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An Experimental Determination of the Velocity of Sound in Dry CO_2-Free Air and Methane at Temperatures below the Ice Point

THOMAS HAROLD QUIGLEY, S.J.*
The Johns Hopkins University, Baltimore, Maryland

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The fixed path acoustic interferometer has been used for the measurement of the velocity of sound in dry CO_2-free air and in methane between 90°K and the ice point. Acoustic resonance in a limited column of gas, coupled to a driven X-cut quartz crystal of fundamental frequency of about 600 kc per sec., is produced by temperature variation. The procedure is such that differences in temperature readings, when the temperature is rising and when it is falling, are reduced to an amount in keeping with the other errors of measurement. No molecular acoustic dispersion has been observed so that the results are made available with especial reference to their value for computations of specific heats. The results are given, within experimental error, by the formulae: for air, $v^2=3.8762\times 10^2T+806+1.8043\times 10^5T^{-1}-2.0364\times 10^7T^{-2}+3.007\times 10^{-2}T^2$ and for methane, $v^2=6.6176\times 10^2T+1.0016\times 10^6T^{-1}-1.3846\times 10^8T^{-2}$.

DEVELOPMENTS in ultrasonics in recent years have made it possible to realize the hopes of early students of acoustics and of thermodynamics that the methods of acoustics could be made to yield results of prime importance in the study of gases, especially with reference to their specific heats. Audible sound waves are of such lengths that sound chambers must be either of prohibitive dimensions or such as to introduce boundary effects, considerably complicating the task of finding the specific acoustic properties of the medium.

It is now well known that a characteristic complication in the study of the specific heats of gases by ultrasonics is the possibility of the presence of acoustic dispersion of the molecular type which may be enhanced in some cases by small traces of gaseous impurity. It has been pointed out, however, that the existence of this dispersion may be immediately detected, its amount evaluated, and it may even be avoided by a suitable choice of pressure and frequency ranges in the experiments.[1–3] This point has been well illustrated in the work of Hubbard and Zartman[4] in the development of the fixed path acoustic interferometer as well as by the work of Herget[5] on the velocity of sound in CO_2 and ethylene.

The object of the present work has been twofold: in part, to develop a procedure of maximum precision for sound velocity determinations; and, in part, to apply it to one or more gases of great purity. Air was chosen because of its ready availability for developing the procedure, and methane because the results would be new and because the gas has been studied extensively in spectroscopy. In neither dry CO_2-free air nor in methane at high purity is there any serious question of molecular acoustic dispersion at the frequency used.

The theory of the ultrasonic interferometer, as used here, has been developed in detail in previous publications[6,7] so that it will be sufficient to outline briefly its principal features. A quartz crystal, used as a resonator after the manner of W. G. Cady,[8] is connected across the condenser of a simple wave-meter circuit whose current is measured by a vacuum thermocouple and galvanometer. The wave-meter is tuned close to the frequency of the thickness vibrations of the quartz. When an exciting oscillator is tuned through this frequency, the wave-meter galvanometer will show the usual electrical resonance peak (i^2 *versus* frequency), except that in the immediate neighborhood of the crystal

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* Since 1940 Professor of Physics at Holy Cross College, Worcester, Massachusetts.

[1] W. T. Richards and J. A. Reid, J. Chem. Phys. **2**, 193 (1934).

[2] A. H. Hodge, J. Chem. Phys. **5**, 974 (1937).

[3] J. C. Hubbard and A. H. Hodge, J. Chem. Phys. **5**, 978 (1937).

[4] J. C. Hubbard and I. F. Zartman, Rev. Sci. Inst. **10**, 382 (1939).

[5] C. M. Herget, J. Chem. Phys. **8**, 537 (1940).

[6] J. C. Hubbard, Phys. Rev. **38**, 1011 (1931); **41**, 523 (1932).

[7] R. S. Alleman, Phys. Rev. **55**, 87 (1939).

[8] W. G. Cady, Proc. I.R.E. **10**, 83 (1922).

frequency the i^2 readings of the thermocouple-galvanometer system will show a falling away, which, under favorable conditions, will reach near zero values. This is the so-called current *crevasse* associated with the quartz resonator, a phenomenon discovered by Cady.[8] When current readings are a minimum, the crystal is vibrating most vigorously and generating a maximum of back e.m.f. If the crystal is immersed in a fluid of a low density, such as a gas, so as to send out sound waves, such waves will represent energy carried away, and the crevasse will not be so deep. If some of the waves are reflected back to the crystal, they will arrive at some phase so related to the phase of motion of the crystal as to modify the current reading of the crevasse. If the phase of the returned radiation is changed while radiation is taking place, the crevasse reading of minimum i^2 will change, becoming greatest when there is resonance in the medium and smallest at anti-resonance. The maxima occurring at resonance in the gas are called reaction peaks. The length of the sound path (distance from crystal to reflector and back) is an integral number of wave-lengths of sound in the medium at resonance. Thus if v is the sound velocity, f the electrical frequency, λ the wave-length of sound, d the distance from resonator to reflector or $2d$ the length of sound path, and n the number of half wave-lengths in the sound chamber we have: $v=f\lambda=2df/n$.

The fixed path interferometer possesses special advantages for work at low temperatures, there being no moving parts and consequently no necessity for packed joints. Then, too, there is no necessity for a screw or connecting rod passing through a temperature gradient for the communication of motion which has always involved a troublesome correction. The sound chamber of the interferometer developed for the present work consists of a hollow cylinder S (cf. Fig. 1) of fused quartz closed at one end by a plane polished plate R of fused quartz and at the other by the crystal Q which has optically plane and parallel surfaces. The fused quartz cylinder has ends optically plane and parallel so that the length between quartz crystal and reflector can be accurately determined beforehand. This does not appreciably change in the course of the experiment as the coefficient of thermal expansion of quartz is negligibly small. This length, d, was found to be 0.62933 cm. The permanent adjustment to parallelism between crystal source and reflector secured in this way ensures symmetry of reaction peaks and a greater accuracy of determination of half-wave-length spacings than is otherwise possible. The internal diameter of the cylinder was 2.2 cm, outer diameter 3.8 cm. A backing plate and guard ring both at less than $\lambda/4$ from the surface of Q were provided to return unwanted radiation to the crystal.[7]

In the case of the present experiments several possibilities of error should be examined. First, a quartz crystal is by no means a simple linear vibrator. Experience, however, shows that when a crystal yields a crevasse curve showing a sharp response to a single frequency, a fluid medium, bounded on two sides by the crystal and a reflector accurately plane parallel to it, tends at resonance to vibrate in a normal mode yielding results for sound velocity of the highest precision. In the second place, in the present work resonance is secured by varying the temperature of the gas instead of the length of the sound chamber, thereby establishing a correspondence between the temperatures at resonance and the values of n. As is well known, however, the temperature-frequency curve of an X-cut quartz plate shows discontinuities so that, for a given crystal, certain small regions of temperature become unavailable for the production of sound fields. In the present study, the crystal used was so unsatisfactory in the immediate neighborhood of the ice point that no measurements could be taken there. Lastly, the abnormally low coefficients of reflection for ultrasonic waves in gases, first observed by J. C. Hubbard,[6] may be expected to give rise to a second-order correction of the acoustic path length. According to the theory of reflection of sound developed by K. F. Herzfeld,[9] there should be a phase change due to irreversible heat exchange between sound wave and reflector. Alleman[7] has made the necessary adaptation of Herzfeld's theory of reflection to interferometer theory, and, by the assumption that the same phenomenon of dissipative loss occurs on emission as on reflection,

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[9] K. F. Herzfeld, Phys. Rev. **53**, 899 (1938).

has found agreement between the predictions of Herzfeld's theory and the results of measurement of reflection coefficients by the interferometric method. A calculation of the effective change of path length owing to phase change on reflection in the present experiments shows it to be insignificant.

The measurement of the velocity of sound by the present method is thus reduced to the measurement of the length of the sound chamber (which in the present work was determined to better than one part in ten thousand); to the measurement of frequency (again, known to about one part in ten thousand); to the determination of the integral number of half wavelengths (uniquely determined), and finally to the measurement of the temperatures of the gas at the times of reaching reaction peaks.

A schematic diagram of the lower section of the cryostat and enclosed interferometer is given in Fig. 1. The cryostat was placed in a Dewar flask (omitted from the diagram) about 53 cm in length and extended from the bottom of the Dewar to a point slightly higher than its opening where it was held in position and supported by a wooden collar which was part of the cover of the wooden box enclosing the flask. This outer box was packed with cotton waste to insulate the flask from the temperature of the room. The cryostat consisted of a long double-walled pyrex glass tube. The outer wall was joined to the inner one by a ring seal near the point where the cryostat reached out of the Dewar flask. The top of the double-walled glass tube was closed by a ground glass stopper, which supported the nickel-silver tubing N and the attached assembly described in Fig. 1.

A thin film of gold was evaporated upon the top surface of the hollow fused quartz cylinder S: in part to make electrical contact with the bottom electrode on the face of the resonator, and in part to make connection with an outside lead (not shown). Thin brass rods, inserted in slots cut into the sides of the reflector and cylinder near the outer diameter served to hold the unit together. Gentle pressure supplied by light springs under nuts on the rods secured close contact between reflector and cylinder and ensured constancy of length of the sound chamber. Electrical contact was made by strips of tin foil, mechanically held in place, between the film of gold on an exposed part of the top of the quartz cylinder and one of the brass rods. This brass rod was connected to one of the leads going to the wave-meter circuit.

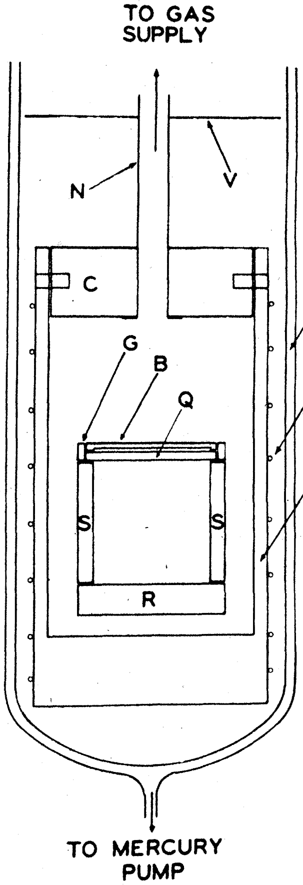

FIG. 1. Details of apparatus. Interferometer chamber, consisting of hollow cylinder S and reflecting plate R, both of fused quartz, the crystal resonator Q with soapstone guard ring G and brass backing plate B. A copper wire lead (not shown) connects backing plate to wave meter circuit. The fused quartz cylinder has inside diameter 2.2 cm, outside diameter 3.8 cm, height 0.62933 cm. This is the value of d (one-half "sound path"). The thickness frequency of resonator is about 587 kc/sec.

Cryostat and temperature control. Air space A between walls of cryostat to control by variation of low pressure, heat flow from inside cryostat to liquid nitrogen outside in Dewar flask (not shown); nichrome heating coil H wound on copper heat distributor C. Aluminum vanes V to reduce convection and radiation supported by nickel-silver tube N. Electrical leads not shown in the diagram.

The temperature of the interferometer unit was measured by a copper-constantan thermocouple (omitted from Fig. 1) soldered to the inside of the copper cylinder C; the leads were brought outside through the nickel-silver tubing *N*. The Copper-Constantan Thermocouple Reference Tables by Southard and Andrews[10] were used for converting from thermal e.m.f. to degrees Kelvin; a correction curve being obtained from the boiling point of oxygen, the freezing point of mercury and the ice point.

The chief difficulty in the measurements was encountered in the determination of the temperature of the gas in the sound chamber when the reaction peak reached its maximum. Since the reaction peaks themselves were very sharp, there was little difficulty in picking the maximum with precision. The determination of the temperature proved to be, as was to be expected, the limiting factor in the accuracy of the work.

Strictly speaking, the temperature measured was that of the copper cylinder *C*, while what was desired was the temperature of the gas within the interferometer. By trial and error it was found necessary to change the temperature not faster than two degrees per hour and in the region of the reaction peaks even more slowly.

TABLE I. Dry CO_2-free air. (Atmospheric pressure.)

n equals the number of half-wave-lengths in the sound chamber.
T equals the absolute temperature (taking 0°C, as equal to 273.1°K).
Δv^2 equals the deviation of the square of the observed value of the velocity from the value of v^2 computed from the empirical equation.

n	T	Frequency (kc/sec.)	Velocity (meters/sec.)	$v^2(10^{-4})$	Δv^2
23*	258.46	587.42	321.46	10.3337	22
23	258.57	587.52	321.56	10.3369	34
24*	237.64	587.73	308.23	9.5006	−22
24	237.66	587.73	308.23	9.5006	−14
24	237.69	587.62	308.17	9.4969	35
25*	219.05	587.88	295.97	8.7598	−74
25	219.30	587.88	295.97	8.7598	26
25	219.24	587.80	295.94	8.7580	19
26	202.88	588.05	284.68	8.1043	3
26	202.98	587.93	284.62	8.1009	77
27	188.21	588.16	274.19	7.5180	−4
27	188.21	588.20	274.20	7.5186	−9
28	175.19	588.22	264.42	6.9918	−49
29*	163.21	588.27	255.32	6.5188	−7
29*	163.14	588.21	255.29	6.5173	−22
30*	152.14	588.42	246.87	6.0945	−196
31*	142.33	588.44	238.92	5.7083	−168
32*	134.23	588.52	231.48	5.3583	−23
33*	126.64	588.54	224.48	5.0391	108
33	126.99	588.50	224.47	5.0387	254
34*	119.03	588.59	217.89	4.7476	−59
34*	119.05	588.62	217.90	4.7480	−55
34	119.89	588.56	217.87	4.7467	285
35*	112.49	588.62	211.63	4.4787	−34
36*	106.43	588.64	205.80	4.2354	−88
37*	100.95	588.67	200.25	4.0100	−101
38*	96.06	588.67	194.99	3.8021	−63
39*	91.74	588.69	189.98	3.6092	43
39	91.83	588.69	189.98	3.6092	80

* Indicates that reading was taken in a run with the temperature decreasing.

Empirical equation for dry CO_2-free air:

$$v^2=3.8762(10^2)T+806+1.8043(10^5)T^{-1}-2.0364(10^7)T^{-2}+3.007(10^{-2})T^2.$$

TABLE II. Methane. (Atmospheric pressure.)

n is the number of half-wave-lengths in the sound chamber.
T is the absolute temperature (0°C = 273.1°K).
Δv^2 is the deviation of the square of the experimental value of the velocity of sound from the value of v^2 computed from the empirical equation.

n	T	Frequency (kc/sec.)	Velocity (meters/sec.)	$v^2(10^{-4})$	Δv^2
18*	252.54	587.53	410.83	16.878	14
18	252.85	587.53	410.83	16.878	34
18	253.10	587.44	410.76	16.872	56
19*	226.09	587.91	389.45	15.167	−33
19*	225.74	587.75	389.35	15.159	−49
19	226.47	587.75	389.35	15.159	0
19	226.05	587.77	389.37	15.161	−30
20	203.53	587.96	370.02	13.692	−64
21*	186.62	588.16	352.53	12.428	61
21	186.30	588.20	352.55	12.429	38
21	184.80	588.11	352.49	12.425	−59
22*	170.34	588.31	336.59	11.329	54
22	168.62	588.24	336.55	11.327	−61
23	154.77	588.34	321.97	10.367	−55
24*	144.18	588.45	308.61	9.524	46
24	144.26	588.36	308.56	9.521	55
25*	133.55	588.50	296.29	8.779	33
26*	124.21	588.54	284.91	8.117	11
27*	115.58	588.62	274.40	7.530	−51

* Indicates that the reading was taken in a run with the temperature decreasing.

Empirical equation for methane:

$$v^2=6.6176(10^2)T+1.0016(10^6)T^{-1}-1.3846(10^8)T^{-2}.$$

It was not difficult to obtain a good estimate of the lag of the temperature of the gas behind that of the copper cylinder by changing the rate of heating or cooling as the bottom of the crevasse started to rise. In many instances, the temperature change in passing through the half-width of the reaction peak was less than one degree, and consequently changes in temperature in the sound field of the order of a thousandth of a degree could easily be detected when readings were taken along the steep slope of the reaction peak. If, when a change of pace in heating (or cooling) was introduced, the temperature of the copper cylinder (as given by the potentiometer) remained practically stationary, while at the same time the bottom of the crevasse continued slowly to rise, then equilibrium would be awaited; and if the lag was so great that the reaction peak was passed, the reading was discarded. Equilibrium to within the desired limit of experimental error between the temperature

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[10] J. C. Southard and D. H. Andrews, J. Frank. Inst. **207**, 323 (1929).

of the copper cylinder and that of the gas in the sound field at the temperatures for the maxima of the reaction peaks was secured by spending one to several hours in slowing traversing the half-width of the reaction peaks.

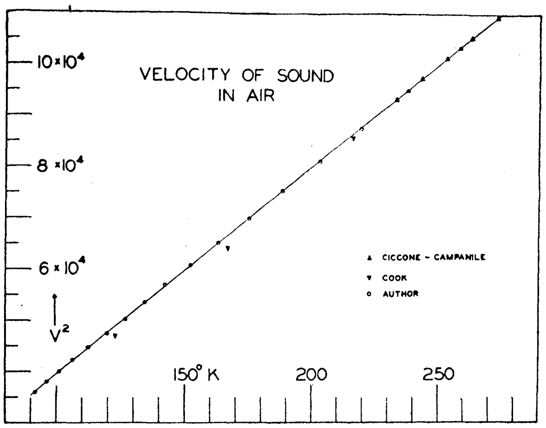

FIG. 2. Graph of velocity of sound in air at atmospheric pressure. Ordinate scale for v^2 in (m/sec.)^2.

The external gas circuit was made of Pyrex glass tubing leading from the gas supply to a Torricelli pump for maintaining the gas at the desired pressure (in the present work, at atmospheric pressure). It then extended to a manometer, a trap, an outlet to an oil pump for evacuating the assembly, then to a mercury safety valve, and finally to the nickel-silver tubing by a short length of rubber pressure tube just long enough to enable the glass stopper and the connected assembly to be removed from the cryostat.

A Dow electron-coupled oscillator, with two stages of amplification, provided an e.m.f. of constant amplitude and frequency for driving the quartz resonator. The output of the second stage of amplification was loosely coupled to the inductance coil of a wave-meter circuit containing, besides the coil, a variable condenser and vacuum thermocouple. The interferometer leads were connected across the variable condenser, and the current in the wave-meter circuit was read from a wall galvanometer connected to the thermocouple.

The electrical frequency was determined by beating the oscillator frequency against the carrier frequency of nearby broadcast stations. A rough calculation from a previously made determination of the velocity of sound at 0°C made it possible to determine uniquely the number of half-wave-lengths in the chamber at the first reaction peak encountered with decreasing temperature. From then on, it was simply a matter of counting.

The results for air and methane are given in Tables I and II, respectively. An empirical equation in each case was found by the method of least squares. The empirical equations are plotted in Figs. 2 and 3, and the experimental readings are indicated by circles. Where two or more readings were too close for separate plotting, the reading of greatest deviation from the curve is given in the figure. In conformity with the tables of Southard and Andrews,[10] 0°C is taken as equal to 273.1°K.

Two other sets of readings are plotted in Fig. 2. Ciccone and Campanile[11] made measurements for each degree from −40°C to 60°C. Their points are in good agreement with the curve. S. R. Cook[12] made several measurements for temperatures throughout the range of the curve. The readings made by Cook in his second series of measurements are found all to lie below the curve. Extrapolating the curve to the ice point gives for the velocity of sound in dry CO_2-free air at 0°C the value 330.6 m/sec. This is lower than the value given by the International Critical Tables, namely 331.45 m/sec. and that given by Kneser,[13] 331.6 m/sec.

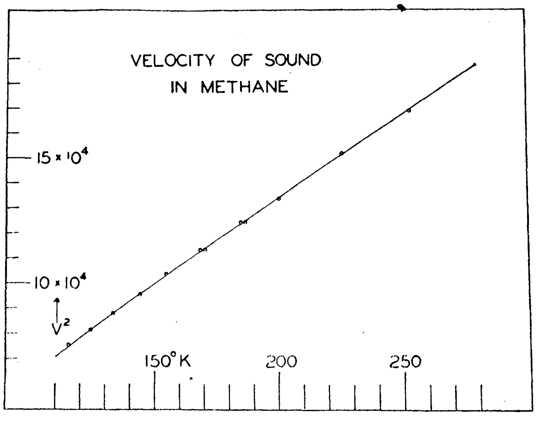

FIG. 3. Graph of velocity of sound in methane at atmospheric pressure. Ordinate scale for v^2 in (m/sec.)^2.

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[11] L. Ciccone and F. Campanile, Rend. di Napoli 5, 187 (1891).

[12] S. R. Cook, Phys. Rev. 23, 212 (1906).

[13] H. O. Kneser, Ann. d. Physik 34, 665 (1939).

Extrapolating the curve in Fig. 3 to the ice point gives for the velocity of sound in methane the value 427.2 m/sec. This is lower than the value 429.2 m/sec. given by Dixon, Campbell, and Parker.[14]

The present design could be improved by admitting the gas through a labyrinth in the wall of the copper cylinder and by reading the temperature of the gas from a resistance thermometer wound in a very thin fused quartz ring fitting snugly within the hollow cylinder of fused quartz, thereby securing greater accuracy in temperature measurement and reducing the temperature lag.

The author expresses his gratitude to Professor J. C. Hubbard for suggesting the subject of the research and for his constant encouragement and guidance throughout the work; to Dr. E. R. Blanchard for advice in designing the cryostat; and to Dr. F. O. Rice, of the Catholic University of America, for suggesting the choice of methane and supplying a sufficient quantity purified by the Podbielniak apparatus.

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[14] H. Dixon, O. Campbell, and A. Parker, Proc. Roy. Soc. Lond. **100**, 1 (1921).

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Approximate Solutions of the Integral Equations in Scattering Problems

C. F. Hsüeh and S. T. Ma
National University of Peking, Kunming, China

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In view of the difficulty of solving exactly the integral equations in the quantum theory of scattering in which radiation damping is taken into account, an approximate method of solution is proposed.

THE investigation of the influence of radiation damping on scattering processes in quantum theory by Waller,[1] Heitler,[2] Wilson,[3] Peng,[2] and others is a very important improvement on the old theory of scattering in which the radiation damping is neglected, both from the theoretical point of view and for interpretation of experimental results. The new theory, however, gives rise to some technical difficulty. The mathematical treatment of the radiation damping in quantum theory involves integral equations. Except in very few cases, the integral equations are so complicated that they cannot be solved exactly. In order to obtain solutions which give essentially correct results, one has often to simplify the problems by neglecting some features of the problems which are comparatively less important, such as transition to negative energy states, the recoil of the heavy particle, or the angular distribution of the scattered particle. Such approximate treatments are necessary for practical purposes. Owing to the approximations thus introduced, however, the results are somewhat less certain than in the old theory. In view of this difficulty, it is desirable for checking the results to find approximate solutions by various independent methods. The results obtained would be more reliable provided they are in reasonable agreement with one another.

One approximate method which enables us to retain all the physical features of the processes but make approximations in the mathematical treatment is the following. In the notation of our previous works[4] the function U_{fi} which determines the transition from an initial state i to a final state f is

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[1] Waller, Zeits. f. Physik **88**, 436 (1934).

[2] Heitler, Proc. Camb. Phil. Soc. **37**, 291 (1941); Heitler and Peng, Proc. Camb. Phil. Soc. **38**, 296 (1942); Hamilton, Heitler, and Peng, Phys. Rev. **64**, 78 (1943).

[3] Wilson, Proc. Camb. Phil. Soc., **37**, 301 (1941).

[4] Ma and Hsüeh, communicated to the Proceedings of the Cambridge Philosophical Society.