

The rate of vaporization and condensation is affected to a remarkable degree by the state of dryness.

Ammonium chloride which has been dried for ten days at 60° in a high vacuum appears to be completely dissociated in the vapor state.

URBANA, ILLINOIS

---

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE JOHNS HOPKINS UNIVERSITY]

## SONIC STUDIES OF THE PHYSICAL PROPERTIES OF LIQUIDS.

### I. THE SONIC INTERFEROMETER. THE VELOCITY OF SOUND IN SOME ORGANIC LIQUIDS AND THEIR COMPRESSIBILITIES<sup>1</sup>

BY EGBERT B. FREYER<sup>2</sup> WITH J. C. HUBBARD AND DONALD H. ANDREWS

RECEIVED OCTOBER 27, 1928

PUBLISHED MARCH 6, 1929

A number of investigators<sup>3</sup> have studied the velocity of sound in liquids at audible frequencies but the methods are beset with so many difficulties and involve the use of such large quantities of liquids that few results of adequate precision for thermodynamic treatment have been obtained. More recently<sup>4</sup> the field of high frequency sound production using piezo-electric crystals has been entered, and Hubbard and Loomis<sup>5</sup> have developed a method which has yielded very accurate values for the velocity of sound in liquids. The investigation recorded here was conducted according to their method and is a part of the general program of thermodynamic research on organic compounds now being undertaken at this Laboratory. The sonic interferometer has been further developed with especial reference to temperature control, the prevention of evaporation of the liquid being studied and of contamination by water vapor from the air.

#### Apparatus and Method

The electrical equipment is shown in Figs. 1, 2 and 3. When the circuit Y is tuned by means of the condenser (15), a heterodyne is produced between the two oscillating circuits. When the note is made to coincide in pitch with that produced by the tuning fork, the crystal in the interferometer is known to be vibrating with the same frequency

<sup>1</sup> This paper was presented in part at the Swampscott meeting of the American Chemical Society in September, 1928.

<sup>2</sup> From the dissertation submitted by Egbert B. Freyer in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

<sup>3</sup> Schmidt, *Wiener Ber.*, (IIa) **114**, 945 (1905); Dörsing, "Inaug. Diss.," Bonn, 1907; *Ann. Physik*, [4] **25**, 227 (1908); Busse, *ibid.*, **75**, 657 (1924); Pooler, *Phys. Rev.*, **31**, 157 (1928) (abstract).

<sup>4</sup> Boyle, *Trans. Roy. Soc. Canada*, **17**, 141 (1923); 159, 191, 197 (1925); 79 (1927); Langevin, British Patent Spec. N. S. 457, No. 145,691 (1920).

<sup>5</sup> Hubbard and Loomis, *Nature*, **120**, 189 (1927); *Phys. Rev.*, **31**, 158 (1928); *Phil Mag.*, VII, **5**, 1177 (1928).

as circuit X<sup>6</sup> (this being fixed and determined by crystal (7)), plus or minus 1000 cycles, the frequency of the fork. Exact coincidence of the two audible frequencies is indicated by the disappearance of the easily discernible beats heard when the fork is operated.

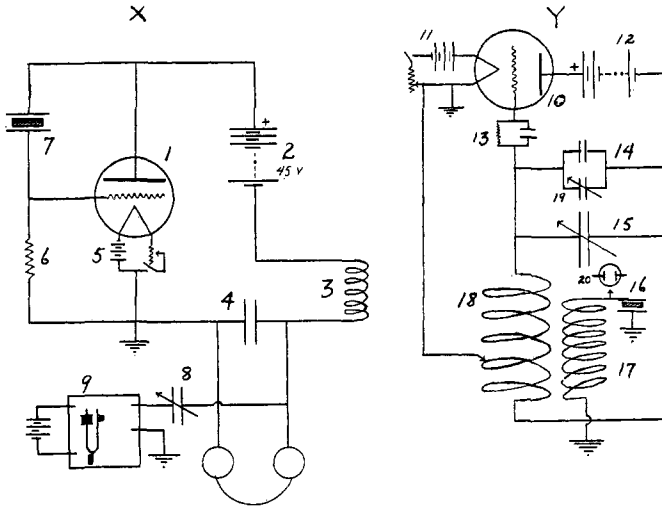


Fig. 1.—X. *The Pierce Oscillator*: 1, UX, 199 tube; 2, 45 volts; 3, choke, 30 millihenries; 4, 0.002 mf.; 5, two dry cells in series; 6, grid leak, 1 megohm; 7, crystal, see Fig. 2; 8, 0.0005 mf.; 9, 1000-cycle electrically driven tuning fork (General Radio). Y. *The Hartley Oscillator*: 10, UX-171 or UX-210 tube; 11, 7 volts, D. C.; 12, 180 to 300 volts D. C.; 13, grid leak, 1 megohm; 0.002 mf.; 14, 1 to 3 mf. (so arranged that 1, 2 or 3 mf. may be used); 15, 0.001 mf.; 16, sonic interferometer, see Fig. 3; 17, 60 to 90 turns of No. 25 B. and S. insulated copper wire, wound closely, diameter of coil, 4"; 18, 30 turns of No. 16 B. and S. bare copper wire, coil 5" in diameter, 6" long, alternate turns provided with projections to clip onto; 19, two plate vernier condenser; 20, neon lamp, see Fig. 4.

The final tuning is effected by means of the vernier condenser. Assuming the lower surface of the interferometer piston to be in a nodal plane, *i. e.*, assuming a system of

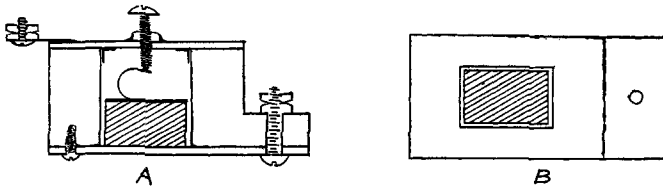


Fig. 2.—Housing for control crystal (7) in Fig. 1.

"stationary waves" in the liquid, the beats will return if the piston is raised or lowered even a very slight distance (0.002 mm.). By a proper simultaneous manipulation of

<sup>6</sup> G. W. Pierce, *Proc. Am. Acad.*, 60, 269 (1925). For other circuits see *Proc. Inst. Radio Eng.*, 15, 9 (1927).

the vernier condenser and the micrometer screw on the interferometer the nodes are located and their relative positions read from the micrometer screw scale. A reading of the screw setting is taken when the beat frequency is zero (piston in node); calling this reading  $x$ , and lowering the piston through the liquid for a distance of about two centimeters, counting meanwhile the number of nodes,  $n$ , a second screw reading,  $y$ , is taken for the position of another node. Then  $(x - y)/n = \lambda/2$  and  $2\omega \times (x - y)/n = v$ , where  $\omega$  is the frequency of oscillator Y, and  $v$  is the velocity of sound in the liquid.

The accompanying drawings illustrate the essential details of the apparatus. Brief mention may be made of the experimental arrangement.

The circuits were mounted on a board bearing a hard rubber panel supporting the condensers and rheostats; this was in turn mounted in a copper-lined box for shielding. The control dials were placed on the outside of this box to be within easy reach. As measurements were made in a number of different thermostats, the entire apparatus was made portable. The box was screwed to the top of a table mounted on rubber-tired casters. Several inches from the floor was a large shelf supported by the table legs; this carried all of the batteries. These and the leads to the circuits above them were shielded by enclosing the whole in copper window screening, using the table to support this. The wire leading from the secondary coil to the sonic interferometer was shielded by running it through a brass tube three centimeters in diameter by thirty centimeters long. It was attached to the side of the box through a universal joint. The lead was maintained rigid in the tube by having it pass through a glass tube supported at either end by corks. As there was a considerable potential between this wire and the shielding (about 1000 volts if a UX 210 tube is used), a pronounced condenser action resulted between the two; to keep this at a minimum, the lead was as short as possible and not too close to its shielding. Contact with the interferometer was made by a clip on the same, the contact itself being shielded by a sheath which slid over the brass tube bearing the lead.

An alternate, though less precise, method of detecting the nodes involves the use of a neon lamp (20). This was mounted in a tube as shown in Fig. 4; whenever the circuit was oscillating, the lamp exhibited a red glow. When the piston was exactly in a node, however, the glow either disappeared entirely (owing to the drop in the value of the current) or so changed in shape and intensity that there was no mistaking the

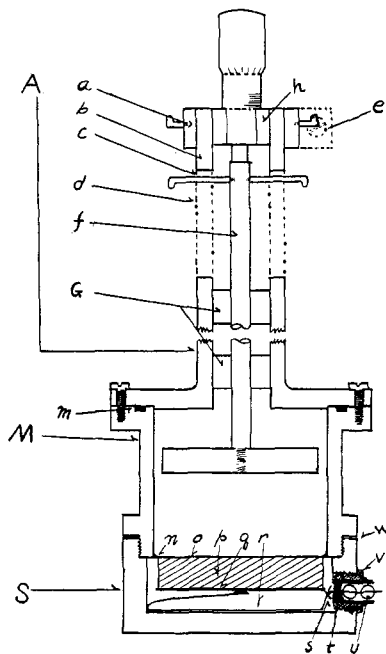


Fig. 3.—The Sonic Interferometer: Materials: A, bronzite; M, iron; S, bakelite; f, "Invar" steel; a, e, clamp; b, four vertical slots, not shown; c, hook for rubber bands; d, slot; g, guide collars; m, rubber gasket, slightly thicker than depth of groove; n, solder; o, phospho-bronze, 0.005" thick; p, quartz disk; q, bronze or brass; r, spring; s, good contact; t, deKhotinsky; u, glass beads; v, brass bushing into which is soldered the copper tube bearing the lead wire; w, water-tight seal. The piston and inside of the cup were gold plated.

position of the node as read on the micrometer screw. Even when this device was not used for the precise determination of the separation of the nodes, it very conveniently served as an indication of when the circuit was oscillating. The character of the glow was determined by the distance between strip (a) and the lamp. Cemented to the screw was a glass tube to insulate the high tension wire against the hand when adjustments were made. In general, for detecting nodes, the distance (a) was such that the glow was quite faint when the piston was *not* in a node. The lens rendered a better view of the glow. The device was mounted by a universal joint to the top of the box containing the circuits and could thus be made visible from any angle.

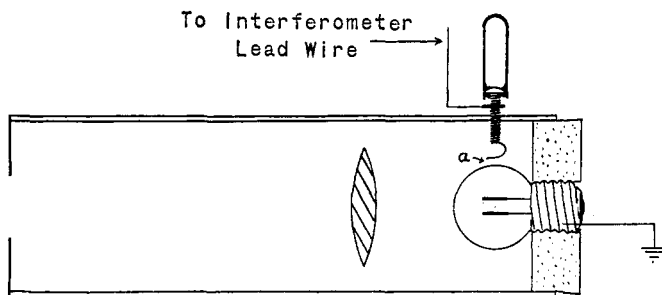


Fig. 4.

**Materials.**—With a few exceptions the samples studied in this investigation were prepared as follows: "Baker's c. p. Analysed" liquids were distilled through a three-foot punched-in column, only those cuts being taken for measurement that boiled within  $0.1^\circ$  of the latest published boiling points. Appropriate barometric and stem corrections were made. Those liquids that tend to dissolve water vapor were carefully dried and protected during storage. The glycerin (Baker's Analysed) was dried for several hours at water-bath temperature through phosphorus pentoxide. The purity of the bromoform and  $\alpha$ -bromonaphthalene was questionable, but these liquids were included in the investigation only because they, like benzene, melt at a convenient temperature and it was desired to ascertain if the break in the velocity of the sound-temperature curve, noticed first in the case of benzene, was a phenomenon of general occurrence. The isomeric heptanes were prepared in the research laboratory of the Ethyl Gasoline Corporation and kindly loaned to us for use in this investigation.

**Sources of Error and the Precision.**—A possible source of error was the absorption of water vapor from the air during the actual measurement. This apparently was quite appreciable in the case of acetone, as manifested by the difference between two readings made an hour and a half apart. It was avoided by using a fresh sample of the liquid for each measurement. This error was borne in mind throughout the investigation and appropriate precautions were taken to avoid it. A new design of the spring mechanism on the piston entirely eliminates this source of error by closing up the slots (d).

For some reason not yet ascertained the oscillations were considerably weakened at temperatures above  $50^\circ$  and with some liquids they disappeared entirely. The values given for the velocity of sound at this temperature are extrapolated ones. If an air bubble is entrapped under the piston

when it is inserted, the sonic "reaction" may be greatly weakened or entirely absent.

As a rule screw readings were taken on three or four adjacent nodes when the piston was near the upper limit of its range and three or four when it was near the lower limit, the number of nodes in the interval being, of course, known. Occasionally, however, the position of each node was determined, as sometimes the  $\lambda/2$  value between two nodes near the center of the liquid column would be a freak one, differing for no apparent reason from all of the others. Such a value was ignored in averaging the values of  $\lambda/2$ . It is felt that this procedure was justified, considering the close agreement between all of the normal values and the great discrepancy between the normal ones and the "freak" datum, as illustrated in a sample determination shown in Table I.

TABLE I  
SAMPLE DETERMINATION  
Alcohol at 20° (A)

Screw reading, $x$ mm.	Diff. = $\lambda/2$	Screw reading, $y$ mm.	Diff. = $\lambda/2$	$x - y$	$\frac{x - y}{n} = \frac{\lambda}{2}$
18.085	1.440	6.590	1.445	11.495	1.4370
16.645	1.440	5.145	1.440	11.500	1.4375
15.205	1.440	3.705	1.440	11.500	1.4375
13.765	1.440	2.265	1.440	11.500	1.4375

$$V = 2 \frac{\lambda}{2} \omega = 1168 \text{ m./sec.}$$

Benzene at 35° (B)

Screw reading	19.460	17.910	16.365	14.814	13.270	11.722
Difference	1.550	1.545	1.551	1.544	1.548	
Screw reading	11.722	10.175	8.625	7.105	5.553	4.008
Difference	1.547	1.550	(1.520)	1.552	1.545	
Mean difference, 1.548.	$V = 1254 \text{ m./sec.}$					

As the data in the last column of (A) represent a precision greater than could be attained using different samples of a liquid, only four significant figures are retained for the most part in the final value of the velocity of sound. Usually independent measurements gave results that checked to one meter per second. The velocity of sound in water, for example, was found on two different occasions to be 1498.6 and 1498.3 m./sec. The average of a large number of determinations by Hubbard and Loomis with a different interferometer and at a different frequency gave 1498.1. The former figures were obtained without making any special effort to attain the maximum precision of which the method is capable.

Mention should be made of the behavior of the frequency control crystal

during these measurements. The crystal and its principal frequency calibration was furnished by the Naval Research Laboratory. In addition to the principal frequency, the crystal exhibited others, as is usually the case: a parallelepipedal oscillator may vibrate along three axes under proper circumstances, each of these periods may have overtones and the crystal may also oscillate with a period which results from the coupling of vibration of two of these modes. When these "overtones" are present they are quite definite and sharp (but easily distinguishable from the fundamental by the character of the audible heterodyne note). At one time, however, the constants of the circuit were such that abrupt changes in frequency occurred, the crystal vibrating now in one, now in the other, fundamental frequency. A careful check showed which liquids had been measured on the new frequency and its value was established in the following manner. Six careful determinations of the wave length in several different samples of pure, air-free distilled water were made. From the accurately known values of the velocity of sound in water at the temperatures of measurement<sup>5</sup> the frequency was calculated. The velocity of sound values used were taken from a curve drawn through a large number of points (about 50) in a 40° temperature interval. They are believed to be accurate to one part in ten thousand. The values of the frequency thus found are as follows: 414.0, 414.1, 414.3, 414.1, 413.8, 413.8—mean, 414.0(1) kilocycles.

These were checked to about 1% with a wavemeter, and, further, at different intervals of time by other sound wave-length determinations. The definiteness and constancy of the new frequency was thus firmly established.

**Results and Calculations.**—In the following tables are given the

TABLE II  
VALUES OF THE ISOTHERMAL COMPRESSIBILITY AND  $C_p/C_v$  CALCULATED FROM THE VELOCITY OF SOUND, ETC.

Temp., °C.	Vel. of sound m./sec.	$\rho$	$dv/dT$	$C_p$	$\beta_T$ , atm. <sup>-1</sup> $\times 10^6$	$C_p/C_v$	$\beta_\phi \times 10^6$ Tyrrer	$B_\phi$ (F., H. and A.) Atm. <sup>-1</sup> $\times 10^8$
Benzene								
0		0.9001	0.00131	0.3970			56.6	
10	1375	.8896	.00134	.4027	87.5	1.449	61.3	60.3
20	1324	.8790	.00138	.4084	94.9	1.441	66.3	65.8
30	1278	.8684	.00142	.4141	102.5	1.435	71.7	71.5
40	1231	.8576	.00146	.4196	111.0	1.422	77.8	78.0
50	1184	.8467	.00151	.4255	119.9	1.420	84.6	85.4
Alcohol								
0	1242	0.8062	0.001286	0.5487	97.6	1.196	83.5	81.5
10	1204	.7978	.001325	.5706	104.4	1.191	89.8	87.6
20	1168	.7893	.001370	.5950	111.3	1.183	95.7	94.1
30	1134	.7809	.001420	.6208	119.6	1.184	102.0	101.0
40	1101	.7722	.001475	.6478	127.8	1.181	109.0	108.2
50	1067	.7632	.001550	.6762	137.8	1.182	116.7	116.6

TABLE II (Continued)

Temp., °C.	Vel. of sound m./sec.	$\rho$	$dv/dT$	$C_p$	$\beta_T$ , atm. <sup>-1</sup> $\times 10^6$	$C_p/C_v$	$\beta_\phi \times 10^6$ Tyrer	$B_\rho$ (F., H. and A.) Atm. <sup>-1</sup> $\times 10^6$
Acetone								
0	1273	0.8125	.....	....	...	...	...	77.0
10	1231	.8014	.....	....	...	...	...	83.5
20	1190	.7905	0.001881	0.514	129.2	1.426	...	90.6
30	1146	.7788	.....	....	...	...	...	99.1
40	1102	.7672	0.002122	.530	158.2	1.456	...	108.8
50	1057	.7554	.....	....	...	...	...	120.1
Chlorobenzene								
0	1362.5	0.8666	0.000850	....	...	...	49.05	47.3
10	1322.5	.8952	.000867	....	...	...	52.30	51.9
20	1284.5	.9040	.000880	0.315	74.8	1.348	55.7	55.5
30	1248.0	.9129	.000895	.322	79.4	1.338	59.4	59.4
40	1212.5	.9220	.000910	.328	84.3	1.325	63.4	63.6
50	1178.0	.9309	.000925	.335	89.5	1.316	67.8	68.0
Toluene								
0	1414	0.8848	0.00124	0.3834	80.8	1.410	59.6	57.3
10	1370.5	.8752	.00125	.3938	85.5	1.388	62.9	61.6
20	1327.5	.8657	.00126	.4042	90.6	1.364	67.4	66.4
30	1284.5	.8563	.00127	.4147	96.2	1.340	72.3	71.8
40	1242	.8470	.00129	.4251	102.7	1.323	77.4	77.6
50	1199	.8378	.00132	.4355	110.4	1.311	83.2	84.2
Chloroform								
0	1069.0	1.5264	0.000810	0.2323	86.6	1.490	58.8	58.1
10	1036.5	1.5078	.000830	.2333	93.1	1.487	63.4	62.6
20	1002.5	1.4888	.000855	.2343	100.7	1.485	68.3	67.8
30	967.5	1.4697	.000884	.2353	109.5	1.486	73.5	73.7
40	932.5	1.4505	.000917	.2363	119.5	1.486	79.4	80.4
50	897.0	1.4310	.....	....	...	...	...	...
Ether								
0	1095	0.7362	0.00203	0.5290	152.7	1.330	114.5	114.8
10	1054	.7248	.002115	.5349	167.4	1.330	127.5	125.8
20	1006	.7135	.002245	.5527	186.8	1.329	141.0	140.6
30	949	.7019	.002390	.5645	210.8	1.328	156.0	158.7
Carbon Tetrachloride								
0	1008	1.6327	0.000730	.2010	89.7	1.468	62.8	61.1
10	970	1.6134	.000742	.2013	97.0	1.452	67.4	66.8
20	935	1.5939	.000756	.2016	104.8	1.439	72.5	72.8
30	904	1.5748	.000777	.2019	113.3	1.437	78.1	78.8
40	873.5	1.5557	.000805	.2022	123.2	1.433	84.2	85.4
50	843	1.5361	.000837	.2025	134.4	1.427	91.1	92.9
Carbon Disulfide								
0	1223.5	1.2931	0.000880	0.2352	80.5	1.536	52.9	52.4
10	1190.5	1.2783	.000908	.2368	86.5	1.544	56.3	56.0
20	1158.0	1.2634	.000941	.2385	93.1	1.556	60.0	59.8

TABLE II (Concluded)

Temp., °C.	Vel. of sound m./sec.	$\rho$	$dv/dT$	$C_p$	$\beta_T, \text{atm.}^{-1}$ $\times 10^6$	$C_p/C_v$	$\beta_\phi \times 10^6$ Tyrer	$B_\phi$ (F., H. and A.) $\text{Atm.}^{-1} \times 10^4$
30	1126.0	1.2483	.000983	.2401	100.9	1.574	63.8	64.1
40	1093.5	1.2327	.001036	.2417	110.3	1.603	68.4	68.8
50	1061.0	1.2168	.001097	.2433	121.1	1.636	73.9	74.0
Methyl Alcohol								
0	1187	0.8100	0.001468	0.563	109.2	1.230	...	88.8
10	1154	.8007	.001505	.594	116.0	1.221	...	95.1
20	1121	.7913	.001554	.632	123.4	1.211	...	101.9
30	1088	.7818	.001609	.679	131.5	1.199	...	109.6
40	1056	.7723	.001670	.732	140.0	1.189	...	117.7
50	1023.5	.7627	.001741	.793	149.6	1.180	...	126.8
Temp., °C.	Vel. of sound, m./sec.	$\rho$	$B_\phi$ (F., H. and A.) $\text{atm.}^{-1} \times 10^6$	Temp., °C.	Vel. of sound, m./sec.	$\rho$	$B_\phi$ (F., H. and A.) $\text{atm.}^{-1} \times 10^6$	
Heptane				$\alpha$ -Bromonaphthalene				
0	1235	0.7005	94.9	10	1402	1.503	34.3	
10	1196	.6920	102.4	20	1372	1.487	36.2	
20	1154	.6836	111.4	30	1341	1.472	38.3	
30	1112	.6751	121.4	40	1311	1.459	40.4	
40	1070	.6665	132.8	50	1280	1.448	42.7	
50	1028	.6579	145.8					
Octane				Glycerin				
0	1277	0.7185	86.5	10	1941.5	1.2671	21.2	
10	1235	.7103	93.6	20	1923	1.2613	21.7	
20	1192	.7021	101.6	30	1905	1.2553	22.3	
30	1150	.6940	110.4	40	1886.5	1.2491	22.8	
40	1108	.6859	120.4	50	1868.5	1.2427	23.4	
50	1066	.6777	131.6					
Aniline				Bromoform				
0	1742	1.0389	32.2	10	953	2.886	38.7	
10	1700	1.0303	34.0	20	928	2.858	41.2	
20	1659	1.0216	36.1	30	907	2.830	43.5	
30	1619	1.0130	38.2	40	886	2.802	46.1	
40	1579.5	1.0044	40.5	50	865	2.774	48.8	
50	1540	0.9957	42.9					
			Vel. of sound, 45°		Vel. of sound, 20°	$d_{44}^{20}$	$\beta_\phi$ at 20° $\text{atm.}^{-1} \times 10^6$	
	<i>n</i> -Heptane		1048		1154.0	0.6836	111.40	
	2-Methylhexane		1014		1120.0	.6789	119.05	
	3-Methylhexane		1033		1135.5	.6870	114.45	
	3-Ethylpentane		1061		1169.5	.6982	106.15	
	2,2-Dimethylpentane		972		1080.5	.6737	128.90	
	2,3-Dimethylpentane		1039		1148.5	.6942	110.70	
	2,4-Dimethylpentane		984.5		1083.5	.6745	128.00	
	3,3-Dimethylpentane		1024.5		1129.5	.6935	114.55	
	2,2,3-Trimethylbutane		1000		1101.5	.6901	121.05	
	2,2,4-Trimethylpentane		998.5		1098.5	.6918	121.45	



TABLE III  
COMPARISON OF ISOTHERMAL COMPRESSIBILITIES OF BENZENE AND ETHYL ALCOHOL  
FROM VARIOUS SOURCES

Temp., °C.	F., H. and A. (1 atm.)	Tyrer 1-2 atm.	Pagliano and Palazzo <sup>a</sup> (1-4 atm.)	Röntgen <sup>b</sup> (8 atm.)	Amagat <sup>c</sup>
Benzene					
17.9	...	...	...	91.7 × 10 <sup>-6</sup>	...
20	94.9 × 10 <sup>-6</sup>	95.3 × 10 <sup>-6</sup>	90.1 × 10 <sup>-6</sup>	...	...
40	111.0	110.7	105	...	...
Ethyl Alcohol					
0	97.6	99.6	97	...	100 × 10 <sup>-6</sup> (extrpd.)
10	104.4	106.6	...	...	...
14	...	...	...	...	101
20	111.3	112.9	105.3	...	115 (extrapolated)
40	127.8	128.6	117.8	...	129

<sup>a</sup> Pagliano and Palazzo, *Ann. Phys. Chem.*, (iii) **44**, 1 (1891).

<sup>b</sup> Röntgen, *Mem. accad. Lincei*, (vi) **19**, 30 (1883).

<sup>c</sup> Amagat, *Ann. chim. phys.*, **29**, 523 (1893).

results of the velocity of sound measurements and the compressibilities and compressibility ratios calculated from them.<sup>7</sup>

The blanks are due to the absence of certain specific heat and coefficient of expansion data. It is hoped to fill these soon by measurements to be undertaken in this Laboratory. The density, specific heat and coefficient of expansion values used were the same as those used by Tyrer,<sup>8</sup> in the cases where comparison is made of the measured adiabatic compressibility data with those calculated from the velocity of sound. They are believed to be very trustworthy. Those not from this source were taken from the Landolt-Börnstein "Tabellen" and the "International Critical Tables." Table III is given to indicate briefly how the calculated compressibilities compare with those experimentally determined. In Figs. 5 and 6 are shown the velocities of sound and adiabatic compressibilities plotted against temperature. Tyrer's values for the compressibility of ether are included, since the compressibility data from the two sources for this liquid show a greater disagreement than do the data for any of the other liquids.

Attention is called to the slight deviation from linearity of the velocity of sound curve for benzene in a short temperature range just above the melt-

<sup>7</sup> The following are the equations used

$$V = \sqrt{\frac{1}{\beta_{\varphi}\rho}} \quad \beta_T = \beta_{\varphi} + \frac{\left(\frac{dv}{dT}\right)^2 \rho T}{J C_p} \quad \frac{C_p}{C_v} = \frac{\beta_T}{\beta_{\varphi}}$$

where  $V$  is the velocity of sound;  $\beta_{\varphi}$  is the adiabatic compressibility;  $\beta_T$  is the isothermal compressibility;  $dv/dT$  is the differential of the specific volume;  $J$  is the mechanical equivalent of heat;  $\rho$  is the density;  $C_p$  is the specific heat at constant pressure at  $T^{\circ}$  absolute.

<sup>8</sup> Tyrer, *J. Chem. Sec.*, **103**, 1684 (1913).

ing point. This behavior suggested the measurements on aniline, bromoform,  $\alpha$ -bromonaphthalene and glycerin. Except in the case of glycerin, somewhat similar breaks in the curves occur. The glycerin did not freeze.

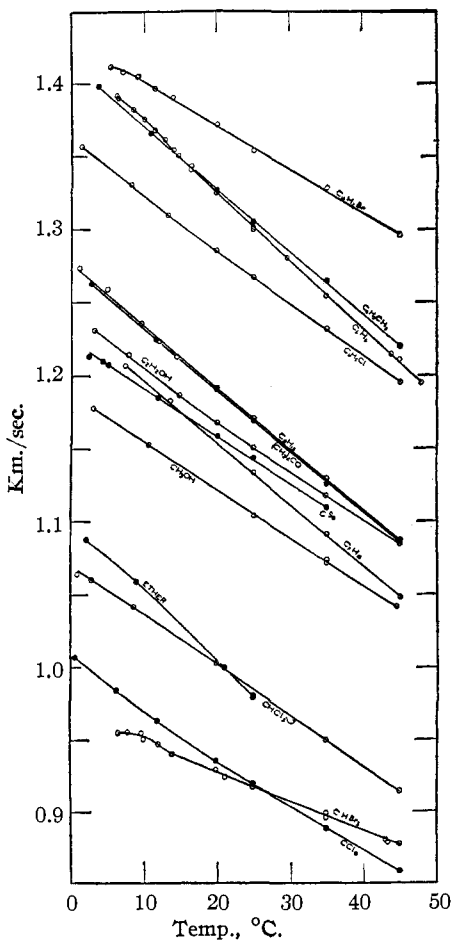


Fig. 5.

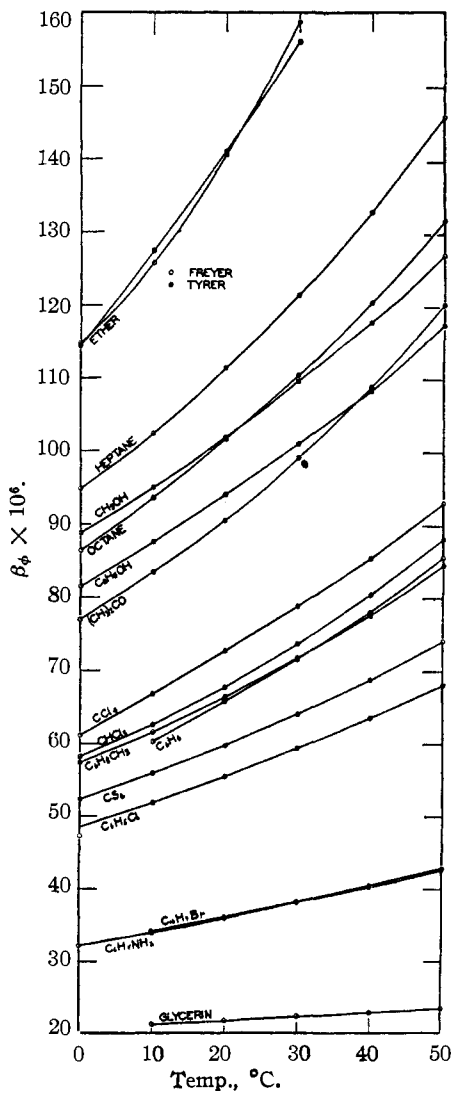


Fig. 6.

It seems reasonable to expect some sort of orientation or grouping of the molecules of liquids to occur preliminary to freezing that would occasion such a change, because the velocity of sound in a liquid is a function of properties directly depending on the molecular arrangement.

Discussing the dipole character of liquids, Gerlach<sup>9</sup> observes, "Dipoles, by their very nature, are favorable to association—after a fashion—a preliminary stage of microcrystalline character; . . . it is not definitely known whether such a character is in evidence during the solidification of substances like benzol whose molecules exhibit not even the slightest dipole nature. Attention may be directed in this connection to certain experiments of Isnardi in which he has observed variations in the dielectric constant of benzene at temperatures slightly above its crystallization point. This would indicate, under such conditions, the existence of a dipole moment, but since Graffunder's results fail to confirm such a conclusion, further experimental evidence must be awaited." Unfortunately the compressibility measurements of Tyrer<sup>8</sup> do not cover the temperature range in question in sufficient detail to permit a confirmation of this irregularity in the velocity of sound in benzene by calculation.

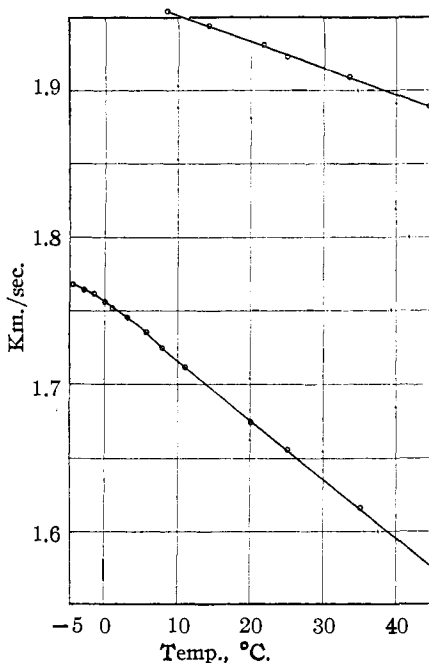


Fig. 7.—Upper curve, glycerin; lower curve, aniline.

The authors are indebted to Mr. Alfred L. Loomis for the use of quartz plates in the interferometer and to the U. S. Naval Research Laboratory for supplying the calibrated quartz frequency control crystal. Grateful acknowledgment is made to Dr. Graham Edgar of the Ethyl Gasoline Corporation for the loan of the isomeric heptanes and for the values of their densities.

### Summary

An explanation of the method developed by Hubbard and Loomis for measuring the velocity of sound in small quantities of liquids has been given. The apparatus consists of an electrical oscillator for producing a high frequency field, an oscillator of fixed frequency to control the frequency of the field, and a "sonic interferometer" for producing and determining the wave length of sound waves. The instrument described in this paper is of a new design. The velocity of sound in and the adiabatic

<sup>9</sup> Gerlach-Fuchs, "Matter, Electricity, Energy" (Translation), 1928, p. 65.

and isothermal compressibility of the following liquids are given: benzene, acetone, ethyl alcohol, methyl alcohol, chlorobenzene, toluene, chloroform, ether, carbon tetrachloride and carbon bisulfide.

The velocity of sound in and the adiabatic compressibility of heptane, octane, aniline,  $\alpha$ -bromonaphthalene, glycerin, bromoform and the isomeric heptanes are given.

Some of the compressibility values have been compared with those found by direct measurement by other investigators.

BALTIMORE, MARYLAND

---

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

## THE PHOTOSYNTHESIS OF HYDROCHLORIC ACID AT LOW PRESSURES

BY GERHARD K. ROLLEFSON

RECEIVED OCTOBER 29, 1928

PUBLISHED MARCH 6, 1929

The mechanism of the photochemical combination of hydrogen and chlorine has been the subject of investigation for many years. The results prior to 1926, summarized by Thon,<sup>1</sup> show that the reaction which occurs with the visible and near ultraviolet light must be considered as proceeding according to a chain mechanism starting with the photo-activated chlorine. The nature of this activation has been the subject of speculation, and the assumptions which have been made fall into two groups; first, those that postulate that the light excites the chlorine molecule to a higher quantum state; second, those that consider that the chlorine molecule is dissociated by the light. From the nature of the absorption spectrum of chlorine the dissociation hypothesis is the more probable of the two,<sup>2</sup> and it is the purpose of this paper to present experimental evidence for this view.

Before describing the experimental procedure let us consider what conditions are necessary to show a difference between the two theories. If we have an excited chlorine molecule it may undergo one of the following changes: (1) return to its normal state by emitting light, (2) lose its energy by collision of the second kind, (3) enter into some reaction. At high pressures an excited molecule undergoes so many collisions in its life period that the number returning to the normal state by fluorescence is negligible, but as the pressure is reduced the number fluorescing increases until, at such low pressures that the time between collisions is long compared to the life period of the excited molecule, fluorescence is practically the only process involved. On the other hand, if the chlorine is dissociated

<sup>1</sup> Thon, *Fortschritte Chem., Physik, physik. Chem.*, **18**, No. 11 (1926).

<sup>2</sup> For this interpretation of the chlorine spectrum see Franck, *Trans. Faraday Soc.*, **21**, 536 (1925); and Kuhn, *Z. Physik*, **39**, 77 (1926).