VISCOSITIES OF CESIUM, SODIUM, AND POTASSIUM NEAR THEIR FREEZING POINTS

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A vibration viscometer has been used to examine the viscosity of cesium (pure and technical grades) up to 200°C and the effects of oxygen on the viscosity. Dissolved oxygen raises the viscosity considerably, and the oscillation amplitude of the plate in the melt decreases considerably near the freezing point because oxides are deposited on the surface. The viscosity has been measured from 400°C to the freezing point and for potassium from 250°C to the freezing point. These metals show no anomaly in the temperature dependence of the viscosity when they have been purified by vacuum distillation.

This anomaly and the hysteresis near the freezing point would indicate structural changes in the liquid and the so-called precrystallization and after-melting.

Not much is known about the viscosities of liquid metals near their freezing points t*.

The above vibration method is automatic and continuous-reading, so it is well adapted to use near t*, even as close as 0.001°C. See [3-6] on the theory of the method, the measuring circuits, and the methods of measurement.

Cesium. Not much has been published [1, 2] on the viscosity of cesium; the results agree well, but only a few points have been recorded near t*.

We used metal containing not less than 99.996% Cs, <0.0018% K, <0.0003% Na, < 0.003% Ca, and <0.0012% Rb.

Gaseous impurities were removed by distillation at 10^{-5} mm Hg. The measurements were done in 99.97% helium at 1.2 atm. The viscometer was calibrated in helium at the same pressure.

Figure 1a shows η(centipoise) from 180°C to t*, where point 1 represents Cs alone, 2 represents Cs + 0.4% O_2, and 3 represents Cs + 1.5% O_2 (all figures by weight).

Temperatures below 100°C were provided by a liquid thermostat, while those above 100°C were provided by a resistance furnace. Various conditions of measurement were used: 1) at stationary points; 2) with slow cooling or heating (up to 0.05°C/min); 3) with fast cooling or heating (up to 10°C/min). All series were in agreement. The relative standard deviation from the smoothed curve was ±0.5%, and the error of measurement for the viscosity was estimated as ±1%. The values agreed with published ones (points 4 [1] and 5 [2]) within the error of experiment. The smoothed η (centipose) for the following relation to T (°K):

$$\ln \eta = -2.322 + 584/T$$

The viscosity was calculated via Basin's [8] data on the density.

We examined η with special care near t*. The apparatus allowed measurements to be made by steps of 0.01°C. The last measurement was made directly before solidification, which was detected from the plate ceasing to vibrate; the temperature of that measurement differed from t* by not more than 0.01°C.

Figure 2 shows the vibration amplitude as a function of T; the upper points 1 and 2 are for pure cesium, with points 1 for cooling and points 2 for heating. The relationship shows no anomalies, so there is no anomaly in η down to t*.

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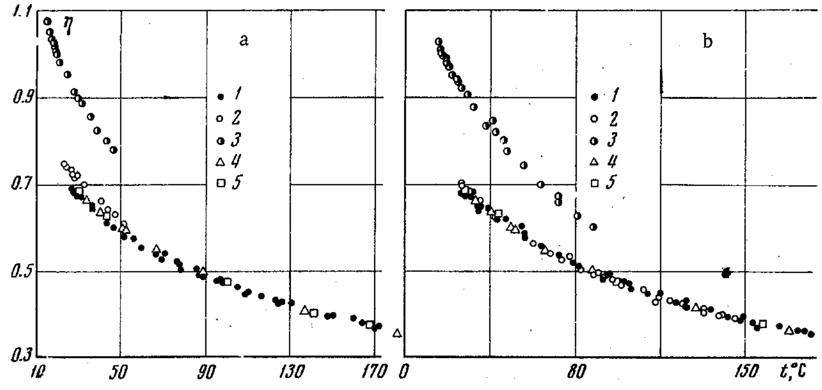

Fig. 1

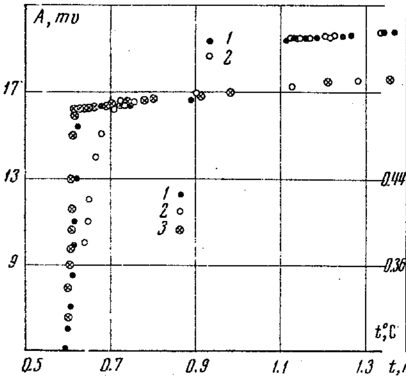

Fig. 2

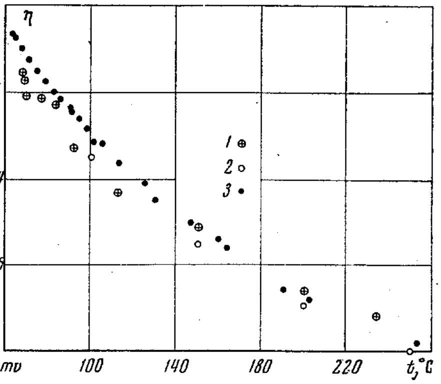

Fig. 3

We also examined qualitatively the effects of oxygen introduced above the metal. The completion of solution in the metal was deduced from the fall in the pressure to the initial level.

Dissolved oxygen raises η (Fig. 1a) and reduces t*. The above three oxygen contents correspond to t* of 27.8, 22.9, and 14.5°C, while the corresponding η at 35°C were 0.63, 0.66, and 0.82 cP.

The dissolved oxygen reduced the vibration amplitude as t* was approached. The lower points in Fig. 2 are for Cs + 1.5% O_2, with points 1 for slow cooling, points 2 for slow heating, and points 3 for stationary values during cooling. The effect is due to deposition of oxides on the plate, as was clear from use of a crucible with a viewing port. The vibration amplitude A as a function of temperature t was deduced from stationary points, with a halt of 15-20 min at each point (steps of 0.1°C). The amplitude fell steadily to zero from the value controlled by η, which would indicate that the proportion of solid in the melt varied from zero to unity. Then the knee on the A(t) curve indicates the liquidus t, while A = 0 represents t*.

The knee on A(t) during heating lies at a t higher than that for cooling (hysteresis), which might be due to differences between the deposition and dissolution processes or to concentration supercooling on the cooling branch. There were no singularities on the data curve for liquid cesium (cooling from 40 to 15°C over 1.5 h), mainly because the impurity content was low and very little heat is evolved when the solid is deposited.

Similar results were obtained with technical cesium (grade RÉTU 117-59, not less than 98%) purified by vacuum distillation. The main initial impurities were <0.5% K, <0.1% Ca, <0.05% Na, and <1% Rb, while the purified material had <0.013% K, <0.018% Na, and <0.12% Rb. The η for the purified material agreed to ±1.5% with those for the high-purity material and with the published data at all t (Fig. 1b).

We measured η for purified technical metal twice (on two samples). In neither case was there any anomaly in η (t) down to t*.

Addition of 1.5 wt.% oxygen increased η by about 30%, and the effects near t* were as for the pure metal.

Sodium. The published results for this metal are better than those for the other alkali metals, and the values from various sources agree well [9-11], but there are only a limited number of points up to 5-10°C above t*.

We made measurements between 400°C and t* on material containing not less than 99.974% Na, the main impurities being <0.013% K, <0.002% Rb, <0.0064% Cs, and <0.005% Ca (all figures by weight). Gaseous impurities were removed by distillation at 10^{-5} mm Hg. Measurements were made: 1) at stationary points; 2) with slow cooling and heating (5-10°C/h); 3) with fast cooling and heating (up to 500°C/h). All the series agreed within the spread of the points. About 40 measurements were made at stationary points, and the error of experiment was estimated as ±1.5%. The values (centipoise) are described (for T in °K) by

$$\ln \eta = -2.470 + 771/T$$

The results agree well with published values, especially those recommended in [9].

The region near t* was examined with special care; a slight supercooling was observed. The crystallization temperature was 97.7°C, while the melting point was 98.5°C, as determined from the plate vibrations. There were no anomalies in $\eta(t)$ down to the crystallization point.

Technical sodium (not freed from gaseous impurities by vacuum distillation) showed an anomaly in A(t), which was similar to that examined in detail for rubidium [6] and cesium; it was due to deposition of oxides and other impurities on the plate.

Potassium. There are many studies on the viscosity of potassium [1, 7, 10, 11], but there are 10-15% differences between the values up to 500°C. We used technical potassium (pure grade, 98.5%), whose main impurity was sodium. Impurities were removed by distillation at 10^{-5} mm Hg. The following were the main metallic impurities in the purified metal: <0.057% Na, <0.006% Rb, <0.003% Cs, and <0.006% Ca (not less than 99.93% K). The temperature conditions were as for sodium. The points had a spread of ±0.8%, and all the series recorded under different conditions agreed within that spread.

The points 3 in Fig. 3 show $\eta(t)$ for the distilled potassium, which at 150-250°C lie 1.5-2.5% above the values recommended by Fomin [1] (points 2 in Fig. 3) but which agree with Solov'ev's results [10] (points 1). Our results for the low-temperature range lie 3-5% above Fomin's values and somewhat above Solov'ev's. We estimated the error of measurement as ±1.5%. The following equation describes η (centipoise) as a function of T (°K):

$$\ln \eta = -2.455 + 636/T$$

No anomaly in $\eta(t)$ near the crystallization point was observed for the purified potassium. Technical (unpurified) material gave an anomaly in A(t), as for rubidium [6], cesium, and sodium, which was due to deposition of impurities on the plate.

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