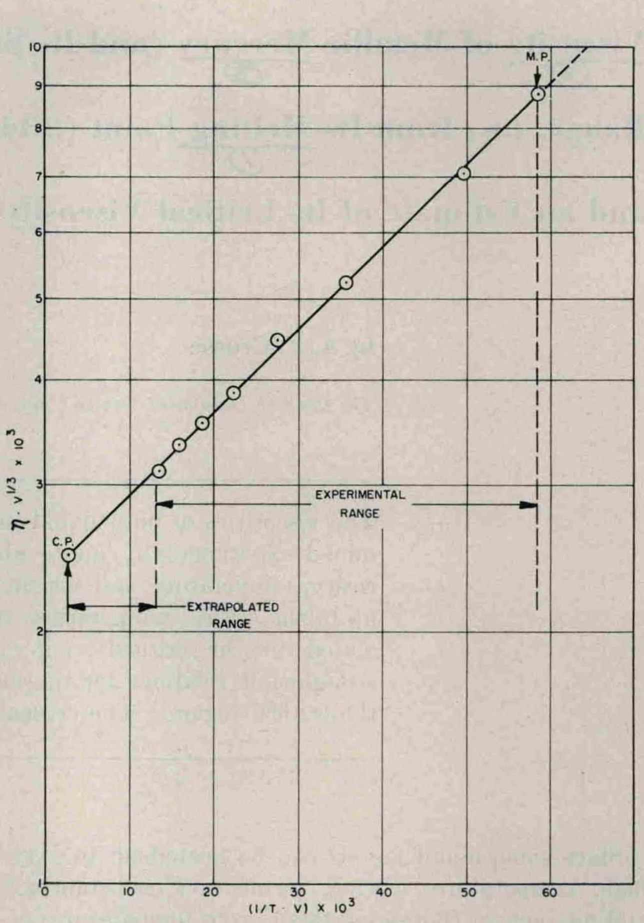

Figure 1. Viscosity, η, of Hg_{liq} using the second Andrade equation.

Our constants A and c are practically identical with the 30-year earlier ones of Andrade. Since the critical temperature of mercury[22] is 1733°K. and the critical density[2] is known, the Andrade line was extended to the critical point (see Fig. 1). The viscosities for set values of temperature were calculated from our Andrade equation since the corresponding specific volumes are known (see Table I); the calculated η-values cover the range from 973°K. to the critical point (the four significant figures given for η_{calcd} should not imply the precision of these values).

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(14) See A. V. Grosse, ref. 2, p. 787, Fig. 8.

(15) R. E. Prange and L. P. Kadanoff, *Phys. Rev.*, **134,** A566 (1964).

(16) A. V. Grosse, *J. Inorg. Nucl. Chem.*, **25,** 317 (1963); *Science*, **140,** 788 (1963).

(17) A. V. Grosse, *J. Inorg. Nucl. Chem.*, **23,** 233 (1961).

(18) E. N. daC. Andrade, *Phil. Mag.*, **17,** 698 (1934).

(19) "Gmelin's Handbook," Mercury, No. 34, Section 1, Verlag Chemie, GmbH., Weinheim, West Germany, 1960, pp. 312–317.

(20) S. Erk, *Z. Physik*, **47,** 886 (1928).

(21) Ch. Chalilov, *Zh. Tekhn. Fiz.*, **8,** 1249 (1938).

(22) F. Birch, *Phys. Rev.*, **41,** 641 (1932).

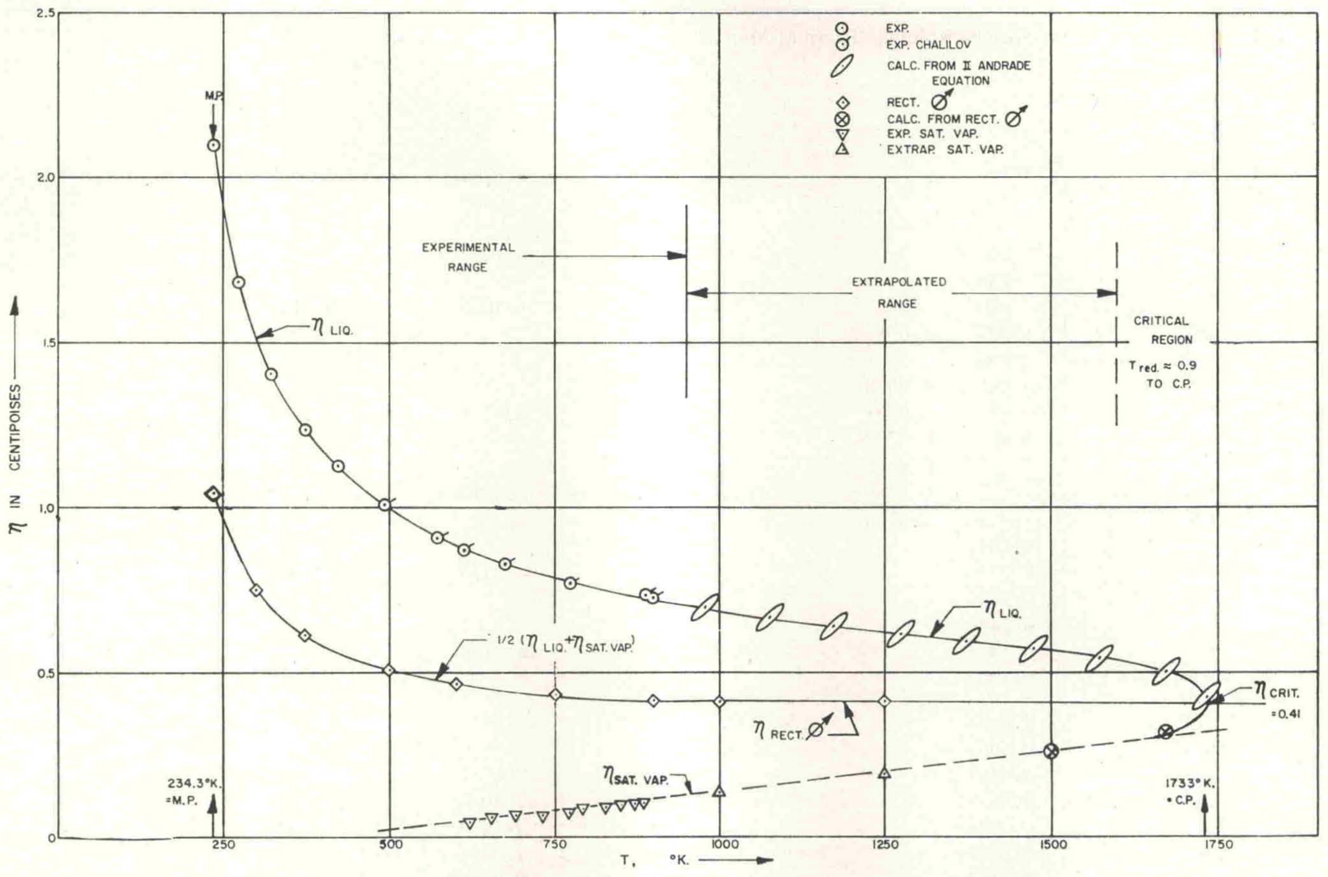

Figure 2. Viscosity, η, of mercury *vs.* T from the melting point (234.3°K.) to the critical point (1733°K.).

Finally, all values of viscosity in Table I are plotted over the entire range from melting point to critical point in Fig. 2; the *average* values of Erk and Chalilov (see Table I) are plotted in their range of overlap (*i.e.*, from 493 to 613°K.).

In addition to the data of Table I, we have also plotted in Fig. 2 the *experimental* values of Chalilov[19,21] for the *viscosity of saturated vapor*, in equilibrium with liquid mercury, in the temperature range of his measurements, namely, from 350 to 610°. In contrast to dilute gases where the viscosity increases proportionally to the $\sqrt{T}$, the η of saturated vapor (because of the much greater pressure) is essentially a straight line function of T, as Fig. 2 shows. Thus, an extrapolation to higher temperatures can be readily made.

An additional empirical fact helps us to correlate the viscosity of the liquid and the viscosity of saturated vapor. In 1908, Phillips[23] was the first to investigate the viscosity of CO_2, *both* of the liquid and the saturated vapor *in the critical region*, and established the main features of the behavior of η *vs.* T and P in the critical region. It could be demonstrated that the change of viscosity of liquid and its saturated vapor *vs.* T showed a similar relationship to the density, namely the law of rectilinear diameter of Mathias and Cailletet (see ref. 2). Thus, the *mean* viscosity, *i.e.*

$$^1/_2(\eta_{\text{liq}} + \eta_{\text{satd vap}}) \qquad (5)$$

is a straight-line function of temperature in the region of $T_{\text{red}} = 0.75$ to the critical point. In contrast to the mean density, *i.e.*, $^1/_2(D_{\text{liq}} + D_{\text{satd vap}})$, which can be extrapolated on a straight line all the way back to 0°K., the mean viscosity curves upward toward the melting point on a *hyperbolic curve*, as Fig. 2 shows.

Recent and precise measurements on *ethane* and *propane* in the critical region by Starling, *et al.*,[24] confirmed this regularity for these two gases. Chalilov's

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[23] P. Phillips, *Proc. Roy. Soc.* (London), **A83**, 265 (1908); see also D. M. Newitt, "The Design of High Pressure Plant and the Properties of Fluids at High Pressures," Clarendon Press, Oxford, 1940, pp. 407–409.

[24] K. E. Starling, B. E. Eakin, J. P. Dolan, and R. T. Ellington, "Progress in International Research on Thermodynamic and Transport Properties," American Society of Mechanical Engineers, New York, N. Y., 1962, pp. 530–540.

Table I: The Viscosity and Specific Volume of Liquid Mercury from the Melting Point to the Critical Point

T, °K.	η, cp.		v, cm.^{3}/g.	$\eta v^{1/3}$, poise cm./g.$^{1/3}$ × 10^3	$1/vT$, g./cm.^{3} °K. × 10^3	
M.p. 234.3	2.10		0.073041	8.7782	58.433	Experimental
273	1.685		0.073554	7.0600	49.801	
323	1.407					
373	1.240		0.074870	5.2262	35.808	
423	1.130					
473	1.052		0.076233	4.4606	27.733	
493	1.027[a]	1.008				
523	0.995					
543	0.985	0.9570				
573	0.950	0.9091	0.077655	3.8786	22.474	
613	0.921	0.8728				
653		0.8405				
673		0.8285	0.079164	3.5510	18.770	
693		0.8165				
733	0.7941					
773	0.7746		0.080802	3.3488	16.010	
813	0.7596					
853	0.7444					
873	0.7385		0.082630	3.2166	13.863	
898	0.7304					
973	0.6987		0.084083	3.0610	12.223	η calculated from second Andrade equation
1073	0.6661		0.087306	2.9550	10.675	
1173	0.6407		0.090212	2.8737	9.450	
1273	0.6178		0.093624	2.8055	8.390	
1373	0.5943		0.098348	2.7432	7.406	
1473	0.5702		0.104613	2.6865	6.490	
1573	0.5472		0.113766	2.6495	5.588	
1673	0.4995		0.135135	2.5632	4.423	
C.p. 1733	0.4249		0.197941	2.4765	2.915	

[a] The data in the left column are due to Erk (ref. 20); those in the right column are Chalilov's (ref. 21).

measurements (see Fig. 2 and ref. 19) established it *experimentally* for mercury, at least with some degree of accuracy at temperatures of about 900°K.

With all these facts and considerations in mind, we can first extrapolate the viscosity of liquid mercury on the one hand and its saturated vapor on the other to a temperature of about 1600°K. Both extrapolations are essentially straight lines because there are no abrupt changes in either viscosity or in specific volume with T; thus the decrease of η from 900 to 1500°K. is only 0.17 cp. The calculated Andrade formula extrapolation and that of Chalilov's saturated vapor measurements give a mean rectilinear diameter viscosity of 0.41 cp. at 1000 and 1250°K. The critical region, which may be defined as the range from $T_{\text{red}} = 0.9$ (or ~1600°K.) to the critical point, is where one has to expect a comparatively rapid decrease in η_{liq} coupled with the rapid increase in $\eta_{\text{satd vap}}$. From the second Andrade equation the viscosity of the critical point is estimated to equal 0.4_2 cp. (see Table I); the law of rectilinear diameter gives the nearly identical and, to us, preferable value of 0.41 cp.

To anyone who has observed or measured the rapid, that is manyfold, change in viscosity over a narrow temperature range of *nearly all* chemical substances, it may seem foolhardy to extrapolate viscosities over a range of 800°K. However, it should be emphasized that our case is an exceptional one in that the critical viscosity is "self-bracketing"; this is to say that the liquid viscosity has to *decrease* constantly from the already low value of 0.73 cp. at 900°K. and, on the other hand, the $\eta_{\text{satd vap}}$ has to increase *constantly* from the experimental value of 0.11 cp. at 900°K. From the known behavior of *all thermally stable* substances which do not undergo chemical change— and mercury is an element[25]—it is known that the two functions *must*

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(25) The only possible change at high temperatures, *i.e.*, ionization of the saturated vapor, sets in, according to the Saha equation and the known ionization potential of mercury at the very much higher temperatures.

meet at the known critical point of 1733°K. Independently, the law of rectilinear diameter leads one to practically the same value. We thus consider the critical viscosity of mercury equal to 0.4_1 cp. at 1733°K. to be a good estimate. To illustrate this further, water has the viscosity equal to 1.00 cp. at 20°; thus mercury, at the critical point, is 2.5 times as fluid as water at 20°.

Since the critical density[2] is equal to 5.0 g./cm.^{3}, the critical *kinematic* viscosity of mercury equals 0.082 centistoke.

The same method may be used to estimate the critical viscosity of a number of other metals whose η_{liq} and $\eta_{\text{satd vap}}$ are known over a substantial temperature range. Such is the case of the alkali metals; the critical temperatures and densities of sodium, potassium, rubidium, and cesium have been estimated (see ref. 3).

Self-diffusion is another transport property which is closely related to viscosity. In a number of papers of the author[26] it has been stressed that the values of the diffusion constant, D, of metals can be obtained from η thanks to the Stokes–Einstein relation.

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(26) The latest one is A. V. Grosse, *Science*, **145**, 50 (1964).