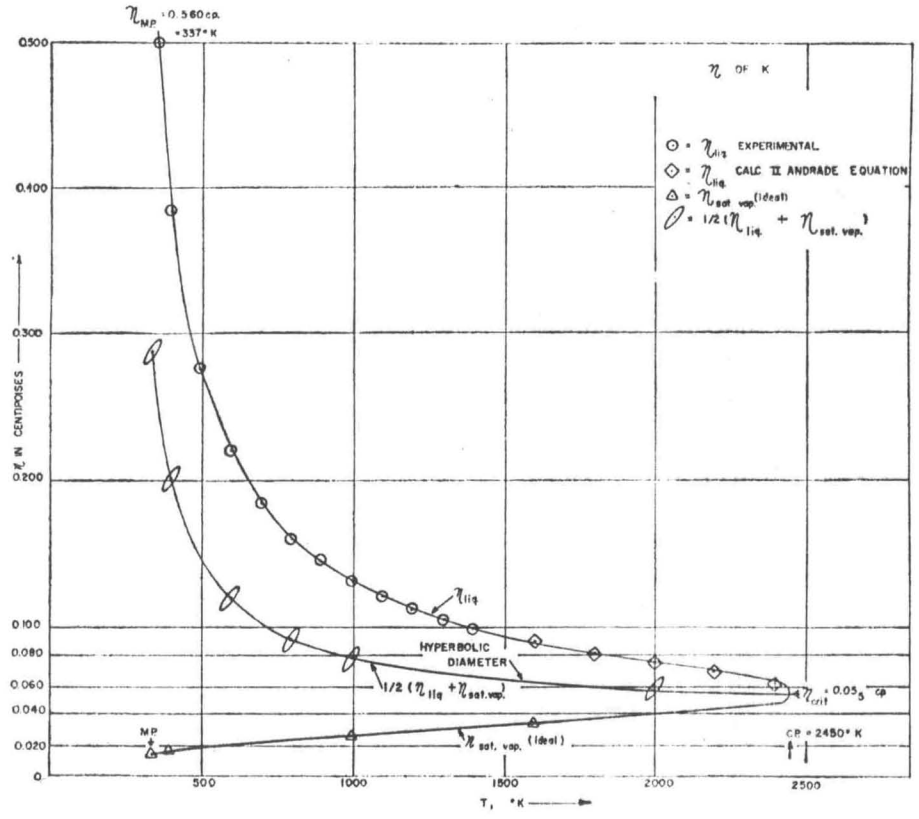

Fig. 3. Experimental and calculated viscosity of potassium from the melting point to the critical point.

where A equals the atomic weight, T is temperature in degrees K, and σ is the atomic diameter in angstroms.

In the higher temperature range, *approaching* the critical region where the saturated vapor pressure is high, it has been found experimentally in the case of Hg (see *6*) that $\eta_{\text{sat vap}}$ increases proportionally to T.

We have found that the $\eta_{\text{sat vap}}$ of Hg (*6*) is adequately described (in the $\sqrt{T}$ region) by using the mean of Pauling's (*11*) metallic diameter and the diameter of the atom for 12 ligands. Using the same procedure we obtained the calculated viscosities of Na and K as shown in Table 3 and plotted in Figs. 2 and 3. These calculations apply to dilute gases; for dense gases additional corrections can be made (see *10*, pp. 611–667)—they increase the calculated vapor viscosity by only 8 percent in the case of Hg. Thus, for the present they can be neglected. It is only in the critical region, which may be adequately defined as the range of $T_{\text{red}} = 0.85$ to the critical point, that $\eta_{\text{sat vap}}$ would be expected to increase more and more rapidly with temperature; this is indicated in the curves of Figs. 2 and 3.

Furthermore, we have an additional *empirical* fact with which we may correlate the viscosity of the liquid and of the saturated vapor, as demonstrated for mercury (*6*). Corresponding to the law of rectilinear diameter for the density of liquid and saturated vapor, we have for the mean viscosity, that is,

$$\tfrac{1}{2}(\eta_{\text{liq}} + \eta_{\text{sat vap}}), \qquad (3)$$

a hyperbolic curve, which becomes practically a straight line in the critical region (*6*). These mean viscosity curves for Na and K are shown in Figs. 2 and 3, and one can readily observe that they are essentially straight lines in the critical region. Therefore, by plotting the "hyperbolic" diameter of the mean viscosities in the region preceding the critical region and by extrapolating the straight line to the critical point we have a second method, besides the Andrade equation, to estimate the critical viscosity.

We thus obtain (and give preference to) slightly higher values for the critical viscosities, as follows:

$$\eta_{\text{crit}} \text{ of Na} = 0.07_2 \text{ cp} \qquad (4)$$

and

$$\eta_{\text{crit}} \text{ of K} = 0.05_5 \text{ cp}, \qquad (5)$$

with an estimated precision of ± 0.01 cp. If and when the experimental range of viscosity measurements is extended (data on $\eta_{\text{sat vap}}$ of Na and K are particularly desirable) adjustments of the above values can be made.

Many years ago Kammerling Onnes (see *10*, p. 620) derived from van der Waals's theorem the following expression for the critical viscosity, η_{crit}, of a liquid:

$$\eta_{\text{crit}} \text{ (in centipoise)} = K \frac{\sqrt{M\,T_{\text{crit}}}}{V_{\text{crit}}^{2/3}}, \qquad (6)$$

where M is its molecular weight and V_{crit} its critical molar volume.

Using our values for sodium and potassium we can calculate the Onnes constant, K, for alkali metals; it equals 70×10^{-4}, if η is in centipoises (*12*). We thus obtain, using our values for T_{crit} and V_{crit} (see *5*, p. 784, Table IV) of Rb and Cs:

$$\eta_{\text{crit}} \text{ of Rb} = 0.074 \text{ cp} \qquad (7)$$

and

$$\eta_{\text{crit}} \text{ of Cs} = 0.080 \text{ cp} \qquad (8)$$

The values of η_{crit} parallel those of D_{crit} of the alkali metals; potassium, as in its density, shows the lowest value for the critical viscosity. This is not only true when compared to the other alkali metals, but even with most other metals, in view of Onnes's relation.

The above is not true for the *kinematic* critical viscosities; they are as follows, in centistokes: Na = 0.40, K = 0.33, Rb = 0.23, and Cs = 0.19 [Hg (*6*) = 0.082].

Now that the absolute critical viscosities of five metals have been estimated it is of interest to compare them with other types of compounds; a selected list taken from the well-known book of Hougen and Watson (*13*) is shown in table 4.

The noble gases, although monatomic liquids like the metals, all show lower values for η_{crit} than K; the same applies for homopolar molecules, such as H_2O, CO_2, or CCl_4. The high critical viscosities of most metals are due primarily to their unexpectedly high critical temperatures (*5*, *7*) and their small critical volumes; the high critical temperatures, in turn, are due to the much greater strength of the *metallic* bond in contrast to the much weaker forces in covalent or homopolar substances of van der Waals type.

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