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Ultrasonic Propagation in Liquids: I. Application of Pulse Technique to Velocity and Absorption Measurements at 15 Megacycles*

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Equipment developed by the Massachusetts Institute of Technology Radiation Laboratory has been applied to the measurement of sound velocity and absorption in liquids at 15 mc/sec. Pulses of one microsecond duration are generated by a transducer, which also picks up the resultant echoes from a plane reflector. Velocity measurements are made by determining the distance the transducer must be moved to delay the received echoes by a specified increment. Absorption measurements are made by determining the attenuation necessary to keep the receiver signal constant as the transducer is moved. The attenuation factor can be measured to an accuracy of about 5 percent and sound velocity to about 0.05 percent. Measurements in homologous series of organic liquids are reported.

I. INTRODUCTION

THE electronic pulsed-circuit techniques and equipments developed during the war are adaptable to the measurement of velocity and absorption of sound in liquids.¹ Preliminary work of this nature took place at the M.I.T. Radiation Laboratory,² and the pulse principle has also been applied³ to the examination of mechanical flaws in metals. For velocity determination in liquids the pulse method is at least as accurate as optical diffraction and acoustic interferometer methods previously employed,⁴ and considerably more accurate for absorption measurements. It is direct and convenient and therefore particularly adapted to investigations involving large numbers of liquids. The present paper reports measurements of sound velocity and absorption in selected organic liquids at 15 mc/sec. and at several temperatures.

The scheme is essentially to use the liquid sample as a "storage medium" for short sound pulses and to measure the time delay and attenuation undergone by the sound in traversing a known path within the liquid. The acoustical pulses are generated from electrical pulses by

means of a crystal transducer and are converted back to electrical form upon completing a transit through liquid; the effects of changing the acoustical path length can be compensated for electrically. Hence the increased delay produced by an increase in path length gives a measure of sound velocity; the attenuation which must be removed from the electrical circuit to balance acoustical losses in the additional distance provide a measure of absorption.

The variation in acoustic path length is accomplished by mounting the crystal transducer on a movable support riding within a tank containing a sample of the liquid. The 15 mc/sec. sound pulses, after being generated from electrical pulses by the transducer, travel through the liquid to a plane reflector and back again to re-excite the crystal at a later time. The resulting delayed electrical signal passes through a calibrated attenuator to a receiver, the output of which is fed to an oscilloscope equipped with a special sweep indicating time delays; the start of this sweep is synchronized with the generation of the original pulse, and calibrated accurately with respect to time. The change of the signal position on the screen as the transducer mount is moved with respect to the reflector is a direct measure of the corresponding delay; simultaneously, attenuation is inserted or removed by means of the calibrated attenuator to keep the receiver input signal constant.

Velocity is obtained directly from the slope of *distance traveled plotted vs. pulse delay*, and absorption is obtained from the slope of *compen-*

* This paper is based on work done for the Office of Scientific Research and Development under Contract OEMsr-262.

¹ This has been reported at the April 1946 meeting of the American Physical Society: J. R. Pellam and J. K. Galt, abstract A12.

² M. Cefola, M. E. Droz, S. Frankel, E. M. Jones, G. Maslach, and C. E. Teeter, Jr. Radiation Laboratory, M.I.T. Report 963, March, 1946.

³ F. A. Firestone, *Metal Progress* **48**, 505 (1945). E. N. Simon, *Metal Progress* **48**, 513 (1945).

⁴ L. Bergmann, *Der Ultrashall* (Edwards Brothers Reprint, Ann Arbor, Michigan, 1944).

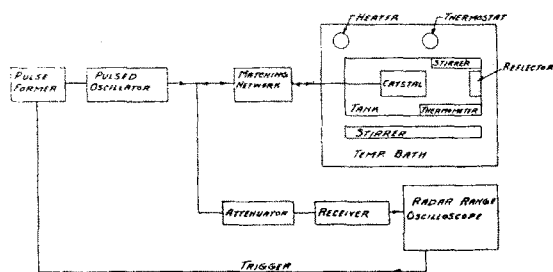


FIG. 1. Block diagram.

sating electrical attenuation vs. distance. Since the method depends only upon observing the effects of differences in acoustical path length, knowledge of exact distance traveled by the sound is unnecessary.

Results obtained in this manner may be regarded as physically equivalent to those obtained by continuous wave methods, since it may be shown that differences in behavior between pulsed sound and continuous sound in liquids should produce negligible effects. For example, no significant dispersion in liquids has been detected at these frequencies⁴ (nor any pulse distortion during these measurements) so that the group velocities measured by pulsing should not differ measurably from the phase velocities ordinarily dealt with. Similarly, although attenuation of sound in liquids varies as the square of the frequency, the band width associated with the pulses used is small enough to prevent appreciable effect on absorption measurements.*

II. EQUIPMENT

(a) Electrical Equipment and Circuits

Figure 1 is a block diagram of the equipment and Fig. 2 is a photograph of the assembled apparatus. The timing sequence is as follows:

* The exponential pressure attenuation coefficient (α), defined by

$$p = p_0 e^{-\alpha x}$$

will have a fractional error given by

$$\frac{\Delta\alpha}{\alpha} = \left(\frac{\Delta\nu}{\nu}\right)^2 \frac{\partial^2 \alpha}{\alpha \partial \nu^2} = \left(\frac{\Delta\nu}{2\nu}\right)^2$$

if measured over a frequency range of width ($\Delta\nu$). The last term results from placing (α) proportional to frequency squared, as is frequently the case. It may be shown that, for pulses of much longer duration than the period of a single oscillation, $\Delta\nu/2\nu$ is just the reciprocal of the number of cycles per pulse. The pulses employed in the measurements reported here contained about 15 oscillations, corresponding to an error of roughly one part in 250.

A crystal controlled circuit in the oscilloscope starts the scope sweep and simultaneously sends a trigger to the pulse generator. The pulse formed by the generator passes through a simple impedance matching network to the transducer; when the resulting sound pulse returns to the transducer after its round-trip within the liquid, the delayed electrical pulse is formed which passes back through the matching network. Since the transmitter is off when the echo signal arrives, very little leakage loss occurs and the main portion travels through the attenuator to the receiver.

All triggering and time measurements are accomplished by the crystal-controlled circuit in the oscilloscope (DuMont Type 256B A/R Range Scope), so that synchronization occurs automatically. In addition to setting off the pulse generator and starting the sweep, this circuit also provides marker pips spaced accurately every 12.192 microseconds thereafter (corresponding to 2000 yards radar range). Minute examination of the front edge of the echo signal is possible by means of an expanded sweep with variable delay and a speed of 1 inch per microsecond. Crystal control is necessary primarily for timing the marker pips accurately; one pip is developed for each oscillation, and since the crystal frequency is accurate to better than 1 part in 10,000 the same is true for the range marker positions.

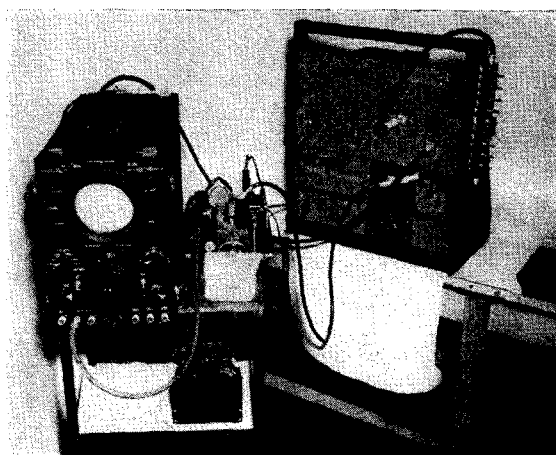


FIG. 2. Apparatus. Left: A/R range scope; center: liquid delay tank; and right: pulse forming network, oscillator, attenuator, and receiver.

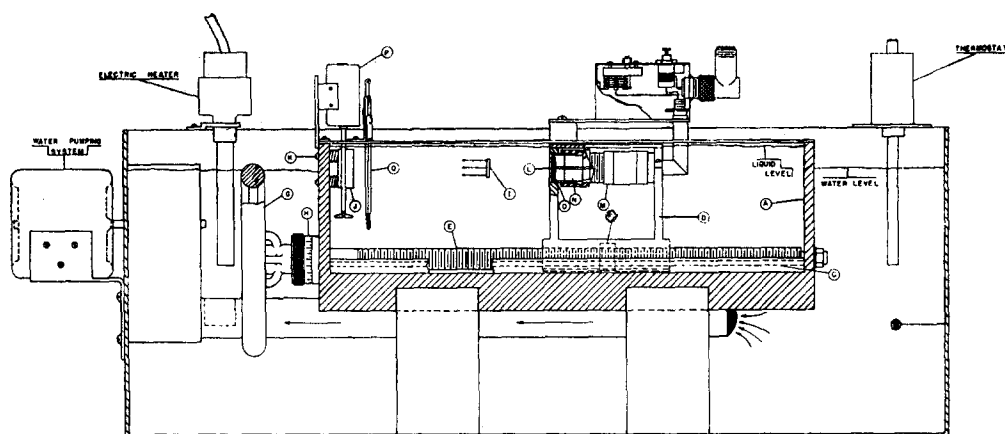


FIG. 3. Liquid delay tank.

The detailed discussion of the design of the pulse generator circuit has been given elsewhere.⁵ The trigger from the oscilloscope passes through a stage of amplification to excite the second stage, a blocking oscillator. The output of the blocking oscillator, after being clipped to form a video pulse, is applied through a switch tube to the 15 mc/sec. r-f oscillator. The latter is driven into oscillation for the duration of the pulse, and the resultant r-f pulsed signal feeds through two stages of amplification. The final signal level put out to the transducer may be controlled by means of a variable power supply to the amplifier.

Since the electrical impedance presented by the crystal is very different from the 70-ohm characteristic impedance of the transmission line leading from the pulse generator, an impedance matching network⁶ is provided to improve the response of the transducer. A small coil is used both as an autotransformer to match the line and as a means for tuning out the dead capacity of the crystal to give a purely resistive load (see Fig. 3). A coil of about 3 microhenries total inductance with a 6 to 1 turns ratio fulfills both requirements.

The receiver includes: (1) four stages of amplification at 15 mc/sec.; (2) a 15 mc/sec. local oscillator and mixer; (3) two stages of amplification at 30 mc/sec. (each stage consisting of three tubes with circuits tuned to slightly different

frequencies for broad banding); (4) a detector; (5) two stages of video amplification; (6) a video amplifier in the oscilloscope. The 30 mc/sec. stages were used only because of equipment availability; a receiver operating at 15 mc/sec. throughout is now under construction.

The calibrated attenuator has steps of 1 db and up. Shielding is adequate to prevent leakage from introducing appreciable errors, even though attenuations as high as 110 db are inserted.

(b) Sound Delay Tank for Liquids

A sample of the liquid being investigated is placed in a sturdy brass tank (A) (see Fig. 3) within a constant temperature bath (B). The bottom of the tank is sufficiently thick ($\frac{1}{2}$ ") to accommodate a milled track (C), with adjustable side plate for tightening, and upon which the transducer mount (D) travels. Motion is produced by turning the phosphor bronze micrometer screw (E) which threads through a stainless steel nut (F) set in the transducer mount. A hand-wheel (G) is provided and a dial (H) which indicates travel in thousandths of an inch. Calibration of the screw against size blocks makes it possible to read the transducer position significantly to 0.0001".

The sound pulse (I) is reflected at the end of the tank by a disk (J) of stainless steel, ground and lapped optically flat. This reflector is supported by three adjustment screws (K), and may thereby be set perpendicular to the sound beam by aligning for maximum returned signal strength.

⁵ S. Frankel, M.I.T. Radiation Laboratory Report 645-8.

⁶ The authors are grateful to Messrs. Jones and Frankel of the Radiation Laboratory for the design constants used in this network.

The transducer element (L) is an X -cut 15 mc/sec. quartz crystal plate, $\frac{1}{2}$ " in diameter and gold plated on both sides. This crystal is held in place within a cartridge (M) by a Lucite bead (N) so that a diameter of about 1 cm is exposed to the liquid. A metal foil (O) between the bead and the quartz establishes electrical contact with the back surface.

(c) Temperature Control

Temperature equilibrium is maintained by balancing the effects of dry ice in the bath against the warming action of a thermostatically controlled electric heater. A water pumping system improves temperature uniformity outside the measuring tank, and a motor-driven stirrer (P) maintains constant temperature within the liquid sample itself. Temperature is read by thermometer (Q) and must be maintained to within less than 0.03°C for velocity measurements accurate to 0.01 percent.

III. MEASUREMENT TECHNIQUES

The velocity of sound within most organic liquids is of the order of 1.5×10^5 cm/sec. which corresponds at this frequency to about 100 wave-lengths per cm. Hence the crystal radiating surface is about 100 wave-lengths across, so that the pulses travel out within a very sharp beam (0.7° to the first minimum). It may be shown that this spread produces less than $\frac{1}{2}$ db of geometrical attenuation over the range employed; therefore readings of attenuation are suitable, without corrections, for computing liquid absorption coefficients directly.

Velocity readings are taken at 2000-yard (radar) range intervals by placing the returned signal pip at definite positions with respect to successive scope range markers, and recording the setting of the micrometer screw. By properly adjusting the scope these markers appear as very short (dark) breaks in the sweep, and if consistent positioning criteria are adopted, accurate range difference readings result. It turns out that careful adjustment of attenuation is necessary for consistent velocity readings. Consequently simultaneous readings for velocity and attenuation are preferable.

This interdependence between measurements

exists because the signal pulses never build up instantaneously, even though they are sharp; as a result the front edge of the pulse may actually be shifted with respect to the range marker by varying the attenuation level. Therefore by adjusting attenuation to bring the signal peak always to the same arbitrary height on the screen (chosen within the linear range of scope amplification), the identical portion of the signal may be obscured by successive range markers. Once this condition is satisfied, the crystal position may be set more precisely if a predetermined attenuation is then arbitrarily removed; this allows setting on a lower, and therefore steeper, portion of the pulse front. Consistent results are obtained in this manner providing the same quantity is removed for each range reading, and a value of 10 db was found convenient.

It is evident that if this adjustment of the returned signal to a pre-determined level is attained by means of the attenuator leading to the receiver (see Fig. 1) without disturbing the gain of the remainder of the system, absorption data follow as a by-product of the velocity measurements.

For accurate absorption readings the sharpness of the beam requires that (1) the reflector disk be adjusted carefully, and (2) temperature gradients within the liquid sample be avoided. *The proper operation of the stirrer (P) is absolutely*

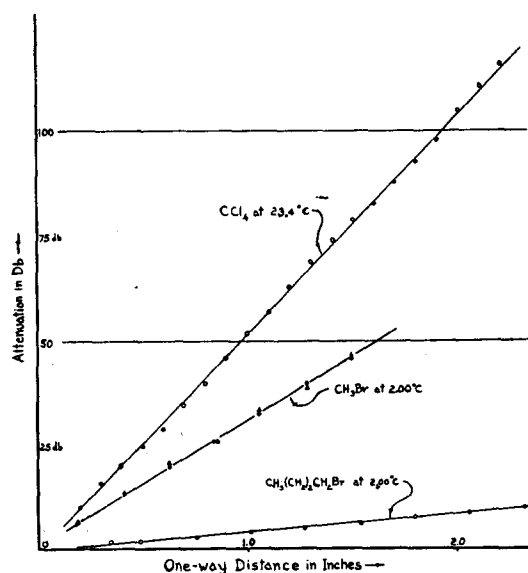


FIG. 4. Plot of sound attenuation vs. distance.

TABLE I. Experimental values of the pressure attenuation and velocity in liquids.
Frequency $f = 15$ mc/sec. $p = p_0 \exp [-\alpha x]$.

Substance	(1) Temp. °C	(2) Velocity cm/sec.	(3) Attenuation cm ⁻¹	(4) $(\alpha/f^2) \times 10^{17}$ sec ² /cm experimental	(5) classical	(6) $\alpha^{-1}(\partial\alpha/\partial T)_p$ exper. °C ⁻¹	(7) $c^{-1}(\partial c/\partial T)_p$ exper. °C ⁻¹
Methyl bromide CH ₃ Br	2.0	0.905 × 10 ⁸	0.684 (±1%)	304	—	—	
Ethyl bromide CH ₃ CH ₂ Br	2.0	0.959	0.136 (±5%)	61	10	+0.010	-0.0036
	10.0	0.932	0.14	62	—		
	20.0	—	0.14	62	10		
	30.0	—	0.18	80	—		
<i>n</i> -propyl bromide CH ₃ CH ₂ CH ₂ Br	2.0	1.0326	0.088 (±5%)	39	11	—	
<i>n</i> -butyl bromide CH ₃ (CH ₂) ₂ CH ₂ Br	2.0	1.083	0.11 (±10%)	49	13	—	
Methyl iodide CH ₃ I	2.0	0.888	0.555 (±1%)	247	10	+0.0087	-0.0031
	6.5	—	0.588	262	—		
	20.0	—	0.711	316	—		
	30.0	0.815	0.751	334	—		
	35.0	—	0.765	340	—		
	40.0	—	0.776	345	—		
Ethyl iodide CH ₃ CH ₂ I	2.0	0.9235	0.09 (±10%)	40	12	—	
<i>n</i> -propyl iodide CH ₃ CH ₂ CH ₂ I	2.0	0.982	0.122 (±5%)	54	14	—	
<i>n</i> -butyl iodide CH ₃ (CH ₂) ₂ CH ₂ I	2.0	1.022	0.109 (±5%)	48	17	—	
<i>n</i> -propyl chloride CH ₃ CH ₂ CH ₂ Cl	2.0	1.158	0.095 (±10%)	42	8	—	
<i>n</i> -butyl chloride CH ₃ (CH ₂) ₂ CH ₂ Cl	2.0	1.213	0.242 (±2%)	108	10	—	
Methyl acetate (Pract) CH ₃ COCH ₃	19.0	1.195	0.16 (±3%)	71	6	—	
Ethyl acetate (Pract) CH ₃ COC ₂ H ₅	24.3	1.145	0.163 (±3%)	72	8	—	
Amyl acetate (Pract) CH ₃ COC ₄ H ₁₁	29.2	1.173	0.167 (±7%)	74	14	—	
Methyl alcohol CH ₃ OH	2.0	1.186	0.10 (±15%)	45	15	-0.011	-0.0032
	19.3	1.123	0.084 (±10%)	37	14		
Ethyl alcohol CH ₃ CH ₂ OH	2.0	1.246	0.052 (±10%)	23	29		
<i>n</i> -propyl alcohol CH ₃ CH ₂ CH ₂ OH	2.0	1.288	0.195 (±2%)	87	55	-0.0086	-0.0028
	27.5	1.1976	0.157 (±3%)	70	36		
<i>n</i> -butyl alcohol CH ₃ (CH ₂) ₂ CH ₂ OH	2.0	1.324	0.240 (±5%)	54	65		
<i>n</i> -amyl alcohol CH ₃ (CH ₂) ₃ CH ₂ OH	2.8	1.320	0.348 (±2%)	155	113	-0.014	-0.0029
	28.6	1.224	0.231	106	58		
Benzene C ₆ H ₆	7.5	1.382	1.52 (±3%)	680	9	+0.011	-0.0036
	21.8	1.3116	1.79 (±1%)	800	8		
Nitrobenzene NO ₂ C ₆ H ₅	7.5	1.518	0.165 (±5%)	73	16	+0.0048	-0.0023
	23.8	1.462	0.178 (±4%)	79	14		
Chlorobenzene C ₆ H ₅ Cl	7.5	1.333	0.276 (±1%)	123	10		
<i>n</i> -hexane CH ₃ (CH ₂) ₄ CH ₃	21.2	1.085	0.174 (±5%)	77	10		
<i>n</i> -heptane CH ₃ (CH ₂) ₅ CH ₃	22.4	1.150	0.18 (±10%)	80	10		
Carbon tetrachloride CCl ₄	23.5	0.924	1.20 (±1%)	533	20		

essential to the temperature uniformity required for accurate absorption measurements. If the stirrer is stopped there is an immediate change in signal

level and non-linear absorption curves result. The heat developed by attenuation within the beam contributes to these refraction effects.

IV. RESULTS

(a) Linearity of Absorption Curves

Curves of attenuation *vs.* range are given in Fig. 4 for three sample liquids, indicating the degree of linearity found (over a range exceeding 100 db for CCl_4). No effects attributable to geometrical divergence of the beam are evident; the limit of accuracy appears to depend upon the smallest attenuation increment used (1 db) as suggested by the small systematic variation about a straight line.

(b) Summary of Measurements

Part I of this paper is concerned only with the presentation of measurements in the form of raw data, interpretation being reserved for Part II. However, these results are given in terms of quantities or parameters possessing physical significance in view of Part II.

Table I is a summary of measurements obtained for the various series of related organic compounds investigated. The velocity is given in column (2) in units of cm/sec. and the absorption coefficients (α) in column (3) in units of cm^{-1} . (α) is the exponential pressure attenuation coefficient defined by

$$p = p_0 e^{-\alpha x}. \quad (1)$$

Since for a number of liquids (α) varies nearly as the frequency squared, a convenient form for comparing measured results with those computed from classical (viscosity) theory is given in column (4). The classical absorption values were calculated considering viscosity effects alone; heat conduction will increase these values by about 5 percent. Columns (6) and (7) give the experimental temperature coefficients for (α) and velocity, respectively.

These particular series of homologous compounds were chosen with a view to observing the gross effects of substitutions within molecules (such as the revelation for example that replacing an $-\text{H}$ in benzene by a $-\text{Cl}$ cuts absorption by a factor of 5, and that an $-\text{NO}_2$ cuts it by 9). The most complete array examined was the alkyl halide group, of which 10 members were included (the 2°C was chosen just below the boiling point of methyl bromide).

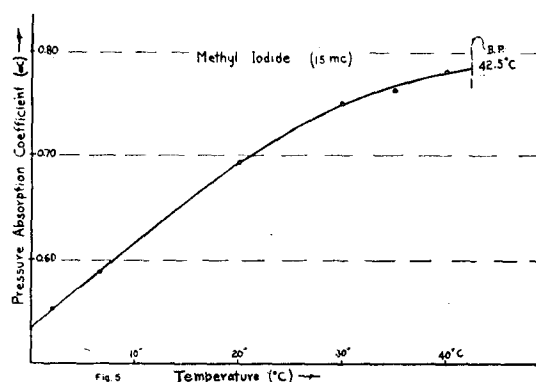


FIG. 5. Sound pressure absorption coefficient α *vs.* temperature.

(c) Accuracy

Velocity results are given here to an accuracy of about 1 part in 1000. It is believed, however, that the pulse method is inherently capable of yielding as high accuracy for velocity measurements as the best diffraction techniques. On the other hand, whereas previous techniques were often incapable of exceeding 25 percent accuracy in absorption measurements, the absorption is given here to about 5 percent on the average. Since the limit of this accuracy is set by the smallest attenuation increment, best results occur for highly absorbing liquids since they provide a greater attenuation range. Thus for liquids such as CCl_4 (α) is given to about 1 percent, but is accurate only to about 10 percent for liquids exhibiting low absorption.

(d) Temperature Dependence of Absorption

The pulse method for measuring (α) is sufficiently accurate for investigating the effects of temperature. For example Fig. 5 shows the absorption coefficient for methyl iodide plotted against temperature (for values up to the boiling point). Temperature coefficients may be obtained from such curves and, as shown in Part II of this paper, have considerable significance with regard to the mechanism of sound propagation.

V. REMARKS

(a) Anticipated Measurements

A new apparatus for measuring velocity and attenuation by the pulse technique has just been

completed. It is designed for operation at liquid helium temperatures. Preliminary measurements have already been made for liquid nitrogen and argon, and measurements in liquid helium will shortly be under way.

(b) Acknowledgments

The authors wish to express their thanks to Mr. Gerald Holton of Harvard University for

aid with the measurement runs and to Miss Ruth Roman and Mr. J. E. Krasinski, Electronics Laboratory, for technical assistance. The ultrasonic measurement program was arranged through the cooperation of Professor J. A. Stratton, Director of the Research Laboratory of Electronics, and Professor R. H. Bolt, Director of the Acoustics Laboratory. The encouragement and advice of Professor P. M. Morse is gratefully acknowledged.

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Ultrasonic Propagation in Liquids. II. Theoretical Study of the Free Volume Model of the Liquid State*

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The free volume theory of liquids is applied to problems connected with sound propagation. The equation of state derived by Tonks for assemblies of hard elastic spheres may be written $pV_a \cong 3NkT$, where the *available volume* V_a is the difference between the actual volume and the volume corresponding to the closest possible packing. It is shown that the molar available volume is approximately given by the increase in molar volume of a substance on heating from 0°K to the temperature considered, so that the pictorial concept of the available volume has a real physical basis. Using the Tonks equation, expressions are derived for the sound velocity, and the temperature and pressure coefficients of sound velocity. These expressions are compared with experimental results. Expressions are also given for the cubic expansion coefficient and the difference of the specific heats on the free volume model. The Herzfeld-Rice derivation of the sound absorption caused by phase shifts in the vibrational specific heat is carried through for the Tonks equation of state. The temperature and pressure coefficients of sound absorption are discussed. Remarks are made on the relation of molecular structure to sound absorption.

I. INTRODUCTION

THE purpose of this paper is to describe the velocity and absorption of ultrasonic waves in liquids in terms of the free volume theory of liquids and the relaxation theory of absorption processes. It is emphasized at the beginning that simple models of liquids may not be expected to give close numerical agreement with observation. We should, however, require that the model give the correct order of magnitude of physical quantities and their variations. This test we propose to apply to the free volume theory of liquids. The implications of the theory with respect to the mechanical properties of liquids have not

previously been considered, to the author's knowledge.

The important experimental facts regarding ultrasonic propagation in liquids are summarized below:

(a) The velocity of sound in a liquid is commonly of the order of five to ten times the velocity in the vapor at the same temperature. For example, the velocity of sound in liquid oxygen¹ at 90°K is 910 m/sec., while the velocity in oxygen vapor² at the same temperature is 180 m/sec.

(b) The temperature coefficient of sound velocity $c^{-1}(\partial c/\partial T)_p$ is of the order of $-3 \times 10^{-3} \text{ } ^\circ\text{C}^{-1}$; in gases the temperature coefficient is of the same order but is positive.

(c) The pressure coefficient of sound velocity $c^{-1}(\partial c/\partial p)_T$ is of the order of $+5 \times 10^{-10} \text{ cm}^2/\text{dyne}$.

(d) The absorption of sound waves in liquids usually exceeds the classical value calculated on the basis of

* This paper is based on work done for the Office of Scientific Research and Development under Contract OEMsr-262.

¹ H. W. Liepmann, *Helv. Phys. Acta* **9**, 507 (1936).

² A. van Itterbeek and P. Mariëns, *Physica* **4**, 207 (1937).