

Effect of Isotopic Mass on Viscosity of Molten Lithium*

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The viscosity of the separated isotopes of molten lithium was measured by observing the damped oscillations of a torsion pendulum whose bob contained a spherical cavity filled with the material under test. For both Li^6 and Li^7 , the viscosity varies approximately as $\exp(B/T)$ over the temperature range 180 to 300°C; B has the value 458°K for Li^6 and 631°K for Li^7 . The viscosity of Li^6 is 4.18 ± 0.05 mP (millipoise) at 180.4°C, its melting point; of Li^7 , 6.00 ± 0.05 mP at 180.7°C, its melting point. A linear interpolation for Li^{nat} (7.4% Li^6 , 92.6% Li^7) gives 5.86 mP at 180.5°C, only slightly lower than the value of 6.02 mP reported earlier by Andrade and Dobbs. The ratio of the viscosity of Li^7 to that of Li^6 is 1.44 at the melting point, in contrast with the value of 1.08, the square root of the mass ratio, as predicted on simple theoretical arguments. Actually, a thorough dimensional analysis shows that the viscosity varies as $(mkT)^{1/2}$ times a complementary dimensionless function containing—among other arguments—the mass as a consequence of quantum effects. The function evidently depends strongly on these effects, as indicated not only by the present results on molten Li^6 and Li^7 , but also by the results of others on other isotopically-substituted liquids.

INTRODUCTION

EVEN though great progress has been made recently in the fundamental theory of the liquid state, most transport processes remain imperfectly understood. Isotopic mass appears to be a variable likely to contribute to an understanding of these complicated processes, since a given property is merely a function of isotopic mass, whereas it is a functional of atomic field. In this vein we have undertaken a study of the effect of isotopic mass on viscosity, with the separated isotopes Li^6 and Li^7 as the subject of investigation. Our experimental work consists of measuring the viscosity of each isotope over a temperature range not far above the melting point. The results are then considered in the light of a careful treatment of the problem by dimensional analysis, and in relation with work by others on other isotopically-substituted liquids.

EXPERIMENTAL CONSIDERATIONS

Apparatus

The high chemical reactivity of lithium and the paucity of its separated isotopes call for special procedures in measurement of viscosity. A suitable method, first used by Helmholtz and Piotrowski,¹ and since developed by other workers, is the observation of the viscous damping of a torsion pendulum whose bob has a hollow cavity filled with liquid. Figure 1 is a schematic diagram of the apparatus as we have adapted it. The bifilar tungsten-wire suspension² supports a bob con-

sisting of an inertia bar connected by a stainless-steel tube to a sample cell. The torsion pendulum is contained within an evacuated housing, the bottom of which is surrounded by a furnace to heat the sample cell. Windows in the housing allow passage of a light beam incident on a small mirror attached to the oscillating bob. The reflected beam emerges through another window onto a photoconductive-cell assembly that permits observation of the damped oscillations.

The sample cell is an austenitic (nonferromagnetic) type 446 stainless-steel cylinder with a 1-in.-diam spherical cavity at its center (cf. Fig. 2). The top of the cavity joins a vertical cylindrical cavity $\frac{1}{16}$ in. long and $\frac{5}{16}$ in. across. Into this neck are inserted radial vanes (not shown) to prevent motion of the sample material outside the spherical region. A stud on top of the cap is threaded to fit into a hole tapped into the upper part of the bob.

The furnace is noninductively wound, and is fed with alternating current from a proportional controller actuated by a recording self-balancing potentiometer sensing the indication of a thermocouple in the furnace wall. Eddy-current losses in the oscillating bob were shown to be negligible by observing the absence of change in residual damping when the furnace was switched on.

Samples

The separated isotopes were provided by the Isotopes Division of Oak Ridge National Laboratory, who also furnished isotopic and semiquantitative chemical analyses.³ The Li^6 sample contained 99.8% Li^6 , 0.2% Li^7 , atomic basis; the chemical impurities were Si 0.01%, Na 0.02%, and several others each less than 0.01%, atomic basis. The Li^7 sample contained 0.01% Li^6 , 99.9% Li^7 ; the chemical impurities were Al 0.01%, Sr 0.02%, and several others each less than 0.01%. At

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¹ H. Helmholtz and G. v. Piotrowski, Sitz. ber. Akad. Wiss. Wien, Math.-naturw. Kl. 40, 607 (1860).

² The wire was obtained from the General Electric Company through the cooperation of Dallas T. Hurd of the Advanced Development Engineering Section. By special arrangement, 2.5-m lengths were kept straight during shipping.

³ The help of Dr. P. S. Baker and E. B. Olszewski in redistilling the samples, analyzing them, and filling the sample cells is appreciated.

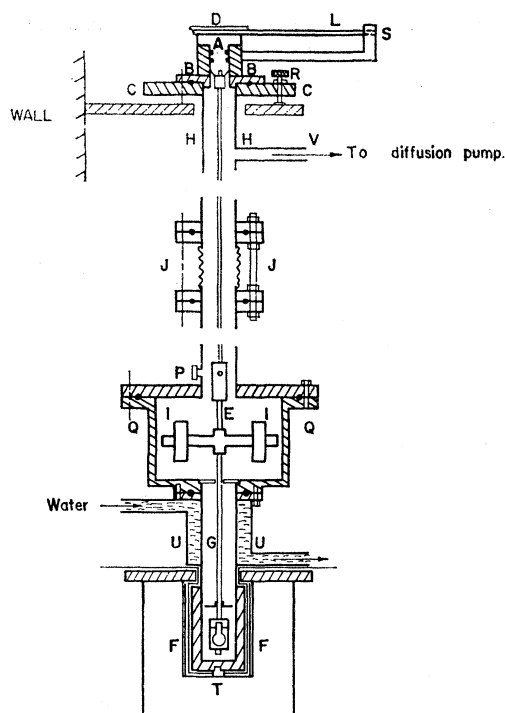


FIG. 1. General view of apparatus. The bifilar tungsten suspension is fastened to the head D at the top of the figure. The head is sealed into B, the top of the vacuum enclosure, with two O-rings at A. The head can be rotated with the aid of arm L carrying a scale S to measure the initial displacement. Leveling screws R allow adjustment of the collar C, carrying the brass vacuum enclosure H. The air can be evacuated from the chamber through V by a conventional vacuum system consisting of a diffusion pump and fore pump as well as associated valves, gauges, and traps. A bellows connection at J permits alignment of the lower part of the chamber to provide clearance between the pendulum and the enclosure. The window P allows light to fall on the mirror attached to the oscillating bob at E inside the brass chamber Q. There are two adjustable masses I which permit the moment of inertia to be varied conveniently. The sample cell, connected to the inertia bar through a stainless-steel tube G, is surrounded by a furnace F, which is controlled by a thermocouple at T. A water bath U and appropriate baffles on the stainless-steel tube G keep the upper section of the apparatus cool. The lower part of the apparatus can be removed with screws at Q allowing samples to be changed and adjustments made. The entire apparatus may be leveled, making the axis of rotation directly below the point of suspension, with the use of leveling screws R. The entire apparatus (with the exception of the furnace) is suspended from these leveling screws which are in turn resting on a shelf rigidly bolted to the wall.

the conclusion of our experiments, one of the samples was analyzed chemically in our own laboratory for possible contamination by the constituents of the sample cell. No impurities were found in amounts greater than those specified by the supplier.

To prepare the samples, lumps of the lithium were melted in a vacuum induction furnace. The molten metal was led into the spherical cavity in the stainless-steel cylinder that later was to be part of the bob of the torsion pendulum. The opening into the cylinder was closed with a stainless-steel cap over a gold gasket that remained in place as a hermetic seal throughout the experiments.

Experimental Procedure

The observed damping cannot be used directly in the analysis, since extraneous ("residual") damping occurs due to mechanical hysteresis in the suspension, imperfect vacuum, energy transfer to the support, and eddy-current losses from stray magnetic fields. Instead the observed damping must be corrected by subtracting from it the residual damping, obtained by observing the damping not resulting from liquid motion. In practice it is simplest to measure the residual damping at temperatures where the lithium is solid, rather than working with the empty cell. The observed value does not change much over the range from room temperature to the melting point, and we assume that it remains constant over the range of temperature covered. Since the residual damping is small, about $\frac{1}{10}$ the liquid damping, the error introduced must be very small.

The first step, then, is to observe the motion of the bob at temperatures below the melting point. The oscillation is started by rotating the suspension head by perhaps 3° , and then returning it immediately to the neutral position. The resulting motion is very nearly a damped sinusoid, with period τ_0 and logarithmic decrement δ_0 . The period is determined by observing successive passages of the light beam through the equilibrium position, with the aid of a photoconductive cell at the center of the swing. The logarithmic decrement δ_0 is calculated from the decreasing maximum excursion of the light beam, as observed by a movable photoconductive cell kept near the end of the swings. Following this run at a temperature below the melting point, the furnace is brought up to temperature. The thermal time constant is about 3 or 4 h, and ample time—about 24 h—is allowed for the apparatus to come to thermal equilibrium.

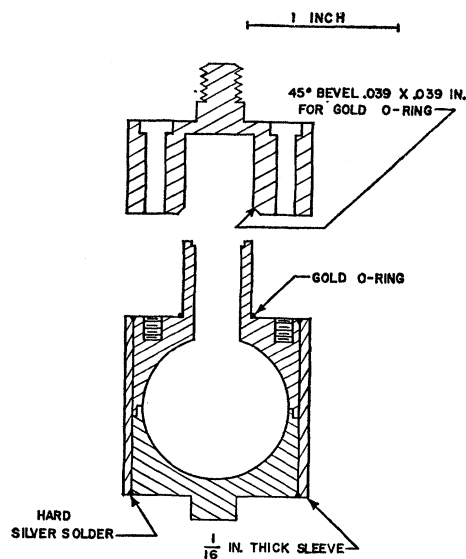


FIG. 2. Detail of sample container.

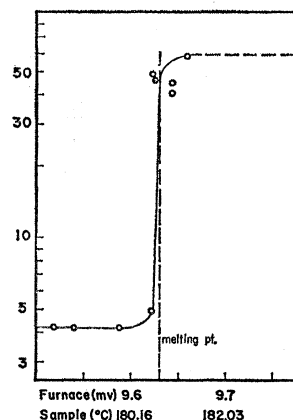


FIG. 3. Variation of logarithmic decrement with temperature near the melting point. Ordinate— $\delta \times 10^5$; abscissas—furnace thermocouple voltage and sample temperature.

The period τ and the logarithmic decrement δ are measured, and then transferred to punched tape along with values of the various other parameters. Appropriate corrections are made for thermal expansion of the sample and the cell. The viscosity η is extracted with the aid of MISTIC, a digital computer at Michigan State University.⁴ The calculation, a straightforward though tedious iteration, may be understood by reference to Andrade and Chiong.^{5,6}

The temperature actually observed is that of the thermocouple in a boss in the furnace wall (cf. Fig. 1). The temperature of the sample cell is inferred from the results of a static calibration with thermocouples cemented at three positions on the sample cell, and read against the furnace-wall temperature. An excellent check on the validity of this procedure is observation of the abrupt increase in damping as the lithium melts (cf. Fig. 3).

Results

A summary of the results for the measurements on the viscosity of Li^6 and Li^7 in the temperature range 180 to 285°C is given in Table I. The consistency of the data for an individual measurement can be seen from Table II, which shows the data taken at what was intended to be a constant temperature over a period of several days. The data presented here agree well with most of the data obtained on the same apparatus several months earlier.⁷ Figure 4 shows a plot of the data in Table I.

⁴ The help of Frank Taylor of Michigan State University with the experimental work and data processing is very much appreciated.

⁵ E. N. da C. Andrade and Y. S. Chiong, Proc. Phys. Soc. (London) **48**, 247 (1936).

⁶ A simplification of the calculation of Andrade and Chiong has been published recently by R. Roscoe, Proc. Phys. Soc. (London) **A72**, 576 (1958).

⁷ N. T. Ban and D. J. Montgomery, Bull. Am. Phys. Soc. **5**, 278 (1960). The preliminary value for Li^7 was the result of only one measurement before trouble developed with the sample container. Immediate repetition of the work on other samples of Li^7 gave values which agree well with the later results as reported in the present work.

TABLE I. Viscosity of lithium-6 and lithium-7, in millipoise.

Lithium ⁶		Lithium ⁷	
Temperature (°C)	Viscosity η (mP)	Temperature (°C)	Viscosity η (mP)
182	4.20	185	5.88
188	4.14	186	5.97
198	4.14	187	5.86
204	4.04	188	5.89
221	3.93	200	5.71
243	3.77	215	5.41
265	3.63	239	5.12
267	3.60	240	5.15
287	3.48	264	4.84
		266	4.79
		286	4.61

DISCUSSION

None of the current theories of the liquid state can be applied directly to predict the effect of isotopic mass on viscosity at moderate temperatures. Consequently, we consider general arguments, based on dimensional analysis, to see what conditions are imposed on any formulas connecting viscosity with atomic parameters.

For our model we take a fixed number of spherically-symmetric particles each of mass m , placed in a large container of volume v at an absolute temperature T and under an external pressure p . We describe the interaction of the particle by a potential function $\phi(r)$ representing, say, a weak attraction at large distances and a strong repulsion at short distances (cf. Fig. 5). We characterize the potential by two parameters, the first a spatial coordinate representing a range of some kind, the second an energetic coordinate representing a depth of some kind. For definiteness, we take as the former s , the distance of the potential minimum from the center of the particle. For convenience, we take as the latter b , the second derivative of the potential curve evaluated at the minimum, recognizing that for curves of a fixed form the depth of the well and the second derivative of the function at the bottom of the well are proportional. The parameter b has the interpretation, of course, of the spring constant for an oscillator in the harmonic approximation.

The methods of dimensional analysis are now applied to this model, which in the present form could apply

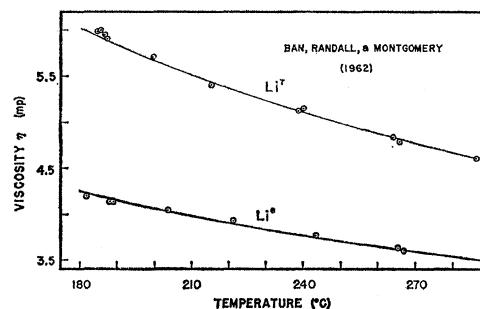


FIG. 4. Viscosity of Li^6 and Li^7 as a function of temperature.

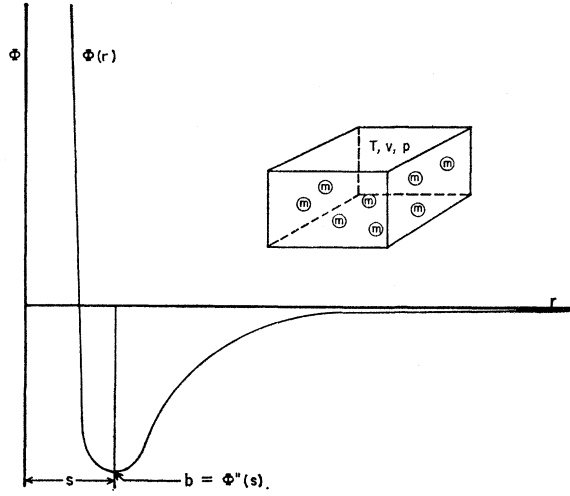


FIG. 5. Model for dimensional analysis.

to any state of matter. We consider as the parameters likely to appear in the equation of motion for the system the set m , b , and s , characterizing the individual particles; the set p , v , and T , characterizing the conditions imposed on the system; and \hbar (Planck's constant divided by 2π) which will enter when any quantum effects are present. The fundamental dimensions could be taken as mass, length, time, and temperature; such a procedure, however, merely introduces another fundamental constant, k (Boltzmann's constant), and thereby complicates the algebra without yielding additional information. We believe that it is better to take k and T together in the form of a thermal energy kT . Moreover, we introduce \hbar by combining it with an angular frequency $(b/m)^{1/2}$, to get expressly a term in the form of a quantum of energy, $\hbar b^{1/2} m^{-1/2}$. Because an equation of state exists, only two of the three quantities p , v , and T are independent, and only two (say p and T) need be included in the analysis. The seven variables to be related are then m , b , p , kT , $\hbar b^{1/2} m^{-1/2}$, s , and η . The three fundamental dimensions are mass, length, and time. Hence, there exists a functional relation among $7-3=4$ dimensionless products of these variables. There is some arbitrariness in the manner in which this function is expressed, and in the choice of the dimensionless combinations. A form convenient for our use is

$$\eta = [(mkT)^{1/2}/s^2] \eta^* (b/sp, bs^2/kT, \hbar b^{1/2} m^{-1/2}/kT). \quad (1)$$

The validity of this equation is independent of the state of the substance. As an illustration, consider a model consisting of perfectly elastic spheres of diameter s with vanishing interaction when not in contact, whence b may be taken as zero. Then η^* becomes constant, independent of p , T , and m . Hence, the dependence of η on these three quantities is contained in the factor external to η^* , namely, $(mkT)^{1/2}/s^2$, a result identical with that obtained by kinetic theory on this model. For the permanent gases, this model is a good repre-

TABLE II. Observations at constant temperature (lithium-7).

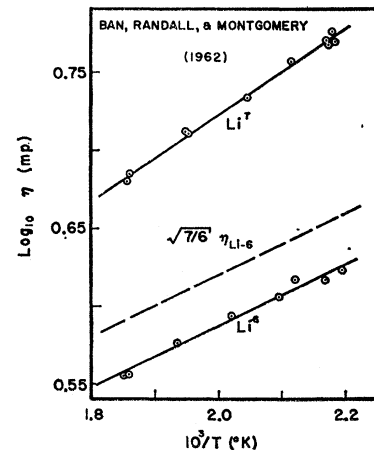
Temperature (°C)	Logarithmic decrement ^a δ	Viscosity ^b η (mP)
187.7	577.3×10^{-6}	5.84
187.5	577.3	5.83
187.7	579.2	5.91
187.3	577.2	5.83
187.1	578.5	5.88
187.2	580.1	5.94
187.3	576.3	5.80
187.2	577.0	5.84
187.6	577.4	5.84
187.6	576.9	5.83

^a Statistical analysis of logarithmic decrement δ : Mean, 577.7×10^{-6} ; standard deviation, 1.18×10^{-6} ; 95%-confidence interval, $(577.7 \pm 0.84) \times 10^{-6}$.

^b Statistical analysis of viscosity η : Mean, 5.85 mP; standard deviation, 0.043 mP; 95%-confidence interval, (5.85 ± 0.03) mP.

sentation, and experiment indeed shows that for these substances the viscosity is proportional to $T^{1/2}$ and $m^{1/2}$, and independent of p over ranges compatible with the requirements of the model. In contrast, for liquids—which would not even exist in the absence of intermolecular attractions— b cannot be zero. Consequently, η^* may be far from constant, and indeed as we know, decreases so strongly with rising temperature that it more than overcomes the increase due to the factor $(mkT)^{1/2}$. We shall see that η^* varies with isotopic mass m as well, though not nearly so strongly as with temperature T .

Equation (1) shows that m enters in η^* only through the argument $\hbar b^{1/2} m^{-1/2}/kT$. Hence, η^* will become insensitive to m only (1) when $b \rightarrow 0$, that is, when the attractive interaction vanishes, as just discussed; or (2) when $T \rightarrow \infty$, that is, when temperatures are so high that equipartition sets in. For the specific case of separated isotopes of the same material in the liquid state, we may take b (necessarily different from zero) and s as the same for both substances, neglecting the very small differences arising from the shift in atomic radii resulting from the difference in reduced mass of the electron-nucleus combination. We can expect η^* to

FIG. 6. Plot of $\log_{10} \eta$ (mP) against $10^3/T$ for Li^6 and Li^7 .

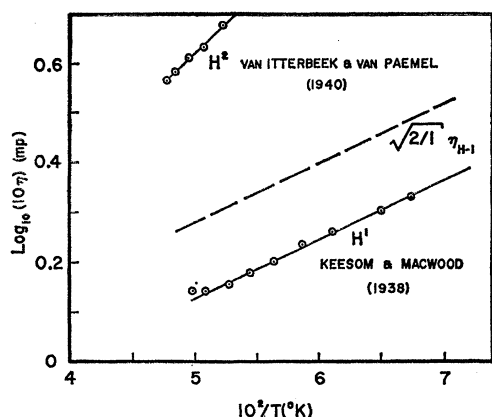


Fig. 7. Plot of $\log \eta$ (mP) against $1/T$ for H_2 and H_2 .

vary with isotopic mass at lower temperatures, but to be independent of m at high temperatures. The mass dependence of viscosity η itself should then approach the dependence $m^{1/2}$ at high temperatures.

We now examine our experimental data in the light of these considerations. To remove part of the strong dependence of viscosity on temperature we make use of the empirical relation, attributable to de Guzman,⁸ that

$$\eta = Ae^{B/T} \quad (p = \text{const}). \quad (2)$$

Here, A and B are supposed to be nearly constant. A plot of $\log \eta$ against $1/T$ would then yield a nearly straight line. Figure 6 shows such a plot for the data of Fig. 4.

We note first that the curves are indeed nearly straight. A dashed curve corresponding to the limiting value $(7/6)^{1/2} = 1.080$ times the viscosity of Li^6 is included in Fig. 6. We note that the separation between the experimental curves is greater than the expected value. We note moreover that the separation between the curves for the two isotopes becomes smaller as the temperature increases. The ratio of the viscosities for the two isotopes just above the melting point ($\sim 180^\circ\text{C}$) is 1.44. The ratio decreases gradually with increasing temperature, becoming 1.32 at 287°C , the highest temperature utilized.

Although the observed behavior seems to be in accordance with the theoretical considerations as outlined above, it is perhaps surprising that quantum effects should be appreciable at temperatures where lithium is molten. The Debye temperature for solid lithium is about 400°K , the melting point is about 450°K . Our temperatures of observation, 450 to 575°K , are too high to let us insist on the appearance of quantum effects, yet too low to ensure their absence. Let us look at other substances to see if this type of behavior is unique.

⁸ J. de Guzman, *Anales ffs. y qufm.* (Madrid) **11**, 353 (1913); **12**, 432 (1914), as mentioned by B. R. T. Frost, *Progress in Metal Physics*, edited by B. Chalmers and R. King (Interscience Publishers, Inc., New York, 1954), Vol. 5, p. 96.

Figure 7 shows the data for liquid hydrogen as measured by Keesom and Macwood⁹ (H_2), and by van Itterbeek and van Paemel¹⁰ (H_2); Fig. 8 shows the data for liquid helium (He^3 and He^4 , nonsuperfluid) as given by Zinov'eva.¹¹ Again we show dashed curves to represent the viscosity of the lower-mass isotopes multiplied by the square root of the mass ratio. The same trend found for the lithium isotopes is evidenced. It might be objected that the comparison with hydrogen is not justified, since hydrogen molecules are not at all spherically symmetric. The ratio of the moment of inertia of H_2 to H_2 is nearly the same as the ratio of the masses, however, and therefore the conclusions from the dimensional analysis should not change much.

It is difficult to find additional substances for which isotopic mass alone may be varied. Study of other elements for one reason or another is not practical. Study of compounds is practical, but theoretical interpretation of the results is not clear cut because rotations and possible vibrations must be taken into account. Then additional parameters will usually be necessary to specify the behavior of the molecules. With respect to viscosity, however, transport of *linear momentum* is the primary phenomenon; as a consequence, the *angular momentum* would appear to have only second-order effects. This consideration gives us more confidence in the results for liquid hydrogen. Accordingly, it might be useful to consider the viscosity of isotopically substituted compounds even though the moment of inertia is not proportional to mass.

Hardy and Cottingham¹² have measured the viscosity of H_2O and D_2O as a function of temperature, with the results shown in Fig. 9. The value of $(18/16)^{1/2} = 1.06$ times the viscosity of H_2O cannot be distinguished from the viscosity of H_2O itself on the scale of the graph. The empirical relation of Eq. (2) fails to describe the temperature dependence of water, a fact not surprising in view of the high degree of association. The mass dependence, however, does appear to be qualitatively similar to that of the elements just cited.

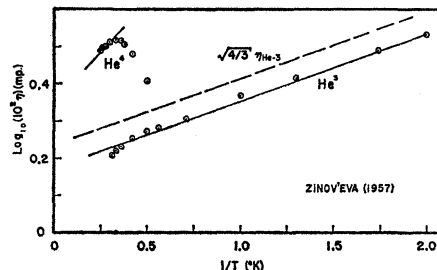


Fig. 8. Plot of $\log \eta$ (cP) against $1/T$ for He^3 and He^4 .

⁹ W. H. Keesom and G. E. Macwood, *Physica* **5**, 745 (1938).

¹⁰ A. van Itterbeek and O. van Paemel, *Physica* **7**, 208 (1940).

¹¹ K. N. Zinov'eva, *J. Exptl. Theoret. Phys.* (USSR) **34**, 609 (1958) [translation: *Soviet Phys.—JETP* **7**, 421 (1958)].

¹² R. C. Hardy and R. L. Cottingham, *J. Chem. Phys.* **17**, 509 (1949); *J. Research Nat. Bur. Standards* **42**, 573 (1949).

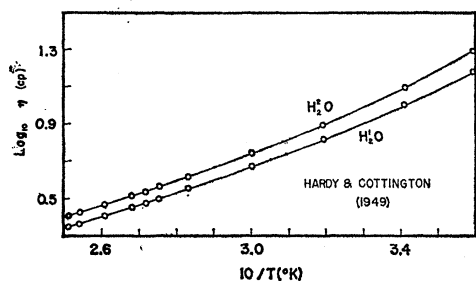


FIG. 9. Plot of $\log \eta$ (cP) against $1/T$ for H_2O and H_2O .

For the nonassociated substance methane, Bresler and Landerman¹³ have reported the viscosity at only one temperature, 90.1°K, as 2.34 ± 0.01 mP for CH_4^2 and as 2.10 ± 0.01 mP for CH_4^1 , to give a ratio of 1.113 ± 0.005 , as compared with $(20/16)^{1/2} = 1.119$. The order of the ratios is opposite to that found for the other materials, just within the limit of precision of the experiment. Further measurements from the melting point (89.2°K) up to and beyond the normal boiling point (111.7°K) would be desirable to see if this order is real and persists.

In summary, it appears likely that quantum effects may be significant in transport processes in liquids even at fairly high temperatures. As to the detailed mechanism, we can only suggest that some sort of clumping might occur, the size of the aggregates being highly sensitive to isotopic mass. However, the difference in melting point between the lithium isotopes¹⁴ is much smaller than expected on certain theoretical arguments. Hence, we are left with the dilemma that the difference in melting point between the lithium isotopes is un-

expectedly small, and that the difference in viscosity is unexpectedly large.

We may speculate as to whether light may be shed on this problem by examining the patterns of x rays or neutrons diffracted by separated lithium isotopes. Unfortunately the scattering power of lithium ($Z=3$) for x rays is small, and the capture cross section of Li^6 for slow neutrons is high. Neutron-diffraction experiments on Li^7 , though, as a function of temperature might yield evidence of clumping. Gingrich¹⁵ has reported results for Li^7 just above the melting point; but at present we do not know exactly how to analyze the results for evidence of clumping. The difficulty is that diffraction studies, as usually performed, represent an average over time as well as over space. The type of clumping that we are suggesting may consist simply of a number of neighboring particles temporarily moving more or less as a unit. Such groupings would not show up as an anomalous density function in an experiment averaging over times long compared with the lifetime of association.

We may speculate also as to the viscosity of "isotopic alloys" made up of different proportions of Li^6 and Li^7 . The failure of a simple $m^{1/2}$ law between pure isotopes casts some doubt on an interpolation rule of this form, with m replaced by \bar{m} , the arithmetic-mean mass. Nevertheless, we give the result of a direct linear interpolation for the viscosity of Li^{nat} (92.4% Li^7 , 7.6% Li^6), as 5.86 mP at the melting point (180°C). This value is only slightly lower than the value of 6.02 reported by Andrade and Dobbs.¹⁶ Direct determination of the viscosity of isotopic alloys would be of scientific and technological interest. The point of greatest technological value in the present work is perhaps that the viscosity of Li^6 is considerably less than predicted on the simple $m^{1/2}$ basis.

¹³ S. E. Bresler and A. Landerman, J. Exptl. Theoret. Phys. (USSR) **10**, 250 (1940); Chem. Abstracts **34**, 7679 (1940). A readily accessible account of the results is included in J. S. Rowlinson, Physica **19**, 303 (1953), and discussed by J. A. Pople, *ibid.* **19**, 668 (1953).

¹⁴ J. A. Crawford and D. J. Montgomery, Bull. Am. Phys. Soc. **2**, 299 (1957).

¹⁵ N. S. Gingrich and L. Heaton, J. Chem. Phys. **34**, 873 (1961).

¹⁶ E. N. da C. Andrade and E. R. Dobbs, Proc. Roy. Soc. (London) **A211**, 12 (1952).