

Viscosities of Liquid Sodium and Potassium, from Their Melting Points to Their Critical Points

Abstract. *The viscosities of liquid sodium and potassium were estimated up to the critical temperatures according to the method recently described for mercury. The critical absolute viscosity of sodium is 0.072 centipoise and that of potassium 0.055 centipoise, the estimated precision being plus or minus 0.01 centipoise. The critical absolute viscosities of metals are higher than those of covalent or homopolar substances of van der Waals type.*

The liquid alkali metals are of interest as heat transfer media in reactor technology and in space applications. Their so-called transport properties, particularly viscosity, have been the subject of detailed studies both in this country (1-3) and in the Soviet Union (4). The viscosity of sodium has now been measured up to 1200°K and of potassium, up to 1400°K. To cover the full liquid range, viscosities must be measured over another 1600°K in the case of sodium and about 1000°K for potassium in order to reach their criti-

cal temperatures, estimated as 2800°K for Na and 2450°K for K (5). In view of the difficulties encountered in measuring properties of highly reactive liquid metals at high temperatures, and particularly at high pressures, it will probably be many more years before the entire liquid range of the alkali metals is covered experimentally and before the values for the critical viscosities can be determined directly.

On the other hand, the absolute viscosity of liquid mercury can be estimated (6) up to its experimen-

tally determined critical temperature of 1733°K. It would seem ludicrous for anyone familiar with the usually rapid decrease of liquid viscosity with temperature to attempt to extrapolate the viscosity of any substance over a range of 1600° or even 1000°K. We now report, however, that in their behavior as liquids, sodium and potassium resemble mercury and represent a particularly simple case.

In a manner similar to mercury or any other thermally stable liquid, the absolute or dynamic viscosity of liquid sodium or potassium has to decrease from the end of the experimental temperature range to the critical point; on the other hand, the viscosity of the saturated vapor of the metal, in equilibrium with the liquid, increases over the entire range up to the critical point. The viscosity of saturated vapor can be calculated easily, in first approximation, from simple kinetic theory; it increases proportionally to \sqrt{T} in the lower temperature range and proportionally to T in the medium range (6). Therefore, the estimation of the critical viscosity becomes self-bracketing; as one extrapolates the viscosity, η , of the liquid and the saturated vapor beyond the experimental into the uncertain region, the range of conceivable η -values becomes very small. This is further supported by the fact that $\frac{1}{2}(\eta_{liq} + \eta_{sat\ vap})$, exactly like $\frac{1}{2}(D_1 + D_{sat\ vap})$ in the law of rectilinear diameter for liquid densities (5, 7), is practically a straight line function of T in the critical region.

Table 1. Absolute viscosity of sodium, from melting point (371.00°K) to critical point (2800°K).

T (°K)	η (10 ⁻² poise)	ν (cm ³ /g)	$\eta\nu^{1/3}$ (10 ³ poise cm ³ /g ^{-1/3})	1/T ν [10 ³ g/ (cm ³ ·°K)]
<i>Experimental range</i>				
371.00	0.690	1.078, 75	7.0766	2.4987
473	.450	1.106, 56	4.6544	1.9106
573	.340	1.135, 72	3.5482	1.5366
673	.278	1.166, 86	2.9268	1.2734
773	.239	1.200, 34	2.54057	1.0776
873	.212	1.236, 25	2.2754	0.9266
973	.193	1.274, 37	2.0925	.8065
1073	.179	1.315, 79	1.9615	.7083
1173	.167	1.360, 54	1.8505	.6266
1203	.164	1.373, 62	1.8230	.6052
<i>Extrapolated range</i>				
1400	0.147	1.4705	1.67	0.486
1600	.134	1.5898	1.57 ₁	.393
1800	.123	1.730 ₁	1.48	.321
2000	.115	1.898	1.42	.264
2200	.106	2.128	1.37	.214
2400	.099	2.421	1.33	.172
2600	.091	2.89 ₉	1.29	.133
2700	.086	3.30 ₉	1.27	.112
2800	.069	5.71 ₄	1.23	.062 ₅

Table 2. Absolute viscosity of potassium, from melting point (336.9°K) to critical point (2450°K).

T (°K)	η (10 ⁻² poise)	ν (cm ³ /g)	$\eta\nu^{1/3}$ (10 ³ poise cm ³ /g ^{-1/3})	1/T ν [10 ³ g/ (cm ³ ·°K)]
<i>Experimental range</i>				
336.9	0.560	1.2062 ₇	5.961 ₂	2.4606
400	.384	1.22911	4.113 ₄	2.0340
500	.276	1.26711	2.986 ₆	1.5784
600	.221	1.3075 ₃	2.416 ₆	1.2747
700	.185	1.3506 ₂	2.045 ₀	1.0577
800	.162	1.3966 ₅	1.810 ₄	0.8949 ₇
900	.147	1.4459 ₂	1.6623	.7684 ₆
1000	.132	1.4988 ₀	1.5106	.6672 ₀
1100	.121	1.5556 ₉	1.4020	.5843 ₈
1200	.113	1.6170 ₇	1.3264	.5153 ₃
1300	.106	1.6835 ₀	1.2610	.4569 ₁
1400	.100	1.7556 ₁	1.2064	.4068 ₇
<i>Extrapolated range</i>				
1600	0.092	1.9417	1.150	0.3219
1800	.084	2.1739	1.085	.2555
2000	.077	2.500	1.0495	.2000
2200	.071	2.94 ₁	1.015	.1546
2400	.062	3.92 ₂	0.975	.1062
2450	.05 ₂	5.88 ₂	0.940	.0694

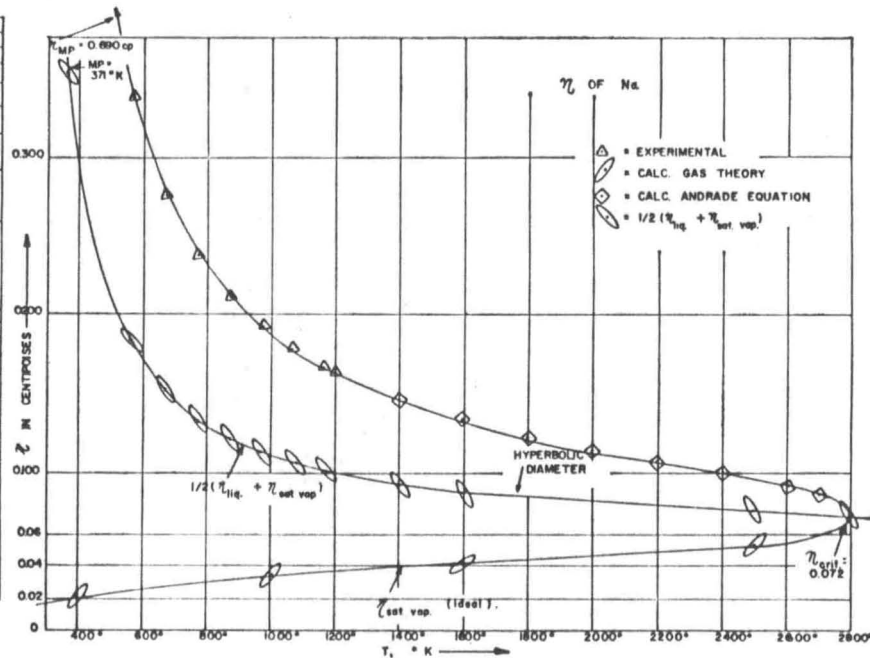
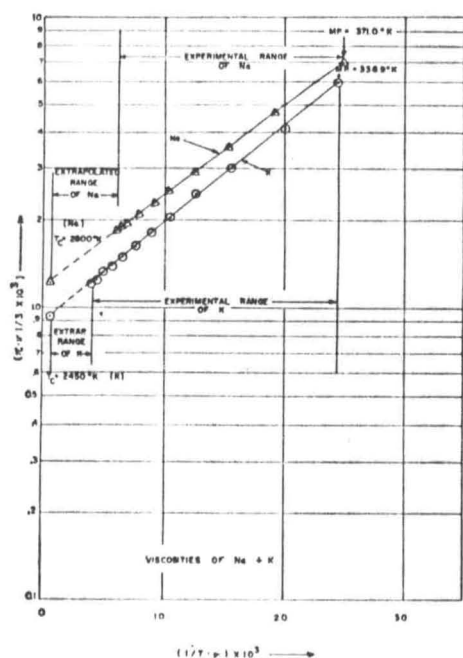


Fig. 1 (left). Dynamic viscosities of sodium and potassium in the form of an Andrade plot (8). Fig. 2 (right). Experimental and calculated viscosity of sodium from the melting point to the critical point.

We proceeded as follows. First we correlated all available liquid η -measurements over the whole experimental temperature range (6) by using Andrade's so-called II-equation (8), that is,

$$\eta v^{1/3} = A e^{c/vT}, \quad (1)$$

where A and c are constants of a particular liquid, η (in poises) being its viscosity and v (in cm^3/g) its specific volume at the temperature T in degrees Kelvin. A plot of $\log(\eta v^{1/3})$ versus $1/(vT)$ is a straight line.

The data for η and v for liquid sodium were taken from Sittig's monograph (9), from the chapter on carefully evaluated physical properties of sodium. For η of liquid potassium we depended primarily on the measurements of Ewing *et al.* (1, 2) up to approximately 800°K and on those of Lemmon *et al.* (3) from approximately 800° to 1400°K; v or D (its density), up to about 1500°K, are from Ewing *et al.* (3). The densities beyond the experimental up to the critical point were estimated as described earlier (5, 7).

When the II-Andrade equation had been set up from the experimental data, it was extrapolated to the critical point and values of viscosity were calculated at set temperatures. All of the experimental data and the variables—that is, $\eta v^{1/3}$ and $1/(vT)$ calculated and η and v data estimated—

are tabulated in Tables 1 (for Na) and 2 (for K).

The two II-Andrade equations—that is, for K and Na—are plotted in Fig. 1; both Na and K, like Hg and most other liquids, follow the relationship demonstrated by Andrade's second (II) equation. Since Andrade showed that this relationship holds up to the critical point, we also extrapolated the Na- and K-lines to their respective critical temperatures ($\times D_{\text{crit}}$, or critical density). The extrapolated range, because of the

nature of the Andrade equation, is very short compared to the experimental range. The viscosities (see column 2 of Tables 1 and 2) up to the critical point were then calculated from the values of $(\eta v^{1/3})$, as read off a large-scale plot of Andrade's straight line, and the estimated v (or D) of Na and K, respectively (see column 3 of Tables 1 and 2).

Both the experimental and calculated viscosities of Tables 1 and 2 are plotted against T in Figs. 2 and 3. The lower curves in these figures are for the viscosity of the saturated vapor, in equilibrium with the liquid metal. No experimental data on these viscosities are available, to our knowledge; work was stopped on this program at Battelle (see 3, p. 58). Fortunately, metal vapors can be expected to behave as the simple kinetic theory predicts (see 10), at least in the low temperature range, thus

$$\eta_{\text{sat vap}} \text{ (in poises)} = 2.6693 \times 10^{-5} \sqrt{AT/\sigma^2} \quad (2)$$

Table 3. Viscosities of saturated vapor ($\eta_{\text{sat vap}}$) of sodium and potassium at set temperatures, calculated with the use of Pauling's diameter of the sodium atom, 3.46 Å, and potassium atom, 4.374 Å, in centipoises.

T (°K)	Na	K
400	0.021 ₃	0.017 ₅
1000	.033 ₇	.027 ₆
1600	.042 ₇	.034 ₀
2500	.053 ₂	

Table 4. Absolute η_{crit} in micropoises (μp) (14) of various substances.

Noble gases	η_{crit} (μp)	Hydrides	η_{crit} (μp)	Oxides and chlorides	η_{crit} (μp)
He	25.4	H ₂ O	495	CO ₂	334
Ne	156	CH ₄	159	SO ₂	411
Ar	264	<i>n</i> -octane	259	CCl ₄	413
Kr	396	NH ₃	309		
Xe	490				

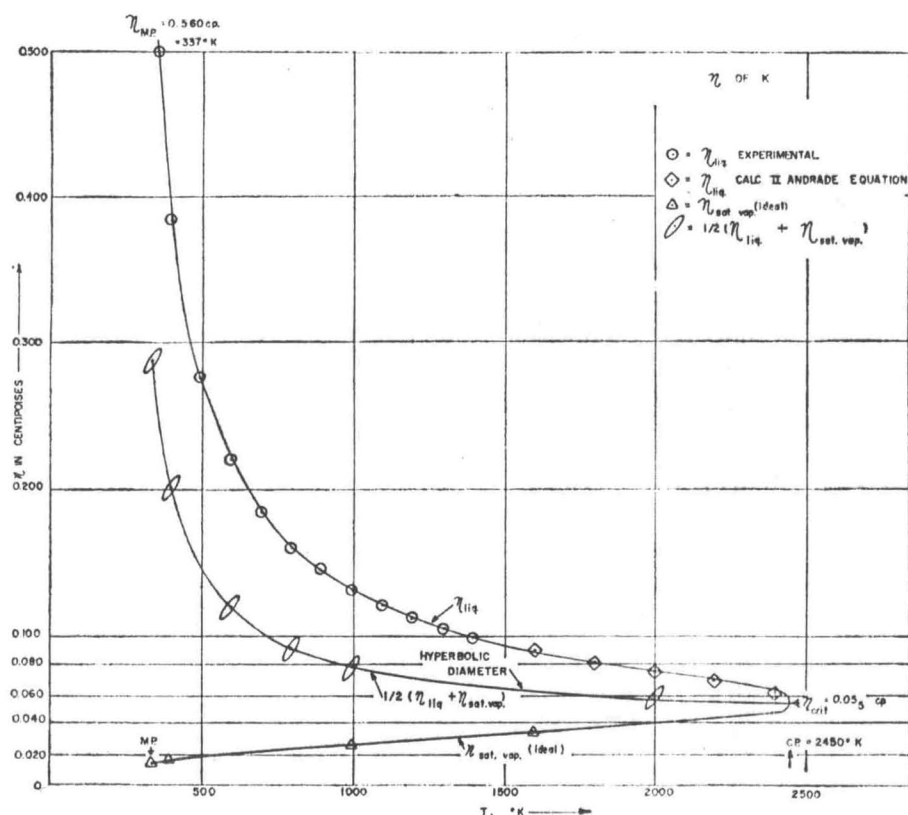


Fig. 3. Experimental and calculated viscosity of potassium from the melting point to the critical point.

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 cor-

relate 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,

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

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:

$$\eta_{\text{crit}} \text{ of Na} = 0.072 \text{ cp} \quad (4)$$

and

$$\eta_{\text{crit}} \text{ of K} = 0.053 \text{ cp}, \quad (5)$$

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:

$$\eta_{\text{crit}} \text{ (in centipoise)} = K \frac{\sqrt{MT_{\text{crit}}}}{V_{\text{crit}}^{2/3}} \quad (6)$$

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:

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

and

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

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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References and Notes

1. C. T. Ewing, J. A. Grand, R. R. Miller, *J. Am. Chem. Soc.* **74**, 11 (1952); *J. Phys. Chem.* **58**, 1086 (1954).
2. C. T. Ewing, J. P. Stone, J. R. Spann, E. W. Steinkuller, D. D. Williams, R. R. Miller, "High Temperature Properties of Sodium and Potassium," *12th Progress Report for U.S. Naval Research Laboratory, NRL Rept. 6094* (Washington, D.C., 9 June 1964).
3. A. W. Lemmon, Jr., H. W. Deem, E. A. Aldridge, E. H. Hall, J. Matolich, Jr., J. F. Walling, "Engineering Properties of Potassium," *NASA CR-54017, BATT-4673-Final* (Battelle Institute, Columbus, Ohio, 1963).
4. I. I. Novikov et al., *J. Nucl. Energy* **4**, 387 (1957).
5. A. V. Grosse, *Science* **140**, 784 (Table 4) (1963).
6. ———, *J. Phys. Chem.* **68**, 3419 (1964).
7. ———, *J. Inorg. Nucl. Chem.* **22**, 23 (1961).
8. E. N. da C. Andrade, *Phil. Mag.* **17**, 698 (1934); both his I and II equations are also fully discussed in ref. 7.
9. M. Sittig, "Sodium, Its Manufacture, Preparation and Uses," *Am. Chem. Soc. Monogr. No. 133* (Reinhold, New York, 1956), pp. 456-461.
10. J. O. Hirschfelder, C. F. Curtiss, R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954), p. 14.
11. L. Pauling, *The Nature of the Chemical Bond* (Cornell Univ. Press, Ithaca, N.Y., ed. 3, 1960), p. 403.
12. For mercury, the constant is 83×10^{-4} ; thus it may change to some extent in the various families of the periodic system.
13. O. A. Hougen and K. M. Watson, *Chemical Process Principles* (Wiley, New York, 1943), vol. 3, p. 873.
14. A. V. Grosse, *Inorg. Chem.* **1**, 436 (1962).
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