

The Dispersion of Sound in Oxygen

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FIG. 2. Ripples in electrodeposited iron produced by ultrasonic radiation (enlarged).

The results seem to indicate that stationary waves are set up in the solution and that the metal ions are relatively more concentrated in layers which are separated by half wave-lengths.

In the case of iron and zinc it appears from the results given in Table I that deposits showing the best ripples are obtained from the more concentrated solutions.

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The Dispersion of Sound in Oxygen

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The velocity of 1000-cycle sound wave in oxygen of various degrees of humidity at 26.5°C has been measured. The velocity behavior indicates that the water molecules are effective in bringing the heat capacity of the first vibrational state of the oxygen molecule into equilibrium with the sound wave. The dispersion change in velocity

amounts to 0.16 percent. Intensity measurements agree with velocity data in fixing the center of the dispersion region between 1 and 3 mm partial pressure of water, which is in agreement with the values calculated from Knudsen's studies of rates of decay at higher frequencies.

THE classical work of Knudsen and Kneser^{1, 2, 3} on the rates of decay of sound waves in mixtures of air and water vapor, and oxygen and water vapor, showed that there was an optimum humidity at which the rate of decay has a maximum value, and showed definitely that the effects observed were due to the efficiency of water molecules in activating the first vibrational state of the oxygen molecule and in returning this vibrational heat capacity to the sound wave. On the basis of the recently de-

veloped theory of sound dispersion^{4, 5, 6} there should be an anomalous behavior in velocity accompanying the appearance of a maximum rate of decay. The velocity of sound in air and oxygen has been determined by several investigators.^{7, 8, 9} Pierce originally reported that at audiofrequencies measurements in dry air and in air at 36 percent and 55 percent humidity indicated no change in velocity with change in humidity within an accuracy of 0.021 percent.

¹ Knudsen, J. Acous. Soc. Am. 5, 112 (1933); 6, 199 (1935).

² Kneser and Knudsen, Ann. d. Physik 21, 682 (1935).

³ Kneser, J. Acous. Soc. Am. 5, 122 (1933).

⁴ Einstein, Ber. d. Berlin Akad. S380 (1920).

⁵ Herzfeld and Rice, Phys. Rev. 31, 691 (1928).

⁶ Kneser, Ann. d. Physik 11, 777 (1931).

⁷ Pierce, Proc. Am. Acad. 60, 286 (1924).

⁸ Reid, Phys. Rev. 35, 814 (1930).

⁹ Brass and Bastile, J. Math. Phys., M.I.T. 2, 210 (1913).

Reid, working in Pierce's laboratory, later modified these results to show that the velocity of sound in air at 20°C was a linear function of the humidity. However, he measured the velocity only at 0, 45 and 100 percent relative humidity using supersonic frequencies.

If we accept Knudsen's data as fixing a dispersion at roughly 0.21 percent water molecules in air and 0.40 percent in oxygen for frequencies of the order of 3000 cycles, then the change in velocity should not be linear with humidity. As water molecules are added to dry oxygen or air, there should normally result an increase in velocity due to decrease in density, and for very small changes in density resulting from the addition of small quantities of water vapor this increase should appear almost linear, since the velocity of sound changes with density according to the familiar equation

$$v = [(p/d)\gamma]^{\frac{1}{2}},$$

where p is pressure, d density, and γ the ratio of specific heats. The change in velocity due to γ for water being less than γ for O_2 is small com-

pared to the density effect. However, if the addition of water molecules serves to activate the first vibrational state of the oxygen molecules with sufficient rapidity so that the vibrational heat capacity is returned to the apparent heat capacity of the gas in the sound wave, then γ must decrease, and correspondingly the velocity must decrease. The density change and dispersion have therefore opposite effects in changing velocity. If, then, velocity is plotted against percent of water molecules present, the curve should have a different character in passing through the dispersion region than in the region where there is no dispersion and the change of velocity with density alone is operative. An apparatus was therefore constructed for measuring the change of velocity in a sound wave passing through oxygen containing various percentages of water vapor, in the hope of detecting the dispersion effect. Oxygen was selected rather than air because of the larger effect observed in the case of oxygen, since dispersion in air is due only to the oxygen molecules present.

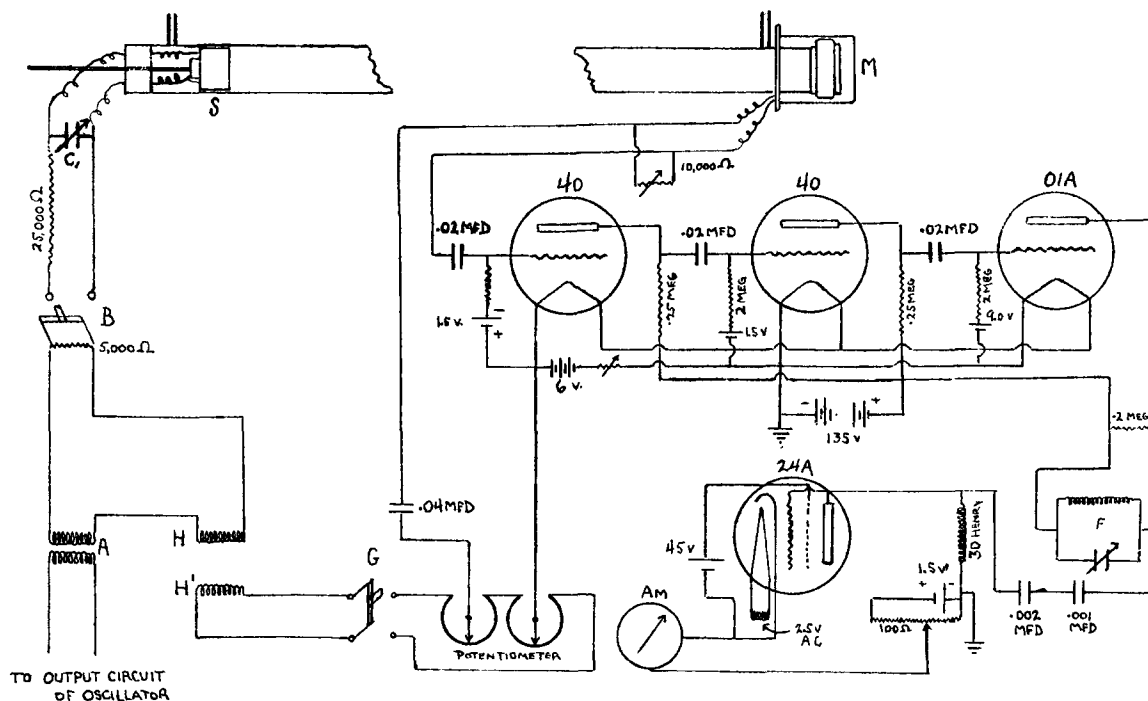


FIG. 1.

APPARATUS

The apparatus shown in Fig. 1 consisted essentially of a resonance tube, with a microphone fixed at one end, and a movable speaker unit in the tube. The resonance cell was a Pyrex glass tube nine feet in length and with an inside diameter of 6.3 cm. Tubes sealed at each end of the cell led to a centrifugal pump and a circulation system whereby the oxygen could be circulated over P_2O_5 or through a glass spiral containing pockets filled with water. The cell was thermostated in a water bath, the temperature being held at $26.50 \pm 0.1^\circ\text{C}$.

The speaker was an American Bell headphone unit held in a brass case, and with a heavy brass plate with a 9.5-mm hole in its center holding the diaphragm. The sender was attached to a long rod which extended out of the cell in a rubber tube, allowing the sender to be moved down the resonance tube.

The microphone, M , was a modified Baldwin speaker unit whose aluminum face had been turned out and a brass plate similar to the one used on the sender, was inserted. These two brass plates offered smooth parallel reflecting surfaces for the sound at each end of the cell. The microphone was mounted at the end of the tube and was enclosed in a glass case. All joints and electrical leads were sealed with a mixture of beeswax and rosin. All free space, except the resonance portion of the cell, was liberally padded with felt.

The oscillator used to actuate the sending unit consisted of an oscillating circuit controlled by a 1000-cycle tuning fork. A headphone unit without diaphragm was mounted close to each arm of the tuning fork. The one serving as a pick-up was connected to the input of a 60-decibel 5-watt amplifier. Part of the output of the amplifier passed through the other phone unit maintaining the vibration of the tuning fork. The output circuit was tuned until an excellent wave form was obtained.

The electrical measurement circuit is shown in Fig. 1. The capacity C across the speaker was adjusted until the speaker had a natural frequency of 1000 cycles, thus giving a sine sound wave free from harmonics. The wave form from the microphone was also excellent when the cell

was set at resonance. The voltage generated in the microphone was amplified by a three-stage resistance coupled amplifier. The plate circuit of the last tube was tuned to 1000 cycles. The output then led to the vacuum tube voltmeter, V . This voltmeter gave very close to a linear response and was well suited for measuring the small AC output of the amplifier.

The electrical set-up, as described to this point, would have required calibration with known voltage inputs to the amplifier, and any subsequent changes in the amplifier or vacuum tube voltmeter characteristics, or change in the output of the oscillator due to long period 60-cycle a.c. voltage fluctuations, would have invalidated the calibration.

A method of eliminating the inaccuracy introduced by any of the above fluctuations, consisted in loosely coupling from the oscillator output by means of the two honeycomb coils H and H' and causing the induced current to flow through the battery terminals of a Leeds and Northrup Student Type potentiometer. The slide wire, or e.m.f., terminals of the potentiometer, were in series with the microphone and input to the amplifier. The procedure in taking readings consisted in opening the switch G and closing the switch B , and observing the swing of the milliammeter caused by the sound wave incident upon the microphone. Switch B was then opened and switch G closed and the potentiometer adjusted so that sufficient induced current from H' was thrown into the amplifier input to duplicate the swing of the milliammeter. As a check, the operation was repeated. The reading on the potentiometer then represented the relative intensity of the sound incident on the microphone. The effect of any variations in the system other than mechanical changes in the sender or microphone units were thus eliminated. However, intensity readings could only be taken between 1 and 5 A.M. when the power lines were free from rapid voltage fluctuations and "static."

In obtaining readings of the change in intensity and velocity with the addition of water vapor to oxygen, the following procedure was used. The resonance cell was first evacuated to 0.1 mm and flushed out several times with oxygen, and then filled to 733-mm pressure. The oxygen was

circulated through the cell and over P_2O_5 to insure its dryness. The sender was adjusted to resonance at seven and one-half wave-lengths from the microphone as indicated by the maximum swing on the milliammeter, and the intensity reading taken on the potentiometer. The position of the sender was noted by means of the position of the adjusting rod relative to a scale at the end of the tube. The oxygen was then circulated through the water spiral until the pressure of the system as registered on the manometer showed a small rise. The water spiral was then cut out of the system and the circulation continued to insure thorough mixing of the water vapor and oxygen. The resonance position and intensity were again determined. This process was repeated a number of times. Readings taken at one-half wave-length showed no appreciable change in end effect with varying humidity. There was only a negligible change in resonance position when the density of pure oxygen was decreased by reducing the pressure. This was not the case until felt padding was introduced to prevent extraneous resonances. Since the change in velocity was less than 0.3 percent, the change in the tube correction can be neglected.

Table I shows a sample series of determina-

TABLE I.

mm H ₂ O	0	1	3	6	10	14	18
INTENSITY	920	870	870	920	926	928	929

tions of the intensity at resonance at various humidities. The results are graphed in the upper curve in Fig. 2. Measurements made on different days give a minimum at the same partial pressure of water but the absolute intensities were not in good agreement. The intensity data merely fix the center of the dispersion between 1 and 3 mm partial pressure of water vapor. Table II shows the change in resonance position of the sender with different partial pressures of water vapor. The position with pure oxygen was 247 cm from the microphone. The relative velocity was calculated as $(2470 + \text{displacement}) / 2470$. In this way it was only necessary to know the absolute velocity in the tube to one part in 250 in order to get the relative velocity accurate

TABLE II.

mm H ₂ O	mm Dis- placement	RELATIVE VELOCITY	mm H ₂ O	mm Dis- placement	RELATIVE VELOCITY
0.	0.	1.00000	5.3	-.5	.99980
.7	-1.0	.99960	5.4	+.5	1.00020
1.0	-2.1	.99915	6.5	1.0	1.00040
1.1	-2.5	.99899	7.9	1.8	1.00073
2.3	-2.1	.99915	13.9	6.0	1.00243
2.5	-2.0	.99919	14.6	6.3	1.00255
3.7	-.6	.99976			

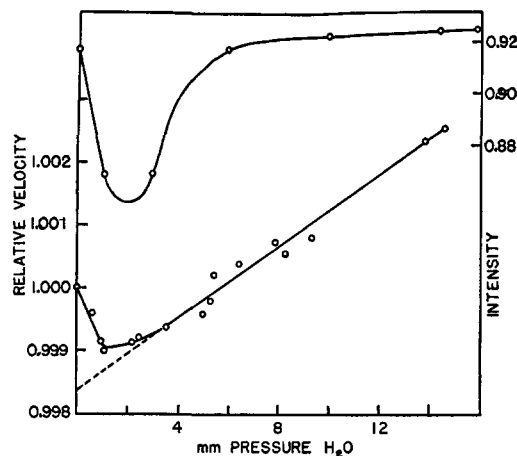


FIG. 2.

to better than 1 part in 10,000. The lower curve in Fig. 2 shows the relative velocity plotted against the mm water vapor present in 733 mm of oxygen. The velocity decreases up to approximately 2 mm water vapor and then starts to increase in a normal manner due to the increase in the ratio of the pressure to the density. Extrapolating the straight-line portion of the curve beyond 4 mm to zero water vapor pressure, we find the relative velocity the sound would have in pure oxygen if the vibrational heat capacity had been present. This extrapolates to 0.9984 of the velocity in dry oxygen, a decrease of 0.16 percent.

Taking the vibrational heat capacity of oxygen at 26.5°C as 0.63 cal./mole/degree,¹⁰ the percentage change in velocity due to dispersion should be 0.19 percent. The agreement is within the error in extrapolating the experimental data. This verifies Henry's¹¹ explanation of the sys-

¹⁰ Johnston and Walker, J. Am. Chem. Soc. 55, 172 (1933).

¹¹ Henry, Nature 129, 200 (1932).

tematic error in the heat capacity of oxygen from velocity of sound measurements.^{12, 13}

Comparison of the reported heat capacity^{12, 13} of oxygen from velocity of sound measurements with the value obtained by other methods, shows that the former is too low by the heat capacity due to the first vibrational state up to

¹² Shilling and Partington, *Phil. Mag.* **6**, 920 (1928).

¹³ King and Partington, *Phil. Mag.* **9**, 1020 (1930).

about 1000°K. At 1400°K, where the second vibrational state should contribute an appreciable amount to the heat capacity, the difference is still greater. This indicates that neither the first or second vibrational levels are activated by the sound wave even at these temperatures.

Measurements of the relative velocity of sound are being continued at higher frequencies where the experimental error will be lower.

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Dielectric Constants of Extremely Dilute Solutions

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The dielectric behavior of unusually dilute solutions of ethyl alcohol in the nonpolar solvents benzol and carbon tetrachloride have been investigated down to 0.00007 mole-fraction concentration of alcohol. This concentration of molecules corresponds to a gaseous pressure of only 1.5 cm of Hg. The effect of an apparently anomalous behavior often present in the usual method of treating data has been eliminated by a slightly different treatment. Effects of association are entirely absent up to concentrations nearing 0.01. Molecular polarizations of alcohol at 24.5°C, evaluated by least squares from data using the two solvents,

agree closely; they also agree well with accepted vapor data. Taking over the molecular refraction of alcohol from optical data, the electric moment of the ethyl alcohol molecule is found to be $(1.700 \pm 0.006) \times 10^{-18}$ from benzol solution and $(1.674 \pm 0.005) \times 10^{-18}$ from carbon tetrachloride solution. These are felt to be unusually reliable for solution values; they compare favorably indeed with the two best vapor values, 1.696×10^{-18} by Miles and 1.686×10^{-18} by Knowles. Accurate density-concentration relationships for very dilute alcoholic solutions are given.

MANY writers have investigated the behavior of polar liquids in nonpolar solvents by way of determining the electric moment of the dissolved molecule. The usual procedure¹ is to assume that the molecular polarization of the solution P_{12} is the sum of the contributions of the solvent and the solute; thus

$$P_{12} = P_1 c_1 + P_2 c_2,$$

where P_1 and c_1 , and P_2 and c_2 are the molecular polarizations and the mole-fraction concentrations of the solvent and the solute, respectively. Calculations of P_2 from observed values of P_{12} at various concentrations, using a fixed value of P_1 observed for the pure solvent, show that the molecular polarization P_2 of the polar solute varies in general with concentration. This varia-

tion is attributed to association. It is customary to plot values of P_2 versus the solute concentration c_2 , and extrapolate this curve to zero concentration. It is assumed that the solute polarization so obtained is free from effects of association. That this is essentially true is evidenced by the fact that electric moments calculated in this way for many molecules agree fairly well with moments obtained from vapor studies. Nevertheless one is impressed by the fact that, to the best of the author's knowledge, no worker has obtained data on sufficiently dilute solutions and at the same time of sufficient accuracy to show that the solute polarization P_2 actually does become constant at some low concentration, thus indicating complete lack of association effects. In fact in certain instances where investigators were forced by sparing solubility of the solute to use extremely dilute solutions, apparently anomalous results were

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¹ See, for example, Smyth, *Dielectric Constant and Molecular Structure* (Chemical Catalog Company, 1931).