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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]

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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.

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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

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

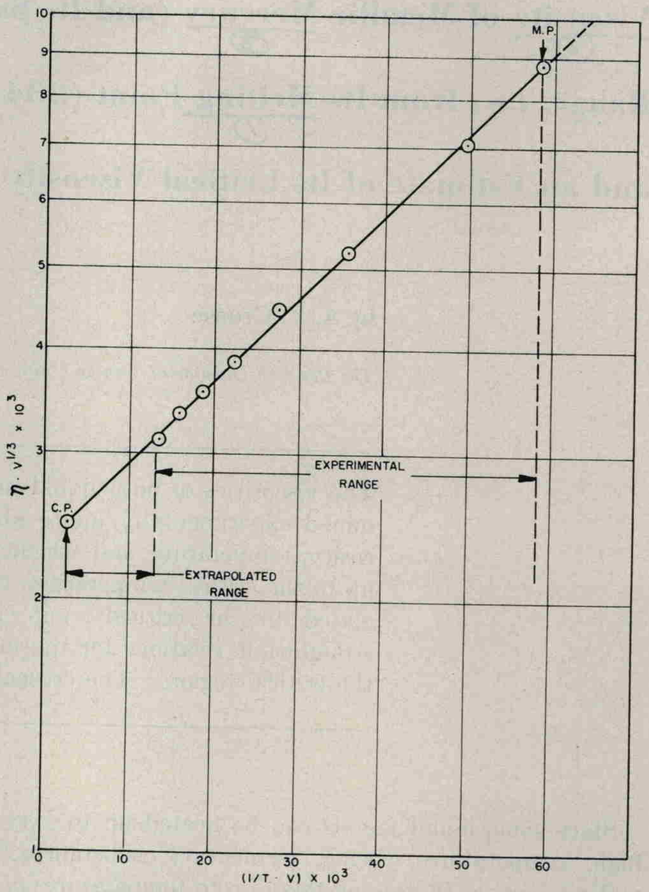

Figure 1. Viscosity, η, of Hg_{liq} using the second Andrade equation.

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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