RP402

ULTRASONIC MEASUREMENTS OF THE COMPRESSIBILITY OF SOLUTIONS AND OF SOLID PARTICLES IN SUSPENSION

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Description is given of ultrasonic interferometer apparatus and a method of measuring ultrasonic velocities in liquids.

Results of ultrasonic measurements on distilled water at temperatures 0° to 86° C. and on aqueous solutions of four kinds of sugar for several concentrations and a series of temperatures are presented in curves and tables. The compressibility of distilled water and of the solutions are determined from ultrasonic velocity measurements.

Pyrex glass suspensions (aqueous) were prepared, the pyrex particles ranging in size from 2μ down. Ultrasonic velocity measurements were made on these suspensions for the purpose of testing the possibilities of a theory for getting the compressibility of a solid by a velocity-suspension method. The results obtained, though largely qualitative, show possibilities and limitations of method.

CONTENTS

I. INTRODUCTION

The ultrasonic interferometer traces its origin to the first application of the piezo-electric quartz crystal in the production of ultrasonic waves in water. In 1917 Langevin [1] brought out for the detection of submarines an echo sounding device which employed as a source of sound a mosaic of quartz crystals faced with steel plates about 4 inches in diameter and 1 inch in thickness. The frequencies which he employed to drive his sounder ranged from 40 to 100 kc. This source of ultrasonic waves proved to have unexpectedly good qualities, both as to its radiating ability and to its directional characteristics.

In the year 1923, R. W. Boyle and his collaborators described in the Transactions of the Royal Society of Canada "A New Photographic Method to Demonstrate the Interference of Longitudinal Wave Trains." For his source of sound he used an ultrasonic generator built similar to that of Langevin, and depending for its action upon the piezo-electric property of quartz. Two of these

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[1] Echo Sounding, Hydrographic Review (Monaco) vol. 2, No. 1, pp. 51–91; 1924–25.

sound generators were placed in a large tank of water opposite each other with their planes vertical and parallel. The same driving potential was applied to the two sound generators in phase. These sound sources were placed at such a distance apart that standing waves with vertical nodal planes were produced in the water. These standing waves were detected by fine coal cinder particles which when placed in the water settled down in the nodal planes and formed rows on a horizontal white plate placed just beneath the beam of sound. The rows formed were then photographed and from their distance apart the half wave lengths in the liquid were obtained. The precision reached in measuring the velocity of ultrasonic waves by this method was not great, about 1 per cent, but this experiment was the forerunner of many more to follow, by Boyle and by others.

Some time later, Pierce [2] developed a method for determining the velocity of ultrasonic waves in gases. There are four distinct differences between Pierce's method and that of Boyle: (1) Pierce used a single source of sound, the second source being replaced by a reflector; (2) the source of sound consisted of one single quartz crystal (in contrast with the mosaic) whose resonant frequency was determined by the dimensions of the crystal itself; (3) a critical reaction of the reflected waves on the vibrating quartz crystal indicated the existence of a system of standing waves between the source of sound and reflector; and (4) successive systems of standing waves were established by moving the reflector a half wave length closer to the source of the sound, the distance between the successive positions of the reflector determining the half wave length.

In Pierce's apparatus, the resonator crystal played the double rôle of resonator and oscillator. This system worked well for gases. Although nodal settings could be made at best to only about 0.02 mm., the accuracy in the wave length measurements for a large span of half wave lengths was very good.

A sonic interferometer for the study of liquids was later developed by Hubbard and Loomis.[3] In their apparatus, a quartz plate serving as the source of the waves was driven by an independent oscillator as in the experiments of Langevin. A system of standing waves was produced in the liquid by a reflector and the half wave length determined from the positions of the reflector for conditions of resonance. The precision obtainable in velocity measurements was found to be even greater for liquids than for gases, owing to the smaller coefficient of absorption in the case of liquids. This method for working with liquids has been extended by Hubbard [4] to the study of sound absorption in gases.

II. PRINCIPLE OF THE ULTRASONIC INTERFEROMETER

The principle of the ultrasonic interferometer depends on the setting up of a system of standing sound waves by reflection. The source of sound used by the author was a piezo-electric quartz disk (Curie cut) 7 cm in diameter and 5 mm in thickness. The schematic arrangement is shown in Figure 1. An alternating potential of high frequency is applied to the condenser plates on either side of the quartz crystal,

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[2] G. W. Pierce, Proc. Am. Acad. of Arts and Sci., vol. 60, pp. 271–302; October, 1925.

[3] Hubbard and Loomis, Phil. Mag., vol. 5, pp. 1177–1190; June, 1928. Loomis and Hubbard, J. Opt. Soc. Am., and Rev. Sci. Int., vol. 17, pp. 295–307; October 1928.

[4] J. C. Hubbard, Phys. Rev., vol. 35, p. 1442; 1930; vol. 36, p. 1668; 1930.

setting up ultrasonic waves of the same frequency in the medium above. The establishment of a system of standing waves requires that the reflector shall be plane parallel with the source of the waves and an integral number of half-wave lengths away from it. Under these conditions the quartz crystal vibrates with a maximum amplitude, since the vibrations of the liquid are in resonance with those of the crystal. If the reflector is out of place this resonance is destroyed and the amplitude of the oscillating crystal is diminished. The crystal in oscillation generates a back piezo-electromotive force proportional to the amplitude of that oscillation. Accordingly, when the amplitude is a maximum the driving current is a minimum. This enables one to adjust the reflector to a nodal position. The distance between successive nodal planes is one-half of a wave length. From a measurement of these half-wave lengths and from the known frequency of the alternating potential, the velocity of the ultrasonic waves may be calculated.

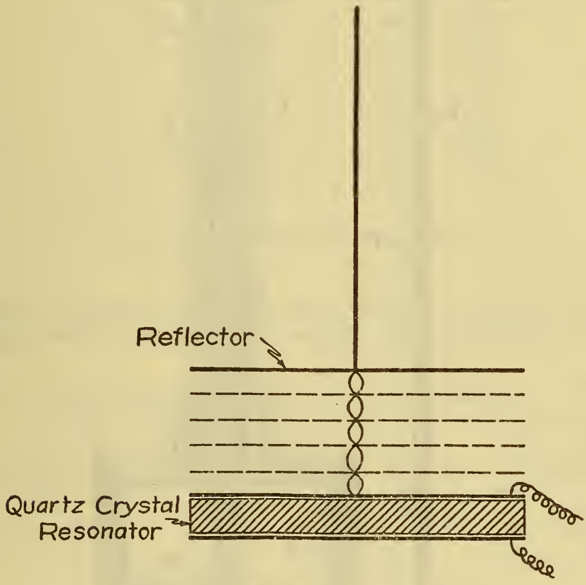

FIGURE 1.—*Principle of ultrasonic interferometer*

III. DESCRIPTION OF THE APPARATUS

A cross-section view of the interferometer itself is shown in Figure 2, which is about one-third actual size. The entire interferometer is made of metal with the exception of the quartz crystal, a bakelite cup holding the crystal, and a rubber tube insulating the alternating potential lead in. Monel metal was used practically throughout.

A cup *C* contains the liquid under investigation and the bottom of the cup, *D* (a phosphor bronze diaphragm), serves as the upper condenser plate of the quartz crystal. The sample of liquid for test may be as small as 180 cm^3. This liquid when placed in the interferometer is brought to temperature by deep immersion in a well-stirred, constant temperature water bath. Water-tight seals on the outside of the interferometer at the top and bottom of the cup are secured by the use of a wax made from beeswax and rosin.

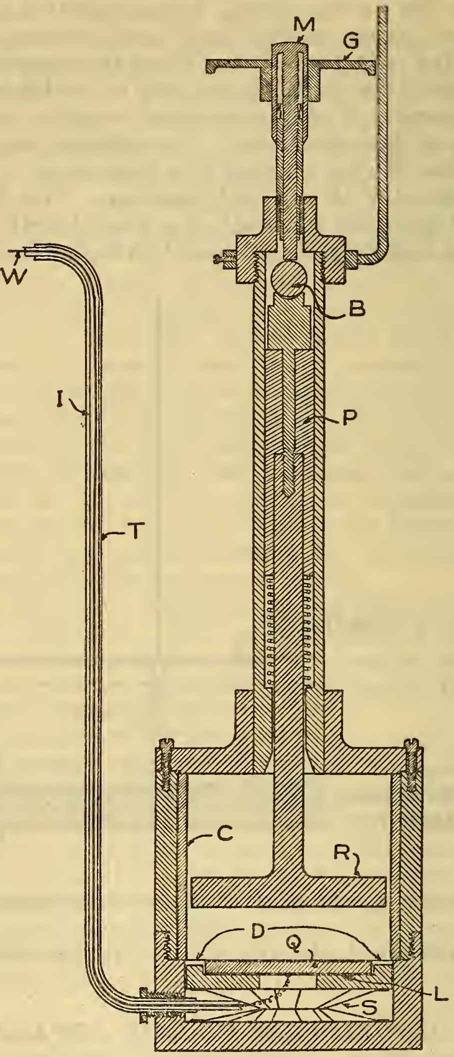

FIGURE 2.—*Ultrasonic interferometer*

R, reflector.
C, cup.
D, diaphragm.
Q, quartz crystal.
S, spring.
P, piston.
B, steel ball.
I, rubber insulation.
T, brass tube.
M, micrometer head.
W, lead wire.
G, graduated disk.
L, lower condenser plate.

Wave-length measurements are made by means of a micrometer screw, which, with the help of a spring, carries the reflector up or down and measures the distance between nodes. Upon the perfection of this screw and of its action the precision of the results is largely dependent, and much care was taken in the selection of this important part. The screw was furnished by the Brown & Sharpe Co. It has a travel of 25 mm. This screw was tested by the gage section, of the Bureau of Standards, and was found to be accurate to 2μ.

Table 1 shows one of the sets of micrometer screw readings taken for a sugar solution and illustrates the precision obtainable. The differences in the readings give wave lengths in millimeters.

TABLE 1.—*Aqueous sucrose solution*

Sugar concentration=30.42 per cent (by weight). Temperature=30° C. Frequency=767.64 kc/sec

Node	Screw readings	Wave lengths
		mm
1	24.366	
		2.107
3	22.259	2.104
5	20.155	2.105
7	18.050	2.105
9	15.945	2.104
11	13.841	2.105
13	11.736	2.104
15	9.632	2.106
17	7.526	2.106
19	5.420	2.107
21	3.313	2.106
23	1.207	
Most probable wave length=2.1051±0.0004 mm		

All possible independent differences between pairs of readings in the above set were used to calculate the most probable wave length.

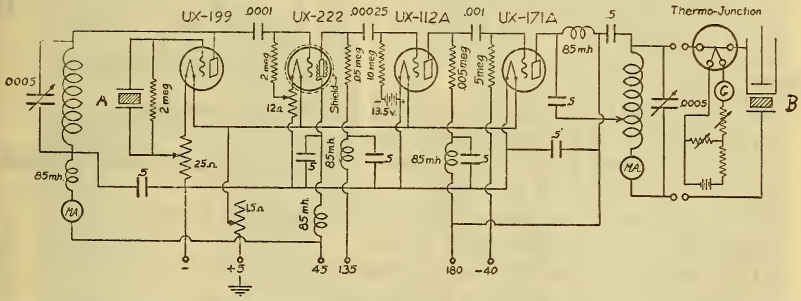

FIGURE 3.—*Constant frequency generator and amplifier used with ultrasonic interferometer*

The estimated possible error in this value was determined from measurements made six months apart on two different aqueous sucrose solutions of the above concentration and at the above temperature, the most probable value for each of four different determinations agreeing to within 0.0004 mm.

Figure 3 shows the constant frequency generator and amplifier which supplies the alternating current of ultrasonic frequency. The quartz crystal *A*, at the left, which controls the frequency, is driven by a small UX–199 tube with a tuned plate circuit. The resonator quartz crystal *B*, on the right, has a natural frequency of 550 kc., but is driven at the frequency of the control crystal, about 750 kc.

Other control frequencies ranging from 200 to 750 kc have been used, but the high frequency was preferable on account of a somewhat increased regularity of nodes for shorter wave lengths. Changes in the current driving the crystal resonator were observed by means of a hot wire-thermocouple unit used in conjunction with a reflecting galvanometer.

A photograph of the assembled apparatus (fig. 4) shows from left to right the constant temperature crystal chamber, the oscillator and amplifier, the water bath of 30 liters capacity, and the interferometer immersed in the water. The temperature of the water in the bath is maintained constant to ±0.02°C. and uniform throughout by means of a heating coil and rotating propeller located in a tube open at its ends near the top and bottom of the bath. The change in temperature of the liquid in the interferometer could be followed by observing the change in the wave length. Constancy of temperature was usually reached in one hour.

IV. THEORY FOR THE PROPAGATION OF SOUND IN SUSPENSIONS

Professor Herzfeld,[5] of the Johns Hopkins University has recently developed a theory for the "propagation of sound in suspensions," and has suggested the possibility of determining the compressibility of solids by making measurements of the velocity of ultrasonic waves first in the suspension and then in the suspending liquid with the solid particles removed by filtration or settling. The compressibility relation is formulated as follows:

$$\frac{K_1-K_2}{K_2}=\frac{V^2{}_2-V^2}{\beta V^2}-\frac{V^2{}_2}{V^2}\;\frac{\left(\frac{\rho_1-\rho_2}{\rho_2}\right)}{1+\frac{1}{3}\beta\left(\frac{\rho_1-\rho_2}{\rho_2}\right)} \qquad (1)$$

where

K_1 = adiabatic compressibility of the solid particles.
ρ_1 = density of the solid particles.
β = fractional part of the total volume of suspension occupied by the solid particles.
K_2 = adiabatic compressibility of suspending liquid.
ρ_2 = density of suspending liquid.
V_2 = velocity of sound in suspending liquid.
V = velocity of sound in suspension.

Formula (1) involves several assumptions—that the particles are small compared to the wave length, that the amplitude of the waves is small compared to the wave length, that the damping of the waves is negligible, and that the accompanying transversal waves are negligible.

V. PREPARATION OF SUSPENSIONS

The preparation of suitable suspensions is a matter of much difficulty. The conditions to be satisfied are: (1) The solid particles should be small enough to remain in suspension for about two hours with the help of only a moderate amount of stirring, (2) the particles

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[5] K. F. Herzfeld, Phil. Mag., vol. 9, No. 59, supplement, pp. 741–751, 752–768; May, 1930. On p. 768 there appears a formula (59) which corresponds to formula (1) above. An error appearing in formula (59) has been corrected in formula (1).

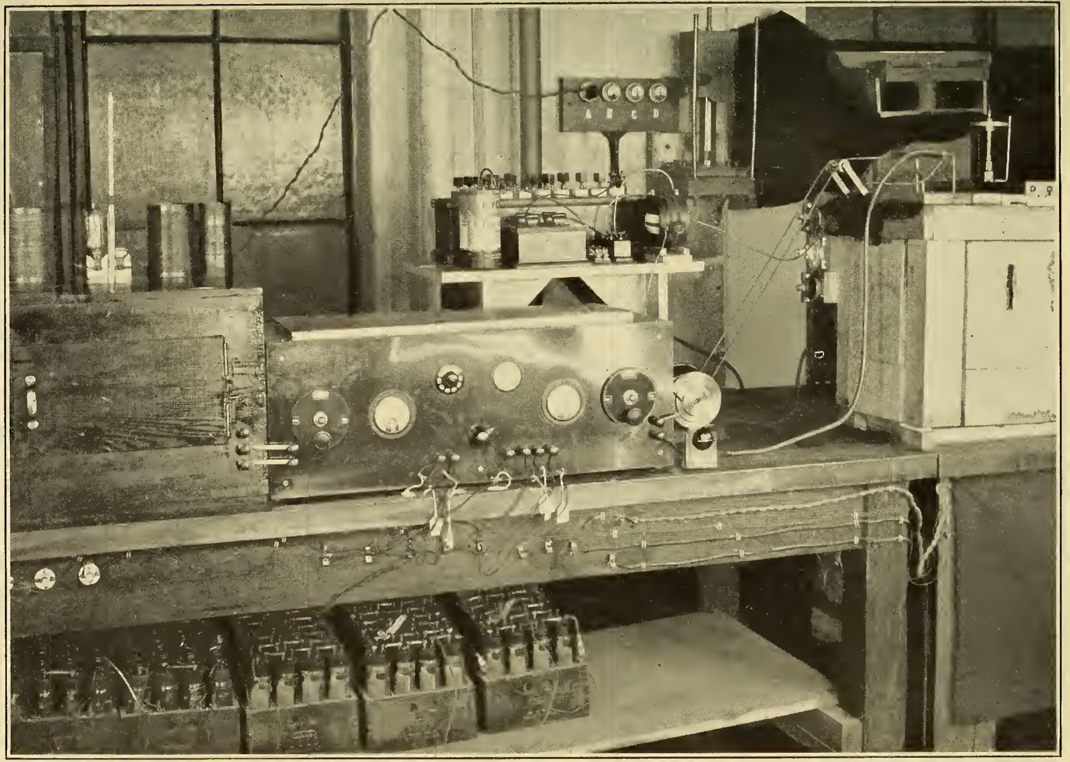

FIGURE 4.—*Ultrasonic interferometer apparatus*

must take up a uniform distribution throughout the liquid, (3) the compressibility ratio of solid to suspending liquid should be large as should also the volume concentration of the solid in suspension in order to determine the compressibility of the particles with only a few per cent of error, and (4) the solid material chosen for the experiment should be one for which the compressibility has been determined by direct pressure measurements in order that a check of the theory may be possible.

Sodium chloride was the first solid to be tried. The suspending liquid adopted was a mixture of bromoform ($CHBr_3$) and tetrachlorethane ($C_2H_2Cl_4$) in such proportions as to produce a liquid of the density of NaCl, 2.160 at 30° C. The NaCl was fused in a platinum crucible and ground with a mortar and pestle. Only those particles which would pass a 200-mesh sieve were chosen for the suspension. As it happened, the labor of pulverizing and sifting the material was entirely lost, for as soon as the fine particles were placed in the liquid they began to cluster in cloud-like masses.

Xylene was tried as a suspending liquid, but while the particles did not seem to cluster so extensively, they could not be made fine enough to remain suspended for more than two or three minutes. Out of 500g of ground material, the amount of NaCl which was fine enough to remain in suspension gave a concentration of only 0.005 per cent.

Zinc oxide particles, all of which were below 1μ in diameter, were tried both in water and in xylene, but the particles showed a tendency to stick together and dropped out of suspension very rapidly.

It was recognized that this tendency to flocculate might be due to traces of water in the liquid or in the salt particles, and special attention was given to this possibility. The liquids were dehydrated as completely as possible, both by partial freezing and by distillation and the salt particles were dried in a current of warm air that had passed through a dehydrating tower, but no appreciable diminution in the flocculation was perceptible.

It was recognized also that electrification might be causing the trouble, and the use of radium compounds in the neighborhood of the particles was resorted to, but without appreciable improvement.

VI. MEASUREMENTS ON PYREX GLASS SUSPENSIONS

The only satisfactory suspensions prepared were those of powdered laboratory pyrex glass in distilled water (containing a very small amount of HCl). Pyrex rod was ground in a steel ball mill for 48 hours. The pyrex was then found to be flour fine. It was placed in a pyrex jar and treated with a 50 per cent HCl solution to remove the iron impurity introduced in grinding. After diluting the acid and allowing the pyrex particles to settle for two days, the acid solution was siphoned off and discarded. Distilled water was then added to the pyrex residue left in the jar and the residue brought into suspension by stirring. After 24 hours' settling, the liquid containing the particles still in suspension was siphoned off and saved. This process of adding water, stirring, settling, and siphoning was repeated many times until over 20 liters of fine suspension had been obtained. A sample of the suspension was examined under a high-power microscope and all the particles were found to be smaller than 2μ in diameter, with no tendency to cling together.

The volume concentration of the solution as obtained was about 0.25 per cent. As this was too small to be suitable for measurements, the suspension was concentrated by evaporation. Two different concentrations were used in the experiments, of strengths 5 and 15 per cent by weight. To insure that the particles did not settle out of suspension during the measurements, the reflector was lowered and raised through its full travel every five minutes while the liquid was being brought to constant temperature. In addition, the reflector was similarly moved just before each reading of the nodal position. Had there been any appreciable settling of the suspended particles during the measurements it would have produced a difference of wave length in the upper and lower levels of the liquid. No such effect was noticed.

The sharpness of the nodes in the system of standing waves was considerably reduced when the particles were present in the suspending liquid. However, the wave length could be determined with a maximum error of 0.04 per cent. For both suspensions, there was a decrease in velocity when the particles were present in the liquid, the more concentrated suspension showing a decrease in velocity of 0.4 per cent. The wave lengths in the suspensions had been determined from the positions of the reflector for minimum driving current. There was, however, considerable damping of the waves which produced a gradual broadening of the pattern of maxima and minima, so that the velocity as calculated from the minima is too large. Calculating from the minima alone, the decrease of velocity in the suspensions is less than half that required by the theory. Substituted in equation (1) this decrease in velocity leads to a negative compressibility for the pyrex particles as shown in Table 2.

TABLE 2

β Pyrex concentration (by volume)	ρ_2 Density of suspending liquid	ρ_1 Density of pyrex particles	V Velocity in suspension	V_2 Velocity in suspending liquid	K_1/K_2 $\frac{\text{Compressibility of pyrex particles}}{\text{Compressibility of suspending liquid}}$
0.0222	0.999	2.23_0	$1{,}511._0$	$1{,}513._0$	−0.10
.0718	.999	2.23_0	$1{,}506._1$	$1{,}513._0$	−.08

The density ρ_1 for the laboratory pyrex glass of the particular lot worked with was determined both for the pyrex rod and the pyrex powder. The density of the rod was obtained from its weight in air and its loss of weight in distilled water; the density of the powder was found by means of a specific gravity bottle using distilled water as the wetting liquid. Both methods gave the same result, the value being 2.230 g/ml.

The volume concentration β for each suspension was determined as follows:

$$\beta=\frac{M_1/\rho_1}{\frac{M-M_1}{\rho_2}+\frac{M_1}{\rho_1}}$$

where

M = mass of suspension.
M_1 = mass of pyrex particles.
ρ_1 = density of pyrex particles.
ρ_2 = density of suspending liquid.

Negative values for the compressibility are, of course, impossible. The broadening effect due to damping seemed to be of sufficient magnitude to account for the negative results obtained. It will be remembered that in the development of formula (1) one of the assumptions made was that the damping was negligible. To see if this were the case, a study of the interference pattern was undertaken, complete curves for the galvanometer readings being taken at distances 4 and 24 mm from the source, the suspension being 18.2 per cent by weight of pyrex glass in water. These curves are shown in Figures 5 and 6.

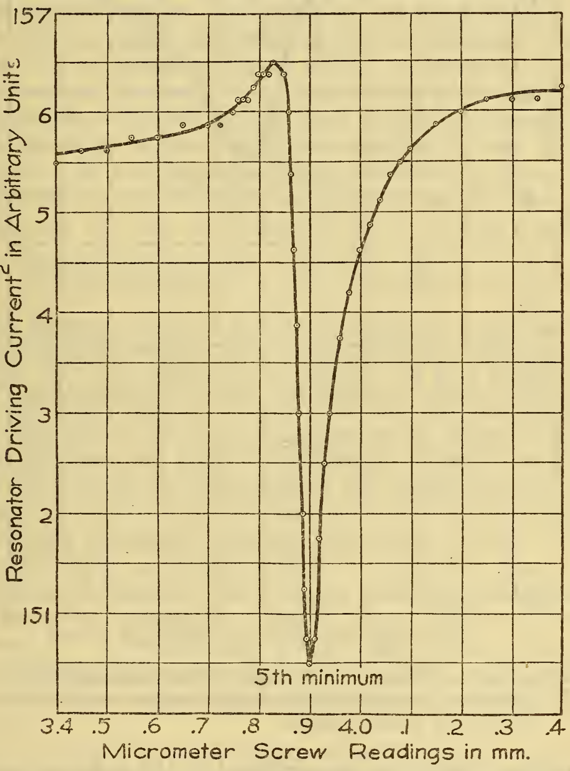

FIGURE 5.—*Wave form for pyrex glass suspension (concentration, 18.2 per cent by weight; temperature, 30° C.), near bottom of liquid column*

To a first approximation the point on the steep part of the curve in Figure 5 cut by a straight line joining the level parts of the curve may be taken as homologous with the corresponding point on the curve in Figure 6. The difference between the velocity as determined from these two points and the velocity determined from the minima is found to be 6.9 $\frac{\text{meters}}{\text{second}}$. This velocity correction applies to a volume concentration of 9.1 per cent pyrex. Assuming that this damping correction to the velocity is proportional to the volume concentration, values are obtained as shown in Table 3 below.

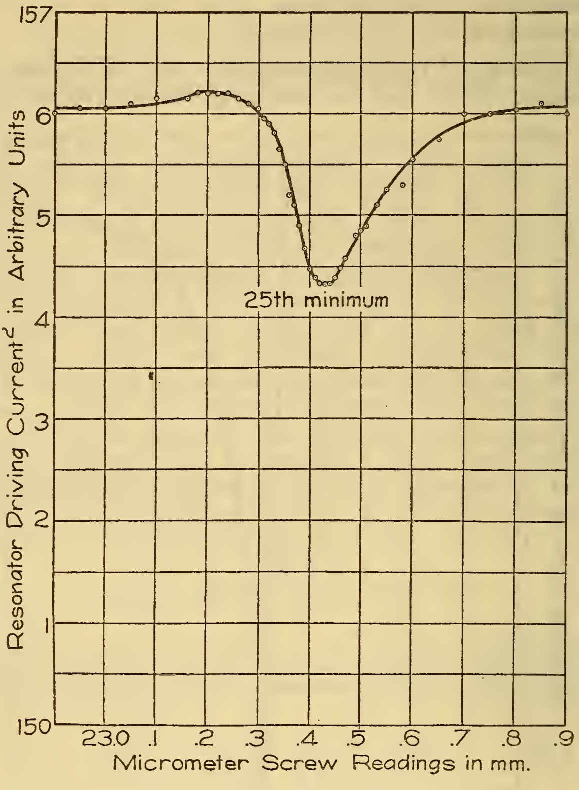

FIGURE 6.—*Wave form for pyrex glass suspension (concentration, 18.2 per cent by weight; temperature, 30° C.), near top of liquid column*

TABLE 3

β Pyrex concentration (by volume)	ρ_2 Density of suspending liquid	ρ_1 Density of pyrex particles	V Velocity in suspension	V_2 Velocity in suspending liquid	K_1/K_2 $\frac{\text{Compressibility of pyrex particles}}{\text{Compressibility of suspending liquid}}$
0.0222	0.999	2.23_0	$1,509._8$	$1,513._0$	−0.006
.0718	.999	2.23_0	$1,500._7$	$1,513._0$	+.013

The precision to be obtained in determining the compressibility of a solid in powdered form by the suspension method is not great. In the present experiment it may be seen that a variation in V of 1 part in 3,000 will alter the value of K_1/K_2 in Table 3 by 0.03 at the lower concentration ($\beta=0.0222$), and by 0.01 at the higher concentration ($\beta=0.0718$). Taking into account the calculated errors the compressibility ratios found for the two concentrations agree well within those limits.

The compressibility of pyrex glass has been determined from direct pressure measurements by Bridgman[6] and by Adams and Gibson[7], the assigned value in both investigations being 3.1×10^{-6} atm. $^{-1}$ at atmospheric pressure. This would give for K_1/K_2 the value 0.07. The difference between this value and the maximum value assignable as found by the suspension method is as yet unexplained.

There are three major limitations in the precision attainable in determining the compressibility of solids in powdered form by the velocity-suspension method: (1) The smallness of the ratio K_1/K_2, (2) the magnitude of the concentration β which it is possible to obtain, and (3) the accuracy of the velocities obtained for the liquid and for the suspension. It is estimated that a precision of 1 per cent might be reached when the above three conditions are the most favorable, provided formula (1) may be depended upon to that extent.

VII. MEASUREMENTS ON SUGAR SOLUTIONS

Ultrasonic measurements have been made on aqueous solutions of four different kinds of sugar: Sucrose ($C_{12}H_{22}O_{11}$), dextrose ($C_6H_{12}O_6$), levulose ($C_6H_{12}O_6$), and raffinose ($C_{18}H_{32}O_{16}$) at five different temperatures (with the exception of raffinose) and for several concentrations. The sound velocities in all these solutions were determined from positions of the reflector for minimum driving current—a procedure to be followed only when the damping of the sound waves is negligible. It was thought that the concentrated solutions might show sufficient damping to make necessary a small correction to the velocities obtained. Accordingly, a determination of wave form near the source of sound and some distance from it was made for a sucrose solution of 30.4 per cent concentration. These wave forms are compared in Figures 7 and 8. A calculation from these curves shows that the maxima and minima both give the same velocity within the accuracy of the measurements. Consequently, there is no damping correction to be applied.

The compressibility of these sugar solutions may be calculated just as for any liquid from sound velocity and density measurements by the following well-known relation due to Laplace

$$V=\sqrt{\frac{1}{\beta_\phi \rho}} \tag{4}$$

where

V = velocity of sound.
β_ϕ = adiabatic compressibility.
ρ = density.

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[6] P. W. Bridgman, Am. J. Sci., vol. 10, p. 363; 1925.
[7] Adams and Gibson, J. Washington Acad. Sci., vol. 21, p. 384; 1931.

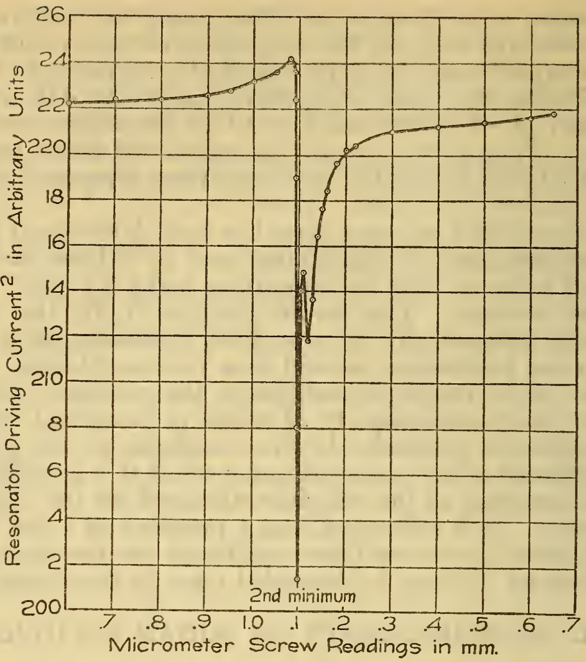

FIGURE 7.—*Wave form for aqueous sucrose solution (concentration, 30.4 per cent by weight; temperature, 30° C.), near bottom of liquid column*

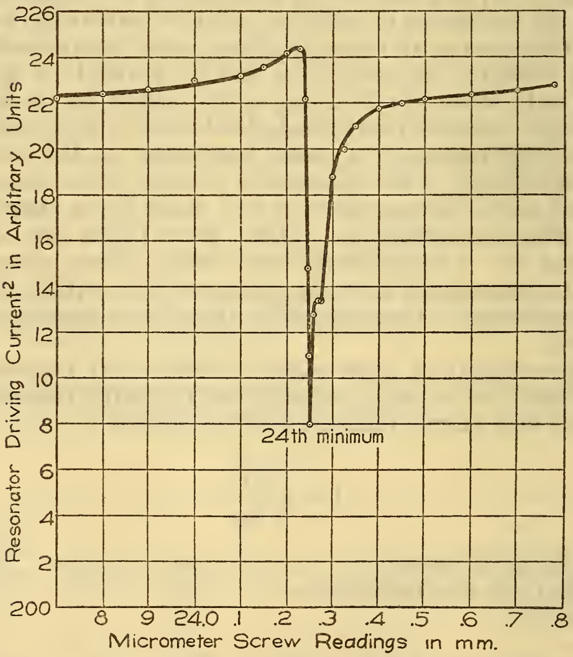

FIGURE 8.—*Wave form for aqueous sucrose solution (concentration, 30.4 per cent by weight; temperature, 30° C.), near top of liquid column*

Values of the compressibility thus obtained are shown in Tables 4 and 5. For the sucrose solutions the values of ρ were taken from Plato's tables. The values of ρ for the other solutions were determined experimentally.

TABLE 4.—*Compressibility (adiabatic) of aqueous sugar solutions at 30° C. for different concentrations*

SUCROSE ($C_{12}H_{22}O_{11}$)

Concentration	Density	Velocity	Compressibility×10 ^{6}
$\frac{g\ sugar}{100\ g\ solution}$	$\frac{g}{ml}$	$\frac{meters}{sec.}$	$atm.^{-1}$
0	0.9957	$1,509._9$	44.6_3
.87	.9990	$1,512._3$	44.3_6
3.95	1.0111	$1,520._1$	43.3_4
7.88	1.0267	$1,531._4$	42.0_8
11.91	1.0432	$1,543._6$	40.7_6
20.13	1.0783	$1,572._3$	38.0_1
30.42	1.1252	$1,615._8$	34.4_9

RAFFINOSE ($C_{18}H_{32}O_{16}$)

4.07	1.0117	$1,520._8$	43.3_1
9.15	1.0326	$1,535._8$	41.6_0
17.30	1.0677	$1,563._2$	38.8_4
27.01	1.1124	$1,603._4$	35.4_3

DEXTROSE ($C_6H_{12}O_6$)

2.11	1.0039	$1,516._9$	43.8_6
9.62	1.0334	$1,544._6$	41.1_0
18.74	1.0712	$1,583._0$	37.7_4
35.27	1,1457	$1,670._0$	31.7_1

LEVULOSE ($C_6H_{12}O_6$)

1.96	1.0033	$1,516._5$	43.9_1
5.96	1.0192	$1,531._3$	42.3_9
11.79	1.0428	$1,554._7$	40.1_9
17.47	1.0668	$1,579._8$	38.0_6

TABLE 5.—*Compressibility (adiabatic) of aqueous sugar solutions at different temperatures*

SUCROSE SOLUTION—PER CENT SUGAR=11.91

Temperature	Density	Velocity	Compressibility×10 ^{6}
° *C.*	$\frac{g}{ml}$	$\frac{meters}{sec.}$	$atm.^{-1}$
0	1.0496	$1,448._3$	46.0_2
10	1.0482	$1,488._8$	43.6_1
20	1.0461	$1,520._2$	41.9_2
30	1.0432	$1,543._6$	40.7_6
40	1.0395	$1,560._7$	40.0_1

SUCROSE SOLUTION—PER CENT SUGAR=30.42

0	1.1348	$1,544._5$	37.4_3
10	1.1322	$1,575._8$	36.0_4
20	1.1290	$1,599._8$	35.0_9
30	1.1252	$1,615._8$	34.4_9
40	1.1208	$1,627._2$	34.1_4

TABLE 5.—*Compressibility (adiabatic) of aqueous sugar solutions at different temperatures*—Continued

DEXTROSE SOLUTION—PER CENT SUGAR=18.74

Temperature	Density	Velocity	Compressibility$\times 10^6$
° *C.*	$\frac{g}{ml}$	$\frac{meters}{sec.}$	$atm.^{-1}$
0	1.0790	$1,499._7$	41.7_5
10	1.0772	$1,535._2$	39.9_1
20	1.0747	$1,562._5$	38.6_1
30	1.0712	$1,583._0$	37.7_4
40	1.0670	$1,597._1$	37.2_2

LEVULOSE SOLUTION—PER CENT SUGAR=17.47

Temperature	Density	Velocity	Compressibility$\times 10^6$
0	1.0756	$1,500._4$	41.8_5
10	1.0735	$1,534._9$	40.0_6
20	1.0706	$1,560._9$	38.8_5
30	1.0668	$1,579._8$	38.0_6
40	1.0623	$1,592._7$	37.6_0

Figures 9, 10, 11, and 12 below show the results of Tables 4 and 5 in the form of graphs. In Figure 9 it may be noticed that the velocity curves for the dextrose and levulose solutions start out together at low temperatures but gradually separate as the temperature rises.

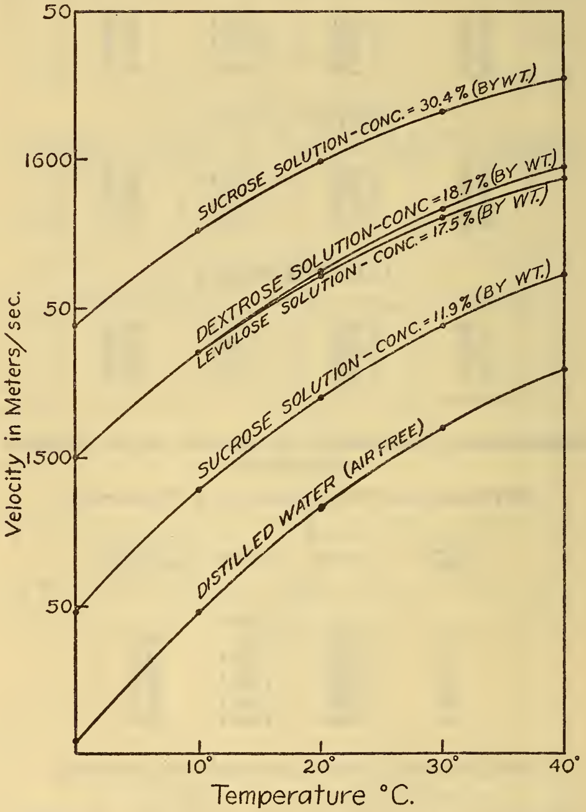

FIGURE 9.—*Variation of velocity with temperature for aqueous sugar solutions*

This is remarkable in view of the fact that both sugars have the same chemical formula, differing only as optical isomerides. Figure 10 shows the same result occurring for increasing concentration; with the curves for raffinose and sucrose also similarly associated. It will be noted that the solutions of dextrose and levulose, with molecular weights less than that of sucrose, exhibit higher velocities than sucrose, but the solutions of raffinose, which has a much greater molecular weight than sucrose, do not exhibit lower, but slightly greater velocities. Figure 12 shows that the compressibility of sugar solutions varies almost linearly with the concentration. The curves are very slightly concave downward.

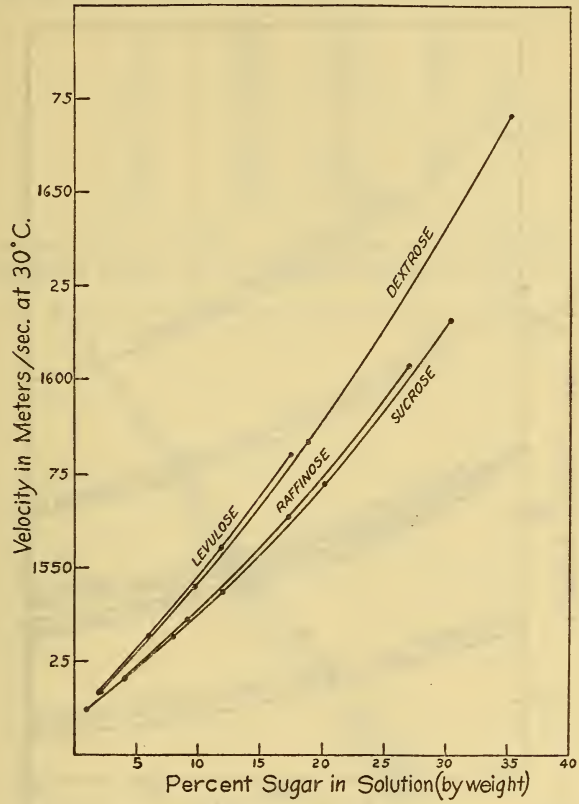

FIGURE 10.—*Variation of velocity with concentration for aqueous sugar solutions*

VIII. MEASUREMENTS ON DISTILLED WATER

Measurements have been made on distilled water over a temperature range from 0° to 86° C. The water was first boiled in a pyrex flask to eliminate dissolved air. The velocity of ultrasonic waves in water and the adiabatic compressibility of water for the above temperature range are given in Table 6 and represented graphically in the two curves of Figure 13. The upper curve shows that the velocity increases the most rapidly at 0° C., reaches a maximum at about 74° C., and then diminishes. The lower curve shows that the compressibility likewise changes the most rapidly at 0° C., with a minimum appearing at about 64° C.

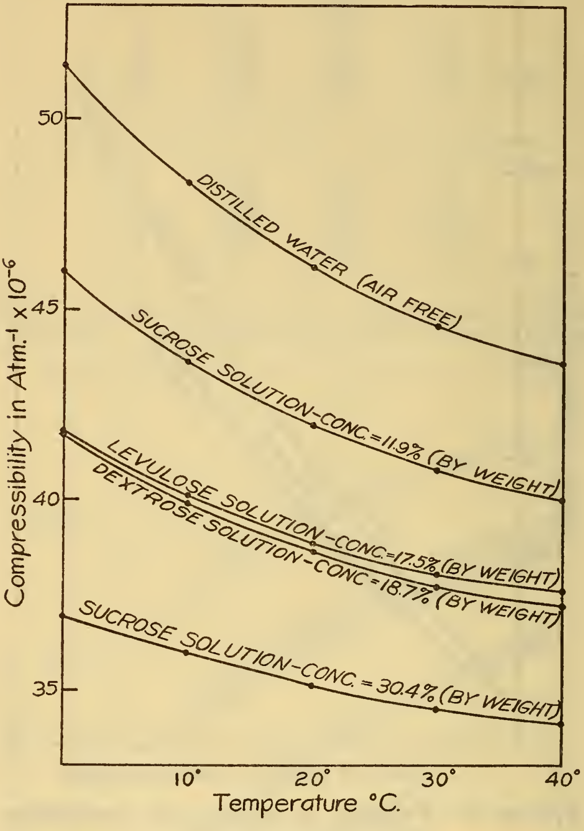

FIGURE 11.—*Variation of adiabatic compressibility with temperature for aqueous sugar solutions*

Table 6.—*Compressibility (adiabatic) of distilled water (air free) at different temperatures*

Temperature	Density	Velocity	Compressibility × 10^6
° *C.*	$\frac{g}{ml}$	$\frac{meters}{sec.}$	*Atm.*$^{-1}$
0	0.9999	1,403.$_5$	51.4$_4$
10	.9997	1,448.$_0$	48.3$_4$
20	.9982	1,483.$_1$	46.1$_4$
30	.9957	1,509.$_9$	44.6$_3$
40	.9922	1,529.$_5$	43.6$_5$
50	.9881	1,543.$_5$	43.0$_4$
60	.9832	1,551.$_5$	42.8$_1$
70	.9778	1,555.$_3$	42.8$_4$
80	.9718	1,554.$_6$	43.1$_4$
86	.9680	1,552.$_4$	43.4$_4$

Pooler[8] working at audible frequencies measured the velocity of sound in distilled water up to a temperature of 70° C. Though he did not reach the temperature for a maximum velocity he did find a minimum compressibility which occurred at about 63° C., practi-

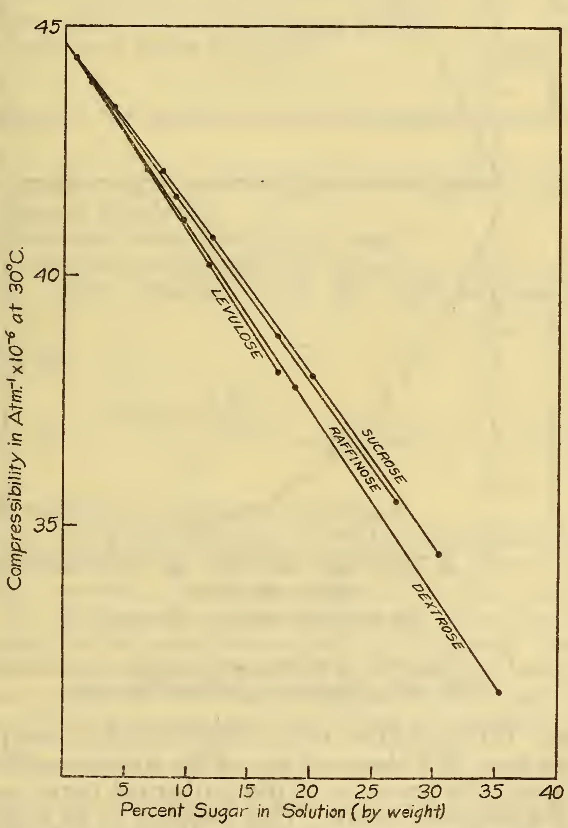

Figure 12.—*Variation of adiabatic compressibility with concentration for aqueous sugar solutions*

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[8] L. G. Pooler, Phys. Rev., vol. 35, pp. 832-847; April, 1930.

cally coinciding with that found at ultrasonic frequencies. By direct pressure measurements Tyrer [9] likewise found a minimum, though at a somewhat higher temperature.

The isothermal compressibility curve for a liquid must lie above the adiabatic curve, but does not necessarily run parallel to it. This curve may be obtained from the adiabatic values plus an additive term determined from specific heat at constant pressure and specific volume data. If the additive term is fairly small in comparison with the adiabatic term and the accuracy of the above-mentioned data is reasonably good, the precision of the isothermal curve may be equal to that of the adiabatic curve. This happens to be true in the case of water. Accordingly Table 7 has been prepared and the results shown graphically in Figure 14.

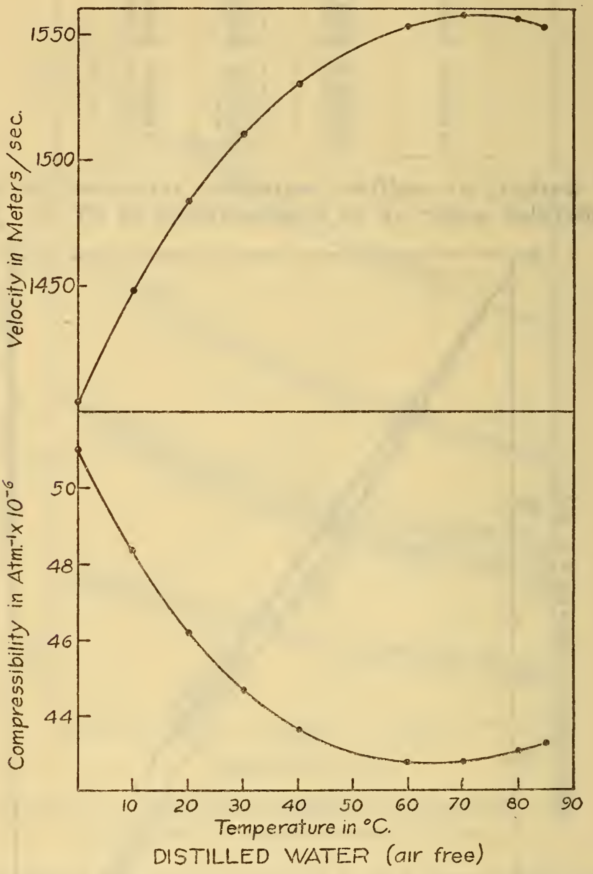

FIG. 13.—*Variation of velocity and adiabatic compressibility with temperature fordistilled water.*

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[9] D. Tyrer, J. Chem. Soc., vol. 103, p. 1687; 1913.

TABLE 7.—*Compressibility (isothermal) of distilled water (air free) at different temperatures*

Temperature	ρ	$\left(\frac{\delta v}{\delta T}\right)_p\times10^6$	C_p	$\frac{0.1013\rho T\left(\frac{\delta v}{\delta T}\right)_p^2}{C_p}\times10^6$	$\beta\phi\times10^6$	$\beta_T\times10^6$
° *C.*						
0	0.9999	−68	4.22	0.03	51.4_4	51.4_7
10	.9997	+88	4.19	.05	48.3_4	48.3_9
20	.9982	207	4.18	.30	46.1_4	46.4_4
30	.9957	304	4.17	.68	44.6_3	45.3_1
40	.9922	387	4.18	1.13	43.6_5	44.7_8
50	.9881	462	4.18	1.65	43.0_4	44.6_9
60	.9832	532	4.18	2.24	42.8_1	45.0_5
70	.9778	597	4.18	2.90	42.8_4	45.7_4
80	.9718	661	4.19	3.63	43.1_4	46.7_7
86	.9680	698	4.19	4.10	43.4_4	47.5_4

In the above table the notation is as follows:

ρ = density of water in g/ml.[10]

$\left(\frac{\delta v}{\delta T}\right)_p$ = slope of the specific volume-temperature curve.[10]

C_p = specific heat at constant pressure expressed in joules/g° C.[10]

T = degrees absolute.

β_ϕ = adiabatic compressibility in atm.$^{-1}$.

β_T = isothermal compressibility in atm.$^{-1}$.

β_ϕ and β_T were obtained from the thermodynamic relations

$$V=\sqrt{\frac{1}{\beta_\phi\rho}}$$

and $\beta_T=\beta_\phi+\dfrac{0.1013\rho T\left(\frac{\delta v}{\delta T}\right)_p^2}{C_p}$ respectively, V being the velocity of the ultrasonic waves in the liquid.

In Figure 14 the compressibility of water as determined by direct pressure measurements by various observers is given for comparison. Specific mention should be made of the fact that the curve represents the isothermal compressibility at atmospheric pressure. The compressibility of water determined by Bridgman [11] was obtained from specific volume measurement over a pressure range of 12,000 atmospheres at pressure intervals of approximately 500 atmospheres for the first 2,000 atmospheres and 1,000 atmospheres for higher pressures. The absolute values of the slope, $\frac{dv}{dp}$, of the isothermal volume-pressure curves are given for the entire range of pressure and for temperatures 0° to 80° C. For pressures 0 to 2,000 atmospheres, the slopes are given at 500 atmosphere intervals. Considering the rapid change of slope over this part of the range, the compressibility values found from the curves at the origin and those found from velocity measurements agree for the most part remarkably well. Tyrer made

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[10] Values obtained from International Critical Tables.

[11] P. W. Bridgman, Proc. Am. Acad. Arts and Sci., vol. 47, pp. 441-558, 1912; vol. 48, pp. 309-362; 1912.

direct adiabatic pressure measurements working between the pressure limits 1 and 2 atmospheres and gives compressibility values which should be identical with the compressibility at atmospheric pressure. His values for compressibility are consistently slightly smaller than those determined from velocity measurements.

Recently direct pressure measurements were made by Jessup[12] for pressure limits 0 to 50 atmospheres by steps of 10. Within the accuracy attainable from the 10 atmospheres pressure changes no measurable variation in compressibility with pressure over the range 0 to 50 atmospheres was found. Consequently the values which he gives represent compressibilities for pressure limits 0 and 50 atmospheres. At the two temperatures, 0° and 60° C. his values fall almost exactly on the curve determined from velocity measurements, the remaining four points falling below the curve. In all cases his

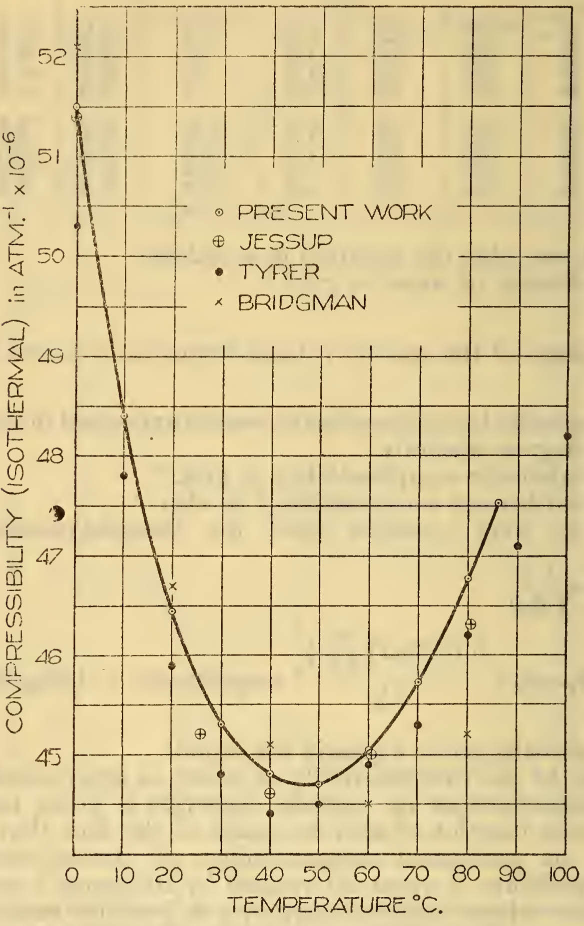

Figure 14.—*Isothermal compressibility of distilled water determined from velocity measurements at atmospheric pressure compared with results of direct pressure measurements*

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[12] R. S. Jessup, B. S. Jour. Research, vol. 5; November, 1930.

results of direct pressure measurements and the present results determined from velocity measurements differ by not more than 1 per cent. This difference may be explained from the results of Bridgman, who worked at the much higher pressures. Bridgman found the compressibility of water at 500 atmospheres to be from 12 to 15 per cent lower than that at atmospheric pressure. Accordingly, the compressibility of water determined from volume differences for pressures 0 and 50 atmospheres might be low for a point at the origin (atmospheric pressure) by 0.6 per cent. The difference between the results of Jessup and those of ultrasonic velocity measurements are thus mainly due to the limitations set by the two different conditions of experiment

IX. SUMMARY

A description is given of ultrasonic interferometer apparatus for measuring ultrasonic velocities in liquids.

Velocity measurements on aqueous solutions of sucrose, raffinose, dextrose, and levulose (and density determinations on the three latter) have been made for concentrations 0 to 30, 27, 35, and 17 per cent, respectively, and for a temperature range 0° to 40° C. The velocities and compressibilities (adiabatic) of the solutions are presented in curves and tables.

Velocity measurements were made on distilled water (air free) covering a temperature range 0° to 86° C. A table of values and curve show the variation of velocity and compressibility (adiabatic and isothermal) with temperature.

Pyrex-glass suspensions in distilled water (containing a very small amount of HCl) were prepared, the diameter of the pyrex particles ranging from 2μ down. Concentrations of 5 and 15 per cent were used for velocity measurements. The velocity decreased as the concentration increased, the decrease in velocity, as determined by minima being 0.4 per cent for the 15 per cent concentration. The change in velocity thus determined, though in the right direction, was less than half that predicted by theory. In these suspensions, however, the waves are strongly damped, the minima being shifted so as to give an apparent velocity which is too large. A correction applied for the damping yields values for the velocity more nearly in accord with those demanded by theory.

X. ACKNOWLEDGMENT

The author wishes to express his appreciation to Dr. J. C. Hubbard for his assistance in the development of the apparatus used in making the measurements on liquids and suspensions; to Dr. K. F. Herzfeld, who developed the theory for solids in suspension with the idea of making possible measurements of the compressibility of solids by the use of the ultrasonic interferometer; and to both for their kindly aid and advice during the many months of experimental work.

The friendly cooperation of the staff of the Bureau of Standards has helped materially in carrying out this research. Especially does the author wish to thank Dr. Paul R. Heyl for his helpful suggestions from time to time and his kindly interest in the work in general.

WASHINGTON, November 11, 1931.