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.*

$$\frac{1}{2}(\eta_{\text{liq}} + \eta_{\text{satd vap}}) \qquad (5)$$

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.*, $\frac{1}{2}(D_{\text{liq}} + D_{\text{satd vap}})$, 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

(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.$^{1/3}$ × 10³	$1/vT$, g./cm.³ °K. × 10²	
M.p. 234.3	2.10		0.073041	8.7782	58.433	↑
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				Experimental
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	↑
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	η calculated from second Andrade equation
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_{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 $\eta_{satd\ vap}$. 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 $\eta_{satd\ vap}$ 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*

(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.