

perature behavior as well as a very strong influence of pressure on solubility. The smoothed atmospheric pressure results were so low that they could not be plotted on Figure 4.

The density results are compared with data for the pure solvents in Figures 5 and 6. As shown, at low temperatures, the small amount of dissolved solute causes a small decrease in solvent density. As temperature increases, solubility increases, and the density departure becomes larger.

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Kinematic Viscosity of Liquid Rubidium from 67° to 688° C.

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The kinematic viscosity of pure rubidium was measured from 67° to 688° C. in an all-metal capillary viscometer. The calibration of the apparatus without the use of a reference fluid is described, and experimental results are compared with low-temperature data for rubidium and with data for potassium and sodium. The correlated kinematic viscosity of rubidium, in centistokes, may be expressed in terms of temperature, in degrees Kelvin, as: $\log (\mu/\rho) = 250/T - 1.15$.

THE ANTICIPATED USE of alkali metals as working fluids, heat transfer media, and lubricants in high-temperature energy-conversion systems has spurred considerable research on the thermophysical properties of these fluids. However, there are still many areas in which reliable data are meager or lacking. Experimental measurement of liquid alkali-metal viscosity is in progress in several laboratories, and new experimental data have been reported recently for potassium (17). The viscosities of cesium, potassium, sodium, and lithium have been measured at temperatures as high as 1150° C. (for potassium) by damped torsional oscillation methods (1, 2, 8, 9, 17), and that of sodium has been determined to 600° C. by capillary viscometry (4, 5). On the other hand, the experimental viscosity of rubidium has not been reported for temperatures above 220° C.

As part of an Air Force sponsored research program on the influence of contaminants in liquid alkali-metal systems, an all-metal capillary viscometer has been developed in this laboratory. Extensive viscosity measurements have been made on pure rubidium from 67° to 688° C., and it is the purpose of this paper to present the resulting experimental kinematic viscosity data.

EXPERIMENTAL APPARATUS AND MATERIALS

Rubidium Samples. Two batches of pure rubidium were obtained commercially for use in this program. Cesium represented the major impurity in each batch, being present to the extent of 0.4 and 0.02 wt. per cent, respectively. The rubidium was analyzed for trace metal constituents by emission spectroscopy; for alkali metals

Table I. Analyses of As-Received Rubidium

Nominal Purity, wt. % Constituent, p.p.m.	Batch No. 1			Batch No. 2		
	Supplier 99.5+	This Work		Supplier 99.9+	This Work	
		Emission spectroscopy	Other methods		Emission spectroscopy	Other methods
O	50
C	119
Al	...	<7	...	8	40	...
B	...	<70	...	<49	<70	...
Ba	<5
Ca	...	31	...	6	45	...
Cu	...	7	...	4	9	...
Cr	...	<3	<3	1	<3	<3
Fe	...	<7	<5	24	<7	12
Mg	...	9	...	<2	9	...
Mn	4
Ni	...	<6	<3	<2	<6	<3
Pb	<2
Si ^a	...	250	...	31	950	...
Sn	<10
Sr	<2
Ti	<2
Tl	<5
Li	30	<49	...	20
Na ^a	...	900	110	<196	900	680
K	...	<1400	200	<196	<1400	200
Cs	~4000	...	3100	216	...	300

^aSi and Na values probably are high because of contact with glassware during analysis.

by flame photometry; for Cr, Fe, and Ni by colorimetry; and for carbon by a combination of wet oxidation and gas chromatography. The results of these analyses are presented in Table I.

With the exception of wet-analysis procedures, all alkali-metal handling and transfer operations were conducted in an atmosphere of pure argon. In most cases, the 99.996 per cent purity argon was bubbled through sodium-potassium eutectic (NaK 78) in order to remove possible traces of oxygen and moisture. Systems were vacuum-pressure cycled repetitively with this argon, in order to minimize residual atmospheric contamination, prior to filling with liquid rubidium.

Capillary Viscometer. A stainless steel, gravity-flow capillary viscometer was developed as part of this research program. The basic unit, which is illustrated in Figure 1, comprises a liquid-metal reservoir (0.635 cm. I.D. by 9.85 cm. high), a helically coiled capillary tube (0.068 cm. I.D. by 125 cm. long by 3.18 cm. coil diameter), and a liquid receiver (22 cc. volume). The lower end of the capillary is "belled," to create a suspended level similar to that in the Ubbelohde viscometer (15) and thus eliminate surface tension corrections of the capillary outlet as well as any question of the lower level placement. In operation, this illustrated portion of the apparatus is surrounded by a pair of semicylindrical electric heaters capable of operating at temperatures up to 1200°C. The entire apparatus is mounted upon a special swivel support which permits 360° rotation in a vertical plane.

Experimental viscosity measurements are based upon determinations of the rate at which the reservoir liquid level descends after the pressure in the reservoir and in the receiver is equalized through an external valve. The changing liquid-level position is detected by measurement of the changing electrical resistance of the reservoir as the liquid-metal "shunt" recedes.

Analysis of Capillary Viscometer. The developed capillary viscometer has certain features which affect the method of calculating viscosity results. The most important feature is the use of a coiled capillary, which requires the use of a semiempirical correction factor developed by White (19)

and refined by Mencik (10). This correction factor, which is presented in Figure 2, has been largely ignored in many viscometer studies. It can be neglected without appreciable error at very low Reynolds numbers, but it becomes significant even at moderate Reynolds numbers such as those encountered in this work.

In most viscometric work, the instrument is calibrated with a standard fluid and the calibration is reduced to "viscometer constants", usually two in number, which express the dimensions of the apparatus and the kinetic energy correction. This approach was not considered suitable for present purposes, for two reasons. First, the "White factor" cannot be adapted readily to incorporation as a "viscometer constant." Second, there is no well-standardized fluid that can be used as a reference point for calibrating this instrument. Data on the viscosity of alkali metals are rather scarce, particularly at high temperatures, and in some cases are contradictory. Unfortunately,

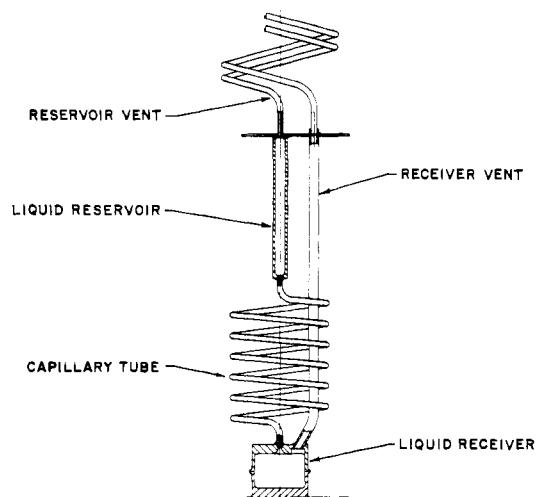


Figure 1. Basic components of liquid-metal viscometer

mercury cannot be used for calibration (the electrical liquid-level gage will not function properly with mercury, which does not wet the reservoir walls), and nonmetallic fluids are unusable because of their insufficient electrical conductivity.

The development of a reliable method for calculating viscosities from capillary flow data without the use of a "standard fluid" was contingent upon including all pertinent parameters in the calculation. Therefore, detailed theoretical relationships were derived for converting experimental measurements into kinematic viscosity data, using known or estimated values of the thermal expansion of type 316 stainless steel (11) and the surface tension (18) and density (15) of pure rubidium. The derived equation thus employed is:

$$\mu/\rho = \pi g r_i^4 H t_i / 8 L q_i \quad (1)$$

where H , the corrected head, is defined as:

$$h = h_m E - h_c - h_\gamma = h_m E - m R^4 (h_1 - h_2)^2 E^2 / t_i^2 r^4 - 2\gamma / g \rho R E \quad (2)$$

The "White factor", C , must then be applied to the calculated viscosity in order to correct for capillary curvature. It will be observed that the function of C vs. k is not adaptable to direct incorporation in the viscosity calculation equations, as it includes Re which in turn includes μ ; thus, iteration is necessary. This is accomplished by first computing μ/ρ , then using this μ/ρ to calculate k and find C from White's correlation or from the tabulated values. If this C (which is designated as C_1) differs appreciable from unity, a new value, $k_2 = k_1 C_1$ is determined, and from this, a new value C_2 is found. This process is repeated until the solution converges; no more than four trials have been required in any case encountered. The final value of C is used as a correction factor:

$$(\mu/\rho) = (\mu_1/\rho) / C_{\text{final}} \quad (3)$$

where μ_1 is the viscosity calculated from Equations 1 and 2.

EXPERIMENTAL

Preliminary Studies with Sodium-Potassium Eutectic. Preliminary experimental viscosity measurements were made on NaK eutectic in order to confirm the efficacy of the viscometer apparatus. The NaK was filtered through a five-micron sintered stainless steel filter at room temperature prior to transfer into the viscometer to minimize its oxide content.

The recording potentiometer trace obtained in one of the NaK runs is reproduced in Figure 3 to illustrate the type of information directly produced during each viscosity run. It can be seen in this figure that a smooth transition in electrical resistance occurs as the liquid level moves between the full position (corresponding to about 240 microhms resistance) and the empty position (corresponding to about 940 microhms resistance). For the purposes of this illustration, a logarithmic curve was penciled in over the recorder trace in the transition region. This was done in order to demonstrate the extrapolation procedure used for obtaining the full and empty intercepts. The chart distance, along the time axis between the full and empty intercepts, is measured with an optical micrometer, and the efflux times is thereby obtained, since the chart speed is known. Knowing the temperature and efflux time, the previously derived calculation procedures are then employed to convert these measurements into viscosity data.

The results of the room temperature NaK viscosity measurements demonstrated close agreement with data reported by Ewing, Grand, and Miller (4, 5). This is gratifying in view of the fact that the viscosity data were computed from efflux times without the necessity of prior calibration with a reference fluid.

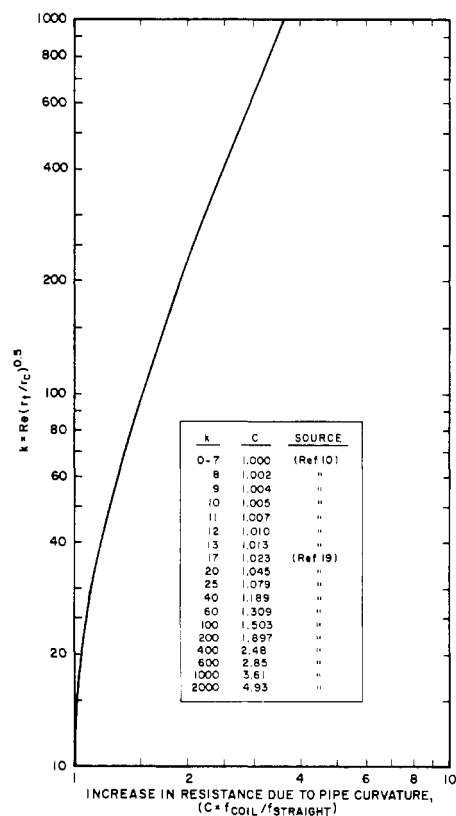


Figure 2. "White-Mencik" correlation of coil-curvature effect

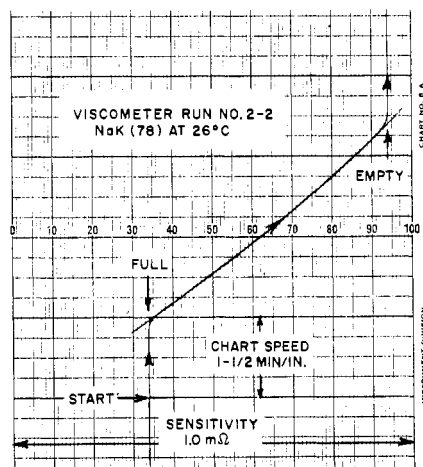


Figure 3. Sample time-of-efflux chart for capillary viscometer

Viscosity of Pure Rubidium. A series of experiments was conducted to obtain viscosity data on rubidium, and the results of these experiments are summarized in Table II.

About 100 viscosity points were measured with the first batch of pure rubidium at various temperatures from about 103–688°C. About 80 additional viscosity measurements were then made at temperatures from about 67–440°C. on the second batch of pure rubidium. Replicate experimental values demonstrated typical standard deviations of less than 1%.

All of these data for pure rubidium are presented in Figure 4 along with prior experimental values. These results, which appear quite reasonable, represent the first experimental rubidium viscosity measurements reported for temperatures greater than 220°C.

Table II. Summary of Experimental Viscosity Data for Pure Rubidium

Reservoir Temp., ° C.	Temperature Difference (Reservoir-Receiver), ° C.	Kinematic Viscosity, Centistokes	No. of Runs Averaged
Batch No. 1			
288.7	18.8	0.203	9
593.3	20.1	0.134	4
181.6	11.6	0.281	3
173.6	6.6	0.273	5
172.5	8.8	0.271	13
293.1	15.2	0.199	12
542.0	15.8	0.143	5
540.2	16.5	0.146	3
297.2	17.1	0.193	6
409.4	18.2	0.164	12
105.3	8.6	0.325	3
102.9	7.6	0.323	8
671.8	15.2	0.127	3
688.0	15.1	0.133	7
Batch No. 2			
170.5	13.6	0.277	12
440.3	12.0	0.161	12
95.6	6.2	0.339	12
344.0	12.7	0.180	11
238.4	9.5	0.227	12
66.8	3.8	0.384	4
97.6	4.7	0.336	4
134.2	6.9	0.291	4
156.7	10.4	0.266	4
183.5	13.4	0.249	4
207.2	10.3	0.233	4

RESULTS AND DISCUSSION

The measured kinematic viscosity values for rubidium are correlated *vs.* temperature quite well by the Arrhenius-type correlation shown in Figure 4. Although this type of relationship is known to apply to the self-diffusion coefficient (12), it is not usually applied to kinematic viscosity. Rather, it is customary to develop correlations of the logarithm of the absolute viscosity *vs.* reciprocal temperature or of the absolute viscosity divided by the cube root of the liquid density *vs.* the ratio of the density to the temperature (1, 2, 12, 13). The latter method was proposed by Andrade, based upon theoretical considerations. However, at least in the case of other alkali metals such as potassium and sodium, it has been observed that these conventional correlation methods do not yield linear Arrhenius-type plots (4, 5, 17).

Without resorting to detailed mechanistic considerations, it does not appear unreasonable to anticipate equivalent characteristics for self-diffusivity and kinematic viscosity (12). In fact, as is shown in Figure 4, the experimental kinematic viscosity data reported for liquid potassium and sodium by Walling and coworkers (17), and Ewing, Grand, and Miller (4, 5), respectively, also yield linear Arrhenius-type correlations. When the viscous-flow activation energy is derived from each of the correlations shown in Figure 4, the resulting values appear reasonable, being 1140, 1230, 1370 (cal./gram. atom) for rubidium, potassium, and sodium, respectively.

Based upon the correlation shown in Figure 4, the pure rubidium viscosity data may be expressed, with an average deviation of ± 3%, by the following relationship

$$\log (\mu / \rho)_{Rb} = 250 / T - 1.15 \quad (4)$$

for temperatures from near the melting point to 688° C., where μ / ρ is the kinematic viscosity in centistokes, and T is the temperature in degrees Kelvin. Similarly, the illustrated data for potassium and sodium may be expressed, respectively, as:

$$\log (\mu / \rho)_{K} = 270 / T - 0.96 \quad (5)$$

for temperatures from near the melting point to 1150° C., and:

$$\log (\mu / \rho)_{Na} = 300 / T - 0.93 \quad (6)$$

for temperatures from near the melting point to 600° C.

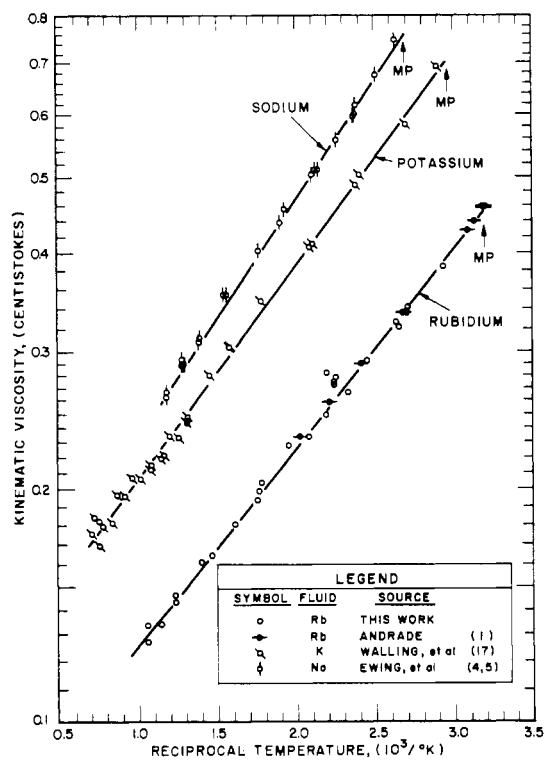


Figure 4. Comparison of experimental rubidium viscosity data with prior data

NOMENCLATURE

- C = "White factor" empirical
 E = linear thermal expansion factor for stainless steel (length at test temperature relative to length at room temperature)
 f = fluid friction factor
 g = acceleration of gravity, cm./sec.²
 h_1 = head with reservoir full, cm.
 h_2 = head with reservoir empty, cm.
 h_m = log mean head, cm.
 h_r = kinetic energy correction, cm.
 h_s = surface tension correction, cm.
 H = corrected head, cm.
 k = "White parameter," = $Re(r_1/r_c)^{0.5}$
 L = capillary length, cm.
 m = factor in kinetic energy correction = (1.12)
 q_f = efflux volume, cm.³
 r_1 = capillary radius, cm.
 r_c = radius of curvature of coil, cm.
 R = radius of reservoir, cm.
 Re = Reynolds number in capillary
 ρ = density, g./cc.
 t_f = efflux time, sec.
 T = absolute temperature, ° K.
 γ = surface tension, dynes/cm.
 μ = viscosity, centipoises

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Heat Contents and Thermodynamic Functions for Thallous Chloride Above Room Temperature

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Heat contents of solid and liquid TlCl were measured to 700° C. These were combined with literature data to calculate the absolute entropy and free energy functions of the condensed phases. Values of the same functions for gaseous TlCl were calculated from molecular constant data.

TO COMPLEMENT a study of the thermodynamics of vaporization of thallous chloride (2), it was necessary to have the heat contents of the condensed phases above room temperature. Goodwin and Kalmus (3) have reported values; however, it seemed worthwhile to repeat their measurements.

Thallous chloride was prepared by dissolving pure Tl (99.95% from American Smelting and Refining) in dilute

nitric acid and precipitating it with hydrochloric acid. The precipitate was collected on a sintered glass filter, then placed in a fused quartz bulb and distilled under pure, dry nitrogen. A sample of the material so prepared was analyzed for chloride and found to contain 14.78% Cl (theoretical 14.78%). About 10 grams were placed in a thin-walled platinum test tube and the end sealed with platinum solder. (The closure was tested by heating the sample above the