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The Temperature Variation of the Compressibility of Molten Sodium*

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The present method for the determination of the adiabatic compressibility of molten sodium depends in the first instance upon the measurement of the velocity of propagation of a short train of ultra-high frequency compressional acoustic waves in the material. This figure is then combined with the best available value of the density to yield the compressibility, on the assumption that the rigidity of the liquid is zero.

The wave trains are produced and detected by a piezoelectric transducer, and the resultant signal is exhibited on the screen of an oscilloscope whose sweep circuit is time-calibrated to permit the measurement of the transit time of a train over a known path length in the medium. A novel acoustic interferometer is employed, with which small changes in velocity can be measured with high precision.

The velocity of compressional waves in molten sodium at the freezing point, 97.6°C, is 252,600±500 cm/sec, and its temperature coefficient remains constant at the value -52.4 ± 0.3 cm/sec °C at least to 545°C. The adiabatic compressibility is 16.85×10^{-12} cgs at 97.6°C, and its temperature coefficient increases from 0.012×10^{-12} cgs at this temperature to 0.013×10^{-12} cgs at 545°C. The relations between these quantities and other elastic and thermal properties of solid and liquid sodium are discussed.

I. INTRODUCTION

CONSIDERABLE information is available concerning the elastic and thermal properties of sodium in the solid state. Thus the principal adiabatic and isothermal elastic constants at zero pressure have been measured between 79°K and 210°K,[1] and the isothermal compressibility at high pressures between 273°K and the melting point, 371°K.[2] The thermal expansion of the material between 79°K and 371°K is known,[3] as is the specific heat at constant pressure over various temperature intervals up to 371°K.[4]

Progress toward an understanding of the process of melting in sodium demands a knowledge of the changes which the aforementioned properties undergo when the substance passes into the liquid state. The thermal expansion[5] and the specific heat at constant pressure[6] of liquid sodium have been measured, as has the change in specific volume on melting,[7] but inherent experimental difficulties have prevented a direct determination of the compressibility of the molten metal.

The present paper describes a series of measurements of the variation of the velocity of sound in liquid sodium with temperature between 371°K and 545°K. The adiabatic compressibility, κ_S, of the material is given in terms of this quantity by the expression,

$$\kappa_S=(\rho V^2)^{-1}, \tag{1}$$

in which V denotes the velocity of a compressional sound wave in the material and ρ the density, and it is assumed that the rigidity modulus is zero. The adiabatic compressibility is related to the isothermal compressibility, κ_T, by the formula,

$$\kappa_T-\kappa_S=T\beta^2/\rho c_p, \tag{2}$$

in which T denotes the absolute temperature, β the volume coefficient of expansion, and c_p the specific heat at constant pressure. The specific heat at constant volume, c_v, may be computed with the formula,

$$\kappa_T/\kappa_S=c_p/c_v. \tag{3}$$

II. EXPERIMENTAL METHOD

Electronic Equipment

The experimental method consists in the measurement of the time of transit of a short train of high frequency compressional acoustic waves over a predetermined path length in the specimen material. The wave trains are excited by a piezoelectric quartz crystal and, after reflection from a plane surface in the medium, are detected by the same crystal. The initial and reflected signals are exhibited on the screen of a cathode-ray oscilloscope, separated by a time-calibrated sweep.

The method has been extensively employed to measure the velocity of acoustic waves in various solids and liquids.[8] Those applications, like the present one, rely in large measure upon special electronic equipment developed by the Massachusetts Institute of Technology Radiation Laboratory for the production and utilization of short high frequency signals. Appropriate references to the published literature of the Laboratory are given here, and detailed description is limited to certain novel features designed to enhance the pre-

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[1] S. L. Quimby and Sidney Siegel, Phys. Rev. **54**, 293 (1938).

[2] P. W. Bridgman, (*a*) Proc. Am. Acad. Arts Sci. **70**, 71 (1935); (*b*) Proc. Am. Acad. Arts Sci. **58**, 166 (1923).

[3] Sidney Siegel and S. L. Quimby, Phys. Rev. **54**, 76 (1938); E. Hagen, Wied. Ann. **19**, 436 (1883); E. A. Griffiths and E. Griffiths, Proc. Phys. Soc. (London) **27**, 477 (1915).

[4] G. L. Pickard and F. E. Simon, Proc. Phys. Soc. (London) **61**, 1 (1948); K. K. Kelley, U. S. Dept. Commerce, Bur. Mines Bull. **371** (1934); Ezer Griffiths, Proc. Roy. Soc. (London) **89**, 561 (1914); E. Rengade, Compt. rend. **156**, 1879 (1913).

[5] E. Hagen, see reference 3.

[6] The available data are reviewed by K. K. Kelley, reference 4.

[7] E. A. Griffiths and E. Griffiths, see reference 3.

[8] H. B. Huntington, Phys. Rev. **72**, 321 (1947); J. K. Galt, Massachusetts Institute of Technology, Research Laboratory of Electronics, Tech. Report No. 45, (Sept. 17, 1947); D. Lazarus, Phys. Rev. **76**, 545 (1949); O. J. Kleppa, J. Chem. Phys. **18**, 1331 (1950).

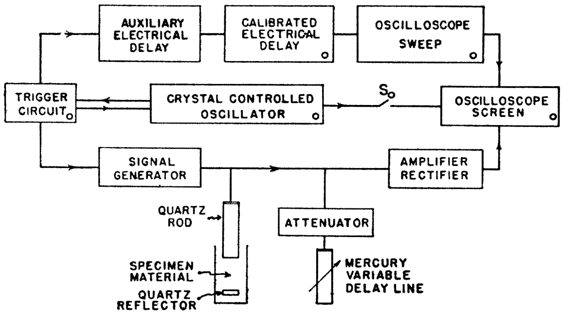

FIG. 1. Functional diagram of electro-acoustic apparatus.

cision of the method and extend its range to high temperatures.

Figure 1 is a functional diagram of the electro-acoustic apparatus. The trigger circuit supplies a 100-volt pulse of one microsecond duration at intervals of approximately one millisecond. Each pulse initiates the following events: (1) the signal generator supplies a sinusoidally varying potential difference of 12.2 megacycle frequency for a period of approximately 3 microseconds; (2) after a measurable time interval, the oscilloscope beam sweeps across the screen; (3) if the switch S is closed, a crystal controlled oscillator of 100 kilocycle frequency registers time markers on the oscilloscope sweep.

The output of the signal generator is impressed on an X-cut quartz crystal cemented to the upper end of a cylindrical rod of optical grade fused quartz, the lower end of which is immersed in the specimen material. The resulting acoustic wave train travels down the quartz rod and into the specimen, with partial reflections at the interface and at a quartz reflector accurately positioned beneath. Both reflected trains are detected by the quartz crystal, amplified, rectified and exhibited as pulses on the oscilloscope screen. The fronts of the two pulses are brought consecutively to the initial point on the sweep by manipulation of the oscilloscope sweep delay, and the associated difference in delay time is then the transit time of the disturbance in the medium. The scale of the sweep delay is calibrated with the time markers on the sweep.

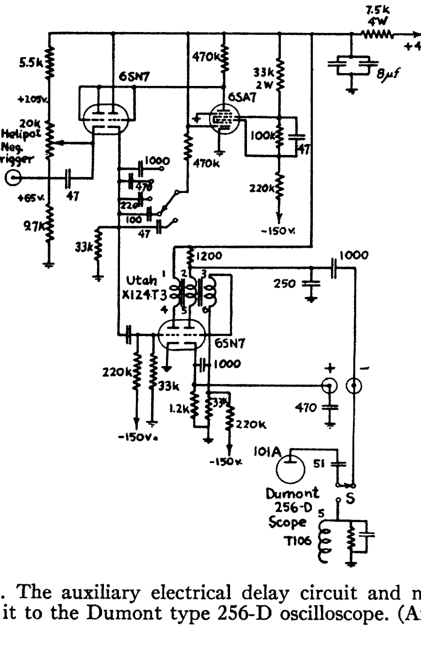

FIG. 2. The auxiliary electrical delay circuit and method for coupling it to the Dumont type 256-D oscilloscope. (After R. M. Walker.)

The transit time is approximately 40 microseconds, and the accuracy with which this can be measured is roughly the wave period, i.e., 0.1 microsecond or 0.2 percent. The consequent percent uncertainty in the measurement of the velocity is the same, but that of the temperature coefficient of the velocity is of the order 10 percent, since the total change in transit time over the temperature range here studied is only 1 microsecond. Therefore the change in the velocity with temperature is measured in the following manner.

The output of the signal generator is impressed on a second quartz crystal mounted at the bottom of a vertical column of mercury which contains a polished steel reflector. The reflector is affixed to the lower end of a spring-loaded piston, the upper end of which is in contact with a fine screw. Thus the position of the reflector, and hence the effective height of the mercury column, can be varied at will and the amount of the variation observed with precision. The length of the mercury column is first so adjusted that the second reflected wave train annuls the train received from the quartz-specimen interface. Next, this adjustment is varied until the third reflected wave train annuls that received from the reflector in the specimen. If, now, the temperature of the specimen is altered, then both these adjustments are likewise altered, the first in consequence of the change in wave velocity in the quartz rod and the second in consequence of the change in the wave velocities in both the specimen and the quartz rod. The change in transit time in the specimen, Δt, is given by the expression $\Delta t = (6\Delta L_2 - 4\Delta L_1)/V_m$, where ΔL_1 is the variation in the length of the mercury column required to annul the wave train reflected from the interface, ΔL_2 that required to annul the wave train from the reflector in the specimen, and V_m is the velocity of sound in mercury. The estimated uncertainty in the values of Δt thus obtained is 0.005 microsecond.[9]

The basic electronic equipment is the Dumont 256-D oscilloscope, in which the items marked with an O in Fig. 1 are incorporated. This instrument permits a choice of either of two values of the full scale range of the calibrated electrical delay, *viz.*, 100 microseconds or 1000 microseconds. The over-all transit time of the disturbance in the quartz rod and specimen is approximately 140 microseconds; therefore, an increase by a factor 10 in the precision of measurement is obtained

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[9] This interferometric method may be contrasted with that devised by Arenberg, Massachusetts Institute of Technology Radiation Laboratory, Report No. 932.

if a fixed electrical delay of suitable magnitude is inserted in series with the calibrated electrical delay. Figure 2 is a diagram of this circuit, which was devised for the writer by Mr. Robert M. Walker of the Watson Scientific Computing Laboratory, and of the method for coupling it to the oscilloscope.

The signal generator and amplifier are essentially those described by Beers and Durand[10] and Galt,[11] respectively. Two 807 tubes are added to the signal generator to increase the output and to obtain cathode-follower coupling to the 100-ohm output cable. This unit yields the peak voltage amplitude in the first quarter cycle; the rise time of the amplifier is 0.1 microsecond.

The variable mercury delay line is mounted in a thermally insulated enclosure, the temperature of which is maintained at 40.7±0.1°C. The uncertainty in temperature corresponds to an uncertainty of 0.001 microsecond in Δt.

The Vacuum Furnace

Figure 3 shows a cross section of the vacuum furnace and associated apparatus. The specimen material is contained in a thin-walled nickel crucible of 200-cc capacity, which is supported by three invar legs on the upper end of a vertical, hollow, stainless steel cylinder. This cylinder floats on a column of mercury contained in a concentric cylindrical well, and the crucible can be raised or lowered at will by altering appropriately the amount of mercury in the well.

The heating element of the furnace is a winding of No. 15 nichrome wire spaced 7 turns per inch on a cylindrical copper tube $2\frac{5}{16}$ in. i.d., $3\frac{1}{2}$ in. o.d., and 10 in. long. The winding is electrically insulated from the tube with a double layer of 5-mil mica sheets, and the turns are held in place with a thin layer of Alundum cement. The element is mounted on three legs of invar and Lavite; these rest on a platform which supports, in addition, two radiation shields, the inner of nickel and the outer of brass.

The quartz rod passes downward through a hole in the top of the brass radiation shield, at which point it is fastened to the shield with a clamp. The quartz reflector is held in position beneath the quartz rod by three clear quartz fingers 3 mm in diameter, which are fused at their upper extremities to the rod and at the lower to the reflector. The latter, constructed by fusing a quartz disk to a half-inch of tubing of the same diameter, has the shape of an inverted cup, and is surrounded by a truncated cone of thin sheet nickel with its vertex down. The cone is open at the bottom so that, as the crucible of molten sodium is raised, the unavoidable surface layer of oxide is guided into the cup and there trapped, and a fresh, clean surface of pure metal is let to form the interface between the quartz rod and the medium. (The cone is not shown in Fig. 3.)

The upper end of the quartz rod emerges from the furnace envelope through a hole in the top. The hole is

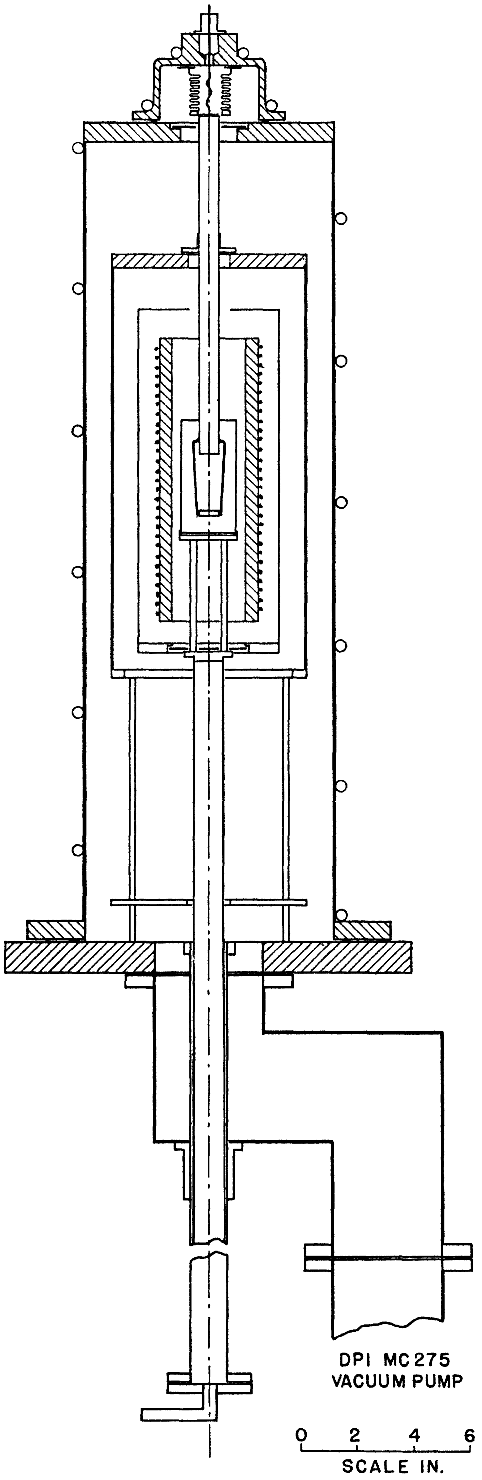

FIG. 3. The vacuum furnace.

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[10] Massachusetts Institute of Technology, Radiation Laboratory Series, *Vacuum Tube Amplifiers* 18, Ch. 8, Edited by G. E. Valley, Jr., and H. Wallman (McGraw-Hill Book Company, Inc., New York, 1948).

[11] J. K. Galt, see reference 8.

covered with a cap which affords a vacuum tight closure of the envelope and carries the electrical connections to the quartz crystal. The latter is an X-cut disk, 0.75 in. in diameter and 0.0098 in. thick, upon which suitable aluminum electrodes are placed by evaporation. The crystal is cemented to the top of the rod with a thin film of beeswax.

A D.P.I. MC275 diffusion pump maintains a vacuum of the order 10^{-5} mm mercury during observation, but changes in temperature near the melting point are facilitated by an atmosphere of a few mm of helium. The temperature is stabilized to 0.1°C with an electronic proportioning temperature controller[12] operated by a Chromel-Alumel thermocouple attached directly to the copper cylinder.

Temperature Measurement

The temperature of the sodium is measured with a Chromel-Alumel thermocouple placed in a thin-walled quartz tube, with the junction near the midpoint of the acoustical path. This thermocouple is calibrated against a platinum resistance thermometer certified by the National Bureau of Standards. A second quartz tube contains a differential thermocouple, with one junction near the surface and the other near the bottom of the specimen. The temperature difference thus revealed varies from 0.2°C at the highest to less than 0.1°C at the lowest temperature. The over-all accuracy of the temperature measurement is estimated to be ±0.5°C; the precision is 0.1°C.

Velocity Measurement

The distance between the quartz rod and the reflector is 5.169±0.002 cm at 25°C, as measured with a Starrett micrometer. Correction is made for the slight variation of this quantity with temperature due to thermal expansion of the quartz supporting fingers. The frequency of the crystal-controlled tuning oscillator is 100,000±40 cycles/sec, as revealed by comparison with the standard frequency broadcast by station WWV. The uncertainties in the measured values of the velocity and its temperature coefficient are estimated to be 0.2 percent and 0.5 percent, respectively.

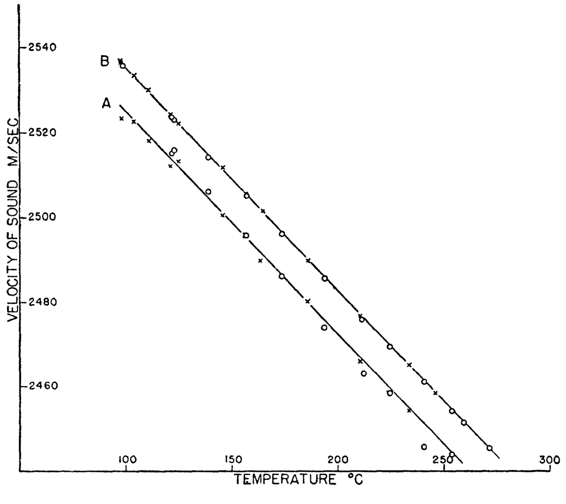

Fig. 4. Curve A, the velocity of sound in molten sodium at various temperatures. Curve B, the temperature variation of the velocity of sound; only the slope of this curve is significant.

III. SPECIMEN MATERIAL

The specimen material is Mallinckrodt analytical reagent grade sodium triply distilled in vacuum, with the rejection of the first and last quarters of the distillate in the first distillation. The still is constructed of nickel, and the final distillation leaves the material in the crucible in which the measurements are made. A lid is clamped on the crucible in an atmosphere of helium, by manipulations made outside the still, and the closed crucible is transferred to the vacuum furnace. The furnace envelope, slightly raised to permit access, is filled with helium maintained is continuous flow; the crucible lid is quickly removed in this atmosphere and the furnace is immediately closed and sealed.

Spectroscopic analysis of the material made after completion of the measurements reveals no nickel or copper, a few thousandths of one percent silicon, and a few hundredths of one percent aluminum and calcium. The analysis of a singly distilled specimen is the same, except for the presence of a few hundredths percent copper. Measurements of the velocity of sound made upon the singly distilled specimen are indistiguishable from those made upon the triply distilled specimen.

IV. RESULTS

The present experimental method yields a precise determination of the freezing point of sodium at zero pressure. The thermal insulation provided by the vacuum in such that the temperature and the velocity of sound in the molten material remain constant for half an hour while solidification proceeds from the outside toward the axis of the crucible. Toward the end of this period the disturbance reflected in the medium disappears quickly. The freezing point of sodium at zero pressure is found to be 97.6°C, with an accuracy which is probably better than 0.1°C because this temperature is proximal to the thermocouple calibration point at the steam temperature.

The observed values of the velocity of sound at various temperatures are plotted on Curve A of Fig. 4. Curve B shows the temperature variation of this quantity, as measured with the interferometer. The ordinates of this curve are displaced by an arbitrary constant amount with respect to those of Curve A; only the *slope* of the curve is significant. Circles indicate measurements made on heating the specimen, and crosses measurements made on subsequent cooling. It will be noted (Curve B) that, over the interval here investigated, the velocity of sound varies linearly with the

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[12] D. Lazarus and A. W. Lawson, Rev. Sci. Instr. **18**, 730 (1947).

temperature. The value of the temperature coefficient is -52.4 ± 0.3 cm/sec °C.

Curve A is the straight line which has the same slope as the line B and which, subject to this condition, best represents the plotted points. Observations at lower temperatures are given greater weight than those at higher temperatures in the placement of this line, because the front of the reflected pulse loses its sharpness somewhat as the material is heated. The ordinate of the line A at the temperature 97.6°C is the value of the velocity of sound at the freezing point, *viz.*, 252,600 ±500 cm/sec.

A careful review of the work of numerous investigators indicates that the following are the best available values of the remaining physical constants of liquid sodium which appear in the formulas (1) and (2) above: density at the melting point $=0.930$ g/cc;[13] coefficient of volume expansion $=2.78\times10^{-4}$/°C;[14] specific heat at constant pressure $=7.5$ cal/mole °C, with an accuracy of about 2 percent between 98°C and 178°C.[6] Corresponding values of the adiabatic and isothermal compressibilities of liquid sodium at various temperatures are given in Table I.

It is significant that no change in the temperature coefficient of velocity is detected in the neighborhood of the freezing point. The velocity of a compressional wave in an isotropic medium is given by the expression,

$$V^2=\left(\frac{1}{\kappa}+\frac{4}{3}\mu\right)\Big/\rho,$$

in which μ is the rigidity modulus of the medium. Accordingly, the constancy of the temperature coefficient of V implies that either μ is zero in the liquid at the melting point and above, or the temperature coefficient of μ/ρ is constant over the temperature range here investigated. The former conclusion is the more plausible. It is supported by the concordance, noted below, of data which relate the change of compressibility on freezing to other measurable quantities, and further by the initial results of a detailed study, now in progress, of the rigidity of both solid and liquid sodium in the immediate neighborhood of the freezing point.

O. J. Kleppa measured the velocity of sound in liquid sodium at the melting point by an acoustical method similar in principle to that here described.[8] He obtained the value 2395 m/sec, which is to be compared with the figure 2526 m/sec given above. A possible source of the discrepancy is the lack of purity of Kleppa's specimen material. The latter contained over one percent solid impurity by chemical analysis, and a considerable volume of occluded gas as well. It was not predistilled and the measurements were made with the specimen, protected by a layer of mineral oil, in an atmosphere of nitrogen.

TABLE I. The adiabatic and isothermal compressibilities of liquid sodium. The number of significant figures does not indicate the accuracy of the absolute value.

Temperature, C	$\kappa_S\times10^{12}$ cgs	$\kappa_T\times10^{12}$ cgs
97.6	16.85	19.11
100	16.88	19.16
120	17.11	19.49
140	17.35	19.85
160	17.59	20.19
180	17.84	20.55
200	18.09	20.89
220	18.34	21.26
240	18.60	21.61
260	18.86	21.98
272	19.02	22.19

V. DISCUSSION

The present experimental method cannot be used to measure the compressibility of polycrystalline solid sodium because, first, sodium crystals are highly anisotropic, and second, it is not possible to prepare a specimen in which the linear dimensions of the crystals are small compared with the 0.3 mm acoustic wavelength. Thus, all attempts to transmit a train of compressional waves through as little as $\frac{1}{2}$ inch of polycrystalline material have been unsuccessful. The alternative is to compute the results of acoustic measurements on large single crystals. This work is now in progress. Pending a successful outcome, the compressibility of the solid and its temperature coefficient can be evaluated with the foregoing and other elastic and thermal data as follows.

Let p denote the pressure, v the specific volume, and T the temperature; then

$$dv/dp=[\partial v/\partial T]_p dT/dp+[\partial v/\partial p]_T,$$

and it follows that[15]

$$\frac{d}{dp}(v'-v'')=\left[\frac{\beta'}{\rho'}-\frac{\beta''}{\rho''}\right]\frac{dT_m}{dp}-\left[\frac{\kappa'}{\rho'}-\frac{\kappa''}{\rho''}\right], \tag{4}$$

in which the primed quantities refer to the liquid, the double primed quantities to the solid, and T_m denotes the melting point of the solid. Furthermore,

$$dT_m/dp=T_m(v'-v'')/L, \tag{5}$$

where L denotes the heat of fusion. The following are adopted as the best available values of the several quantities essential to the calculation of κ''; all are expressed in the cgs system of units.

$L=114.3\times10^7$; this is the mean of the values 113.7×10^7 obtained by Rengade[4] and 115.0×10^7 by E. Griffiths.[4] $(v'-v'')=0.02640$.[3] $\beta''=2.34\times10^{-4}$; this is the mean of the values 2.46×10^{-4} given by Hagen[3] and 2.22×10^{-4} by the Griffiths.[3] (It may be noted that

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[13] E. A. and E. Griffiths, and E. Hagen, reference 3. See also, however, Hackspill, Compt. rend. **152**, 259 (1911), who reported the value 0.9385 but who found the freezing point of his material to be 96.5°C.

[14] Reference 13 and E. Rinck, Ann. chim. et Phys. **18**, 395 (1932).

[15] P. W. Bridgman, Phys. Rev. **6**, 32 (1915).

Hagen's expansion curve between 273°K and 360°K is a smooth continuation of that between 80°K and 290°K published by Siegel and Quimby.)[3] $\rho''=0.954$.[16] $d(v'-v'')/dp=-2.58\times 10^{-12}$; this is the slope at zero pressure of a cubic curve which represents at pressures 1, 1000, 2000, 3000 kg/cm^2 the values of $(v'-v'')$ observed by Bridgman.[15] The corresponding value of the isothermal compressibility of solid sodium at the melting point is 16.68×10^{-12} cgs.

The isothermal compressibility of polycrystalline sodium at 298°K in the pressure range 100 to 500 kg/cm^2 has been measured directly by Richards, Hall, and Mair,[17] who observed no significant variation of compressibility with pressure in this interval and obtained the value $\kappa_T=15.6\times 10^{-12}$ cgs. Now there is good reason to believe that the temperature coefficient of the isothermal compressibility of sodium does not depend upon the temperature. Thus Quimby and Siegel[1] noted that κ_T at zero pressure varies linearly with the temperature between 80°K and 210°K, and Bridgman[18] observed that, within the uncertainty of his measurements, the same is true of κ_T at 5000 kg/cm^2 pressure between 273°K and the melting point. In accordance with this assumption and aforementioned values of κ_T at 371°K and 298°K, the temperature coefficient of the isothermal compressibility at zero pressure is 0.015×10^{-12} cgs.

Bridgman's observations at high pressures, cited in the preceding paragraph, can be extrapolated to yield the compressibility at zero pressure provided the coefficient of thermal expansion at zero pressure is known. The temperature coefficient of compressibility obtained in this manner is likewise 0.015×10^{-12} cgs when the mean value of β at zero pressure over the temperature range is assumed to be 2.21×10^{-4}, the value reported by Hagen[3] and the Griffiths.[3,19] The temperature coefficient given by Quimby and Siegel[1] is 0.017×10^{-12} cgs. Since that of the liquid is 0.017×10^{-12} cgs, it thus appears that the temperature coefficient of the isothermal compressibility of sodium is almost constant over the temperature range 80°K to 545°K.

The value of the adiabatic compressibility of the solid at the melting point, computed with Eq. (2) and the value $c_p=1.27\times 10^7$ cgs,[20] is 15.01×10^{-12} cgs. The specific heats at constant volume computed (Eq. (3)) with the foregoing values of c_p and the compressibilities are $c_v(\text{solid})=6.30$ cal/mole°C and $c_v(\text{liquid})=6.61$ cal/mole °C.

The compressibility of a solid or liquid may be regarded as composed of a part which depends simply upon the average intermolecular distance and a part which depends upon any existing regularity in the molecular configuration.[21] It can be argued on the basis of the foregoing data that in sodium the first of these contributions is preponderant. Bridgman's observations[18] yield the pressure-volume curve of the solid material at the melting point, and the slope of this curve the compressibility. The curve may be extrapolated into the region of negative pressure to the point at which the specific volume of the solid, and hence the average interatomic distance, is the same as that of the liquid at the same temperature. If, now, the compressibility is determined principally by the interatomic distance, then the compressibility of the solid computed from the slope of the curve at this point must be nearly the same as the observed compressibility of the liquid. The former is, in fact, 18.9×10^{-12} cgs, while the latter is 19.1×10^{-12} cgs. The closeness of the agreement must be regarded as fortuitous, since the accuracy of the extrapolation does not warrant it.[19]

In conclusion, the writer gratefully acknowledges his indebtedness to Mr. A. W. Costello, of the Columbia University Radiation Laboratory, for his assistance in calibrating the oscilloscope crystal; to Mr. R. M. Walker, of the Watson Scientific Computing Laboratory, for the delay circuit shown in Fig. 2; to Dr. T. I. Taylor, of the Chemistry Department at Columbia University, for the spectroscopic analysis of the sodium; and to Dr. S. L. Quimby, who suggested the research and followed its progress with helpful counsel and encouragement.

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[16] Both Hagen and the Griffiths obtained this figure. See reference 3.

[17] Richards, Hall, and Mair, J. Am. Chem. Soc. **50**, 3304 (1928).

[18] See reference 2*a*.

[19] The compressibility at 25°C and zero pressure obtained by this extrapolation is 16.5×10^{-12} cgs, which is to be compared with the measured value, 15.6×10^{-12} cgs.

[20] K. K. Kelley, reference 4.

[21] J. Frenkel, *Kinetic Theory of Liquids* (Oxford University Press, London, 1946), p. 171.