Reports

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 critical 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 experimentally 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.

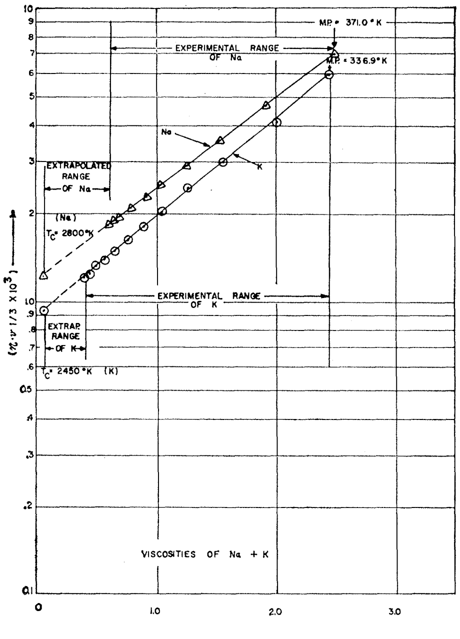
In a manner similar to mercury or any other thermally stable liquid, the absolute or dynamic viscosity of liquid sodium or potassium has to decrease from the end of the experimental temperature range to the critical point; on the other hand, the viscosity of the saturated vapor of the metal, in equilibrium 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 ½ ($\eta_{\text{liq}} + \eta_{\text{sat vap}}$), exactly like ½ ($D_{\text{l}} + D_{\text{sat vap}}$) 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)	v (cm³/g)	$\eta v^{1/3}$ (10^3 poise cm/g$^{-1/3}$)	$1/Tv$ [10^3g/(cm³ · °K)]
		Experimental range		
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
		Extrapolated range		
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_0	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)	v (cm³/g)	$\eta v^{1/3}$ (10^3 poise cm/g$^{-1/3}$)	$1/Tv$ [10^3g/(cm³ · °K)]
		Experimental range		
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_8	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	$.5843_5$
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	$.4068_7$
		Extrapolated range		
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



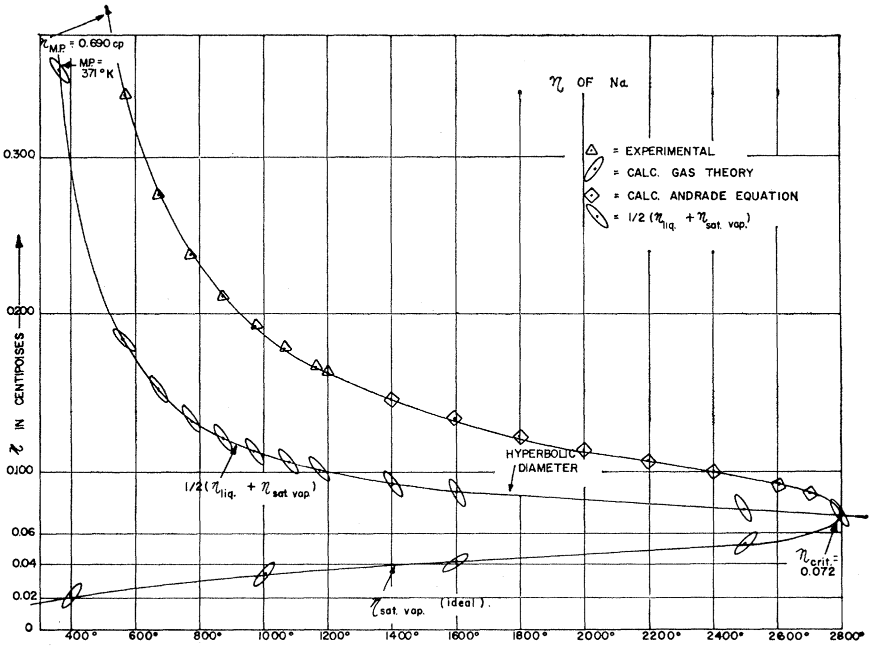


Fig. 1 (left). Dynamic viscosities of sodium and potassium in the form of an Andrade plot (*8*). Fig. 2 (right). Experimental and calculated viscosity of sodium from the melting point to the critical point.

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,

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

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_{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).

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_8 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	$.042_6$	$.034_0$
2500	$.053_2$	

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

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

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_2O	495	CO_2	334
Ne	156	CH_4	159	SO_2	411
Ar	264	*n*-octane	259	CCl_4	413
Kr	396	NH_3	309		
Xe	490				

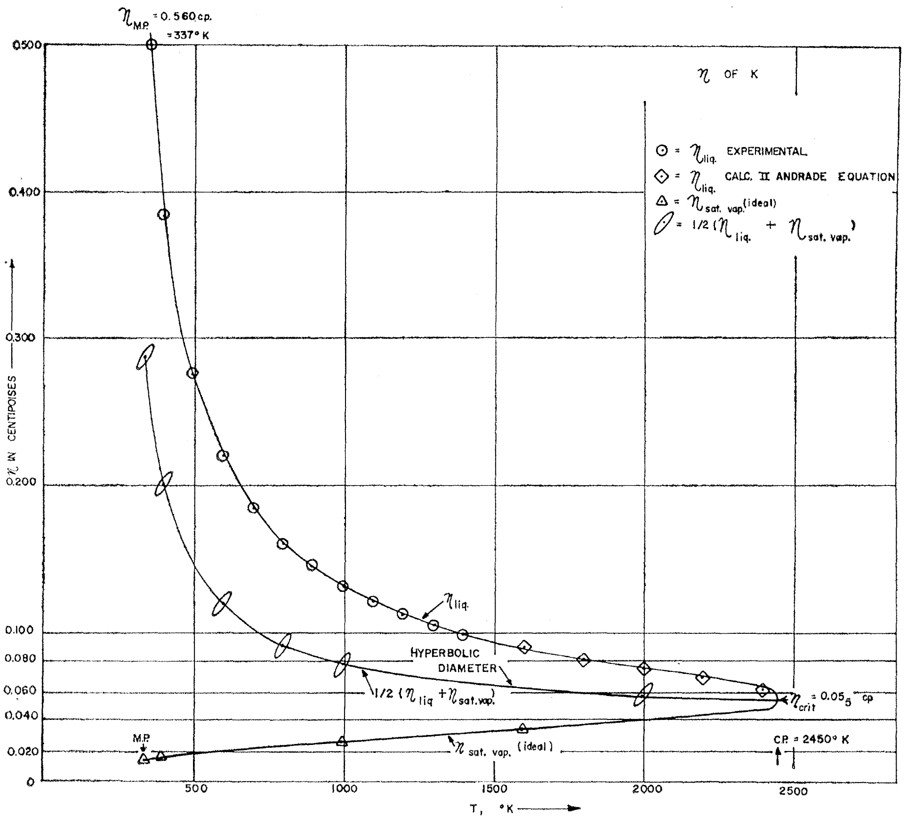


Fig. 3. Experimental and calculated viscosity of potassium from the melting point to the critical point.

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 $\eta_{\mathrm{sat\,vap}}$ increases proportionally to T.

We have found that the $\eta_{\mathrm{sat\,vap}}$ 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 $T_{\mathrm{red}} = 0.85$ to the critical point, that $\eta_{\mathrm{sat\,vap}}$ 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,

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

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:

$$\eta_{\mathrm{crit}}\ \text{of Na} = 0.07_2\ \text{cp} \tag{4}$$

and

$$\eta_{\mathrm{crit}}\ \text{of K} = 0.05_5\ \text{cp}\ , \tag{5}$$

with an estimated precision of ± 0.01 cp. If and when the experimental range of viscosity measurements is extended (data on $\eta_{\mathrm{sat\,vap}}$ 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:

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

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:

$$\eta_{\mathrm{crit}}\ \text{of Rb} = 0.074\ \text{cp} \tag{7}$$

and

$$\eta_{\mathrm{crit}}\ \text{of Cs} = 0.080\ \text{cp} \tag{8}$$

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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15. This work was supported by AEC contract AT(30-1)-2082.

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Superconducting Gallium Antimonide

Abstract. *A metallic phase of gallium antimonide, obtained by quenching at approximately 120 kilobars to 77°K and then releasing pressure, is a superconductor. The transition temperature depends on the annealing conditions; for samples annealed at 250°C under pressure before quenching, it is 4.24° ± 0.10°K, and H_{c2} (the critical field) equals 2640 gauss at 3.50°K. This temperature is higher than the 2.1°K reported for metallic indium antimonide.*

Gallium antimonide transforms from a semiconducting to a metallic state at approximately 70 kb at 25°C (*1*). X-ray powder photographs taken at high pressures show that the metallic phase has a structure similar to that of white tin (*2*). Recently the high-pressure phase has been retained by quenching the sample to 77°K before releasing pressure (*3, 4*). X-ray powder photographs taken at 77°K and 1 bar confirm the "white tin" structure and indicate that the high-pressure phase has been retained (*3*). Because the metallic phase of indium antimonide is superconducting at 2.1°K (*5*), we have determined the superconducting properties of metallic gallium antimonide in order to compare them with those of InSb.

Three different sources of gallium antimonide were used: (i) single-crystal material from Merck and Co., (ii) single-crystal GaSb doped with about 0.01 percent Te to reduce the possibility of excess gallium (*6*), and (iii) *p*-type polycrystalline material from American Smelting and Refining Co. (Asarco). The samples were compressed between tungsten carbide anvils with 2.4-mm faces to an average pressure of 120 kb and then cooled to 77°K before pressure was released; some were annealed by heating the anvils before quenching. The resulting samples were discs ~ 0.05 mm thick and 2.5 mm in diameter. The samples were transferred at 77°K to a helium cryostat and tested for superconductivity by the alternating-current method (*7*).

Superconducting properties of the quenched gallium antimonide apparently depend on the annealing conditions (Table 1). The transition temperature, T_c, and the hardness (that is, the relative strength of the magnetic field necessary to destroy the superconducting state) vary differently with annealing. Annealing at temperatures above 100°C causes T_c to drop from 5.9° toward 4.2°K; annealing at 50°C appears to make the samples magnetically softer. An annealed and an unannealed sample were reconverted by warming them to room temperature. X-ray powder photographs of the reconverted material showed two broad halos centered around the first few lines of the zinc-blende structure. These samples were tested for superconductivity, and the negative result indicated that the retained phase is responsible for the observed superconductivity. X-ray diffraction patterns taken at 77°K of annealed (200°C) and unannealed samples show the "white tin" structure. The data were not sufficiently accurate to determine whether there was a small systematic variation in lattice parameter with annealing. The samples annealed at 200°C also showed two faint additional lines at 3.3 and 1.65 Å. These lines may be attributable to small amounts of $GaSbO_4$, but when an annealed sample was reconverted by heating for 1 hour at 200°C an x-ray photograph showed only the diffraction lines of the zinc-blende form of GaSb. If the additional lines at 3.3 and 1.65 Å were from $GaSbO_4$ they should have appeared in the film of the reconverted material.

The large change in T_c for GaSb observed on annealing may result from an order–disorder transition or from the relief of strains in the sample. The extra faint lines observed in the annealed samples may be superstructure lines; for example, the 111 and 222 reflections for a cell with the *c*-axis of the "white tin" structure doubled. However, available data do not permit an unambiguous description.

It is also known that strain can substantially change the transition temperature. For example, a difference of > 1°K was observed in annealed and unannealed specimens of Nb containing 10 percent Cr (*8*). There was similar change in samples of InTe quenched from high pressures and tem-

Table 1. Superconductivity of GaSb; eight independent experiments.

Sample	T_c (°K)	H (gauss)	Annealing		Source
			Temp. (°C)	Time (min)	
2544	4.20–4.28 3.46	0 2640	250	60	Merck
2522	4.24–4.38 3.82 3.50	0 1640 2640	200	90	Te "doped"
2530	4.24–4.38 4.12	0 660	200	15	Merck
2529	4.45–4.90 (4.2 ± 0.5)*	0 (1000)	100	45	Merck
2534	5.85–6.05 (3 ± 1)*	0 (4600)	50	30	Asarco
2519	5.85–6.15 5.44	0 4600			Te doped
2523	5.75–6.05	0			Merck
2507	5.40–6.15	0			Merck

* Obtained by cycling the magnetic field at about constant temperature.