THE RICE INSTITUTE

AN EXPERIMENTAL DETERMINATION
OF ACOUSTIC VELOCITY
IN NORMAL HEPTANE BY ULTRASONICS

BY

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Woodburn.
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INTRODUCTION

Acoustic measurements in gases, particularly at high pressures and temperatures, are of interest to the engineer. From the experimentally determined acoustic velocity, it is possible to calculate the ratio of specific heats of the gas in question if the equation of state is known.

It has been only within recent years that work on acoustic dispersion by Herzfeld, Hubbard, and others and work on the absorption of sound in gases by Knudsen and Curtis has been appreciated.

The use of interferometers with gases has been limited to low pressures and temperatures. Therefore, if an interferometer could be designed to withstand moderate pressures and high temperatures, the experience gained in the operation of such an instrument would lead eventually to the construction of an interferometer for studying gases at high pressure and temperature.

It is the purpose of the present work to design and construct an interferometer to withstand a maximum of 400 lbs/sq.in. at a temperature of 700°F, and capable of using various hydrocarbons, such as heptane, octane, and decane.

It is of extreme advantage to use a high frequency sound source because the acoustic chamber can be made small and at the same time the troublesome tube correction factors experienced by using audible sound waves is avoided.

In the present work a crystal having a fundamental frequency of 575 kc at room temperature was used and the apparatus so designed to use higher sound frequencies at a later date. The crystal was an "X" cut
crystal which is commonly used for ultrasonic work in gases.

The interferometer is of the movable piston type being made entirely of stainless steel. The reason for using such material was to avoid scaling of the metal at high temperatures and to prevent rusting by the steam condensate which would collect in the steam heated bath during shut-down periods. A steam heated bath was used because of simplicity of operation and construction for keeping the gas inside the interferometer at constant temperature.
HISTORY

The determination of the velocity of sound in air has been the subject for many investigations for several centuries. Older physics texts amply describe and record the results of the experimental work performed, some of which is interesting and some amusing. One of the early French physicists used the Paris sewers as an acoustic chamber to avoid the wind velocity effects in timing the report from a pistol shot.

During the first World War, Professor Langevin developed the underwater sound technique for detecting submarines, which was a problem assigned to him by the French Government. Such work stimulated other investigators but it was not until George W. Pierce in 1925 used the quartz crystal as a means of generating sound waves. Other investigators quickly adapted Pierce's work and in 1928 K. F. Herzfeld and F. O. Rice demonstrated the change in the velocity of sound in CO₂ due to the frequency of the sound source. Professor J. C. Hubbard in 1928 at Johns Hopkins University made a very complete study of several liquids and liquid mixtures and it was possible to obtain accuracy using samples of only a few cubic centimeters. In 1930 R. W. Wood and A. L. Loomis undertook the first serious study of the physical and biological effects of ultrasonic radiation with quite interesting results.

It was established by G. W. Warner and in 1938 by A. H. Hodge, a student of J. C. Hubbard, that the acoustic velocity in N₂, air, H₂, and H₂ increased with higher pressure but decreased in the case of CO₂. Warner's results indicated that the acoustic velocity was both a function
of the frequency of the sound source and also the temperature of the gas.

In 1947 J. Woodburn developed an interferometer for determining the velocity of sound in superheated steam at temperatures up to 700°F.

In 1948 Woodburn and Chapmang developed an interferometer for determining the velocity of sound in Freon 12 at various pressures and temperatures.
Fig 1. Pierce’s Type of Crystal Electric Circuit

Fig 2. Quartz Crystal
T H E O R Y

(A) Introduction

Ultrasonic generators may be divided into a relatively small number of classes: mechanical, thermal, magnetostrictive, and piezoelectric. Mechanical generators include the Galton whistle, the gas-jet generators of Hartmann, and high-speed air sirens. Thermal generators of sound waves at frequencies up to 500 kc/sec include both spark and arc types. The discovery of the magnetostrictive effect in a ferromagnetic material is usually credited to Joule in 1847. To magnetize a specimen, certain changes occur in its internal structure, and the resulting stresses produce small changes in its physical dimensions. This phenomenon is referred to as magetostriction. Magnetostrictive sonar transducers function in this manner. Most of modern studies in ultrasonics have utilized radiators and receivers which depend for their operation upon the piezoelectric properties of crystalline quartz.

(b) Piezoelectric Effect

The Curie Brothers discovered the piezoelectric effect in 1880 and Cady, precisely defined it as "Electric polarization produced by a mechanical strain in crystals belonging to certain classes, the polarization being proportional to the strain and changing sign with it". This is known as direct effect. In the next year, Lippmann predicted the reverse effect and pointed out that not only by vibrating the crystal mechanically thereby causing an electric charge, but by placing an electric charge on the crystal would in turn produce a mechanical
vibration. This latter action is called reverse effect. The amount of contraction and expansion was calculated by Voight, who showed that the piezoelectric effect in quartz is dependent upon the voltage applied but not on the crystal dimension. For 3,000 volts applied in the X-cut quartz crystal the expansion was $6.36 \times 10^{-7}$ cm.

An electric charge appears on a crystal when it is subjected to a compression or expansion in the proper direction. The amount of charges is directly proportional to the pressure and also determined by piezoelectric modulus. This modulus for quartz crystals is about

$$d = 6.32 \times 10^{-2} \text{ esu/kg}$$

experimentally and remains constant for any one material. In both the direct and reverse effect this modulus is an indication of the efficiency of electromechanical conversion.

My Tae Ze discovered that the limitation of the piezoelectric effect is proportional to the applied voltage up to 3,000 volts and also showed that the temperature should not exceed 300°C. The maximum value of modulus occurs at about 200°C but at 573°C this entire piezoelectric effect would fail.

However, within the limits of temperature cited above, ultrasonic output may decrease with increase of temperature. Such temperature coefficient expressed in cycles per second per megacycle per degree centigrade

$$\text{Temp. Coeff.} = \frac{\Delta f}{f_0 (T_{\text{max}} - T_{\text{min}})}$$

where $\Delta f = \text{change of cycles between the maximum temperature } T_{\text{max}} \text{ and minimum temperature, } T_{\text{min}}$

$f_0 = \text{the nominal frequency of the crystal in megacycles.}$

Many crystals, such as Rochell Salt, Tourmaline, and quartz are known to
possess such a piezoelectric effect, but quartz crystals are most commonly and practically used.

(C) Design of Quartz Crystals

Quartz crystals can be produced over a frequency range from a few hundred kilocycles per sec. to about 15 megacycles per sec, when vibrating in a fundamental mode and at very much higher frequencies when operating at a harmonic.

Either natural or artificial quartz is usually in a shape of a hexahedron with a pyramid as Fig. (2). Connecting both peaks of these pyramids is defined as the optical, or Z, axis. The lines perpendicular to Z axis and passing through the opposite corners of the crystal are called electrical, or X, axis. The mechanical, or Y, axis are defined as the other ones as in three-dimensional coordinates.

The X-cut crystal which two major surfaces of the crystal are perpendicular to the X-axis, is the most commonly used for ultrasonic work, since it generates longitudinal, or L, waves.

Whenever an applied stress produces a strain along either the X-axis or the Y-axis of an X-cut crystal, the crystal becomes electrically polarized and piezoelectric charges of opposite sign appear on the two surfaces perpendicular to X-axis. These two surfaces are covered by a metal foil, and by which an electric field is applied parallel to the X-axis.

To design a quartz crystal for the ultrasonic purposes in liquids or gases a relation among the fundamental frequency and thickness has been derived experimentally as follows:

\[
f = \frac{2670}{t (\text{mm})} \text{ kc/sec} \\
= \frac{0.1120}{t (\text{in})} \text{ mc/sec} \quad \text{.................(2)}
\]
where \( f \) = the fundamental frequency produced by the crystal
\[ t = \text{thickness of the crystal.} \]

As indicated already, a quartz crystal may be made to vibrate at any desired frequency by applying an alternating voltage of the same crystal. The crystal would vibrate with minimum power input and maximum amplitude when the voltage is applied at the fundamental frequency of the quartz crystal. In fact the exact natural frequency of a crystal is difficult to find because it is variable with temperature and will be discussed later.

The relations between the stresses, strains, polarizations, and electric fields existing in a crystal were formulated by Voigt. Thickness oscillations at a direction at right angles to the surface of the plate, are used in general for producing ultrasonics. The detailed analysis of crystals in vibration were derived by imposing the conditions defining a vibration on general equations of piezoelectricity.

(D) Frequency and Wavelength

The natural frequency of a crystal is difficult to determine as mentioned before. However, Cady discovered the fact that when a quartz crystal was oscillating at its natural frequency the required power sharply decreased to a minimum. Passing through the natural frequency, the voltage increased again. The power can be measured by means of a very sensitive voltmeter if the oscillating electrical output be fed to a resonant tank circuit containing the crystal in parallel with a variable capacitance and inductance. One of these methods of vibrating a given crystal at its own natural frequency is shown as in Fig. (3). A condenser and an inductance coil, \( L \), are connected in parallel to the crystal.
The inductance in turn is loosely coupled to the output of a driving oscillator and a condenser in the tank circuit is tuned for resonance. The vacuum tube voltmeter $V$ is used for observing the variations in the voltage across the crystal. A vacuum tube thermocouple, $T$, in parallel with a galvanometer $G$, are connected in series with the crystal circuit for detecting the changes in the resonant current. As the frequency of the driving oscillator is turned slowly to the natural frequency of the quartz crystal, the current in the quartz crystal circuit will decrease rapidly, a minimum voltage occur indicating that the crystal is in mechanical oscillation. A plot of frequency against the voltage across a 575 kc/sec. quartz crystal vibrating in air is shown in Fig. (4). The sharp inverted peak is called the crystal "crevasse" and at the lowest value of current the quartz plate is vibrating at its maximum amplitude.

The sound wave emitting from a vibrating crystal is allowed to impinge on a plane reflector which is placed opposite and parallel to the face of the crystal. The reflected sound waves produce a periodic reaction on the crystal, either damping its vibration or reinforcing them, depending on the distance between the crystal and reflector. As the reflector is moved away from the crystal a series of sound peaks occur which are in reality half wave-length sound intervals of the emitted wave. The interference between original and reflected waves is eliminated and the reaction on the frequency of the crystal vibrator had a negligible effect if the plane reflector is in parallel with the crystal. (2)

When the crystal is being driven at its natural frequency by an electrical oscillator, a frequency meter can be used to determine the oscillating frequency by the best method. Knowing the frequency of the
Fig. 3. Interferometer Electric Circuit
emitted sound wave and the wave-length, the velocity of sound in the medium under investigation is the product of these two factors, or

\[ \frac{\lambda}{V} = f \]  

\[ V = f \lambda \]  

(3)

where \( V \) = velocity of sound in ft. per sec,
\( f \) = frequency in cycles per sec
\( \lambda \) = wave-length in feet.

(E) Relationships of the Sonic Velocity and the Ratio of Specific Heats

As regards the relations between the velocity of sound and the ratio of the specific heats of the gas, several investigators have set up expressions. Some of these are inadequate for use with the best experiments. According to Laplace, the relation was shown by the solution of the differential equation for the propagation of sound in a gas as follows:

\[ \nabla = (\frac{B_a}{\rho})^{\frac{1}{2}} = (\gamma \frac{B_T}{\rho})^{\frac{1}{2}} \]  

(4)

where \( \nabla \) is the sonic velocity, \( \rho \) is the density of the gas, \( B_a \) and \( B_T \), respectively, the adiabatic and isothermal bulk modulus and \( \gamma \), the ratio of specific heats of the gas. This equation is practically exact, providing the amplitude of the sound is not too great, a condition fulfilled in most measurements.

In thermodynamics,

\[ B_T = -\nabla (\frac{\partial P}{\partial V})_T \]  

(5)

and

\[ \rho = \frac{M}{V} \]  

(6)

By substitution, Equation (4) becomes

\[ \nabla = (\frac{\gamma M V^2 (\frac{\partial P}{\partial V})}{\rho})^{\frac{1}{2}} \]  

(7)

where \( M \) = molecular weight of gas.
and \( V \) = the molar volume

For perfect gas, \( FV = RT \) \( \ldots \ldots \ldots \ldots \ldots \) (8)

where \( R \) is the gas constant and \( T \) is the absolute temperature. No known gas obeys the above equation under all conditions, but the relation may be regarded as a very good approximation to the behaviour of all gases.

In particular, the equation of state for real gas is

\[ FV = A^* (1 + B^*/V + C^*/V^2 + D^*/V^3) \ldots \ldots \ldots \ldots (9) \]

The derivative appeared in Equation (7) is conveniently obtained because the virial coefficients \( A^* \), \( B^* \), \( C^* \), and \( D^* \) depend only on the temperature of a given gas (13).

Equation (7) is the useful and exact expression for the velocity of sound under any condition if the molecular weight, the ratio of specific heats, and the equation of state are known. On the other hand the ratio of specific heats may be calculated by means of the same equation if the sonic velocity is found by experiment.

Originally the acoustic interferometer was used for measuring the velocity of sound in gases. Pierce used both thickness and longitudinal vibrations of quartz crystals and stated that the velocity of sound is independent of frequency at frequencies up to 1.5 mc/sec and also independent of pressure for pressures ranging from a few atmospheres down to less than 0.01 atmosphere.

Information as to the absorption of ultrasonic waves in a fluid was also obtained from acoustic interferometer measurements. In a non-absorbing fluid the ratio of the amplitude of a returning reflected wave to that being emitted is independent of the distance between the crystal
and the reflector. However, in an absorbing gas the relative amplitude of the reflected wave decreases as the distance increases, with a resulting decrease in the amplitude of the current peaks. At a frequency below 1 mc/sec an unexpectedly high absorption occurred in CO₂. In Fig. (5) is shown a plot of voltage against the distance between the two faces of the crystal and piston, in n-heptane showing a very small change in absorption of the sound wave.
Fig. 5. Sound Peaks in N-heptane for a 575 KC. Crystal at 346°F
Description of Apparatus

(A) Acoustic Interferometer

The interferometer is shown disassembled in Fig. (8) and assembled ready to place in the heating jacket in Fig. (9). All parts of the interferometer are machined from stainless steel for two reasons as follows: to prevent any rusting of the steel by steam condensate during shut-down or heating-up periods when fastened inside the steam heating jacket or tank and to prevent any oxide formation at high temperatures. The one square inch crystal in Fig. (8) may be used as an index to show the sizes of the various parts of the interferometer. The stainless steel bellows was used in preference to a conventional packing gland which eliminated any leakage of gas from the interferometer between the piston rod and interferometer proper. The piston rod was milled with a small axial groove along its length in order that the gas sample could fill the inside of the bellows. An electrode assembly was mounted on the face of the interferometer which contacted both the crystal and the electrode which passed through the cap of the interferometer. The latter electrode was insulated from the cap by a double type cone soapstone washer and ceramic tubing which worked quite satisfactorily. Since the photographs were taken a thermocouple has been inserted in the cap of the interferometer by which the temperature of the gas inside the interferometer can be determined. The flange between the cap and interferometer has also been redesigned in such a manner that the higher the internal pressure the tighter the seal. The seal between the flange on the bellows which rests against the base of the body of the interferometer has been treated in a similar manner.
In previous designs the inlet and outlet gas connections were located in the cap which necessitated the breaking of piping connections each time the cap was removed. The present design shows the inlet gas connection and outlet gas connections to the acoustic chamber located in the body of the interferometer. In this way only the bolts in the cap need to be removed to replace the crystal, the electrode and thermocouple wires having sufficient length and flexibility for easy removal of the cap. Ceramic fish spline type insulators are used to insulate the thermocouple and electrode wiring against the side walls of the steel tank. In addition the thermocouple and electrode pass through the steel wall of the heating jacket or tank and are insulated by means of double cone type soapstone washers. The inlet and exhaust superheated steam lines to the heating jacket are located in the side walls of the tank. Therefore, if a new quartz crystal is to be used the upper flanged lid to the tank is unbolted and then the cap of the interferometer also. The new crystal is then properly located on the face of the interferometer, the cap bolted down and then the flanged lid to the heating jacket. Such an arrangement is quite proper because no inlet or exhaust steam lines have to be disconnected and neither the gas lines to the interferometer inside the tank. Such a design saves considerable time and it is quite common that leaks will occur in screwed or flare type fittings after being unbolted and reconnected after several times, which is avoided. It may also be mentioned that both the gas inlet and outlet valves to the interferometer are located outside the tank. In previous designs both valves were located inside the tank and two seals or conventional packing glands were used to seal off any steam leakage around the extended valve shafts. It was always a
HEPTANE FLOWING SYSTEM

ELECTRICAL LINE

VACUUM SYSTEM

STEAM HEATING SYSTEM

STEAM DISCHARGE

COLD JUNCTION

BLEED

VACUUM PUMP

SCALE

GALVANOMETER

POTENTIOMETER

TEMPERATURE MEASUREMENT

PRESSURE GAGE

THERMOMETER

INTERFEROMETER

STEAM BATH TANK

VACUUM TRAP

DRAIN

DRIVING MECHANISM

DIAL GAGE

CATHEROMETER

MANOMETER

GALVOMETER

VACUUM TUBE VOLTMETER

DEFLECTION MEASUREMENT

POWER SUPPLY

OSCILLATOR

FREQUENCY METER

PHONE

HEPTANE BOILER

STEAM BOILER

SUPERHEATER

SEPARATION

FIG. 6. LINE DIAGRAM OF APPARATUS FOR MEASURING VELOCITY OF SOUND IN N-HEPTANE
FIG. 7. SECTIONAL DRAWING OF THE ACOUSTIC INTERFEROMETER
Fig. 9 The Assembled Acoustic Interferometer
source of trouble which is the reason for placing the valves on the outside of the tank in the present case.

A cross-section of the interferometer is shown in Fig. (7) which clearly indicates the mode of design of a movable path type acoustic interferometer.

A complete line diagram is shown in Fig. (6) of the apparatus. The system can be evacuated by means of the vacuum pump and the gas under test allowed to enter the interferometer by opening the gas inlet and closing the gas outlet. Heating steam is provided by means of a separately gas-fired superheater, the amount of steam being controlled by a discharge valve at the right side of the tank and a thermometer well, thermometer and gage installed in the line between the tank and discharge valve to indicate the steam pressure and temperature. In this way the steam flow may be controlled properly during heating-up periods. Final temperature conditions are obtained by three thermocouples located 120 degrees apart mounted in wells that are welded in a vertical position in the flange lid of the jacket. Each well projects into the tank at a different depth which serves to indicate an average temperature of the steam inside the tank.

Fig. (14) shows the complete apparatus ready for use. At the time the picture was taken the system was being pressurized with nitrogen to test for leaks within the system.

(B) Driving Mechanism

The driving mechanism used to move the piston inside the interferometer is shown in detail in Fig. (10) and in Fig. (11) it is seen in its proper location below the heating jacket. In previous designs a micrometer screw was usually machined on the end of the piston rod which fitted into the piston. The thread was exposed to high temperatures and could not be
lubricated for fear of contamination of the gas sample. In addition the piston had to be provided with a milled slot and key to prevent rotation in the cylinder. If then the piston rod was rotated and it in turn prevented from moving in a vertical direction by a thrust bearing and collar arrangement the piston would move in a vertical direction in the cylinder. In the present design a stainless steel bellows was used to seal the gas in the interferometer, one end of the bellows being welded to the piston rod, the opposite end of the bellows being welded to a flange which was bolted against the bottom surface of the body of the interferometer. Therefore it was impossible to rotate the piston rod for fear of shearing the bellows. A driving mechanism was desired in which the piston rod could be moved through small positive displacements, also to provide against any axial thrust imposed by the unbalanced force on the piston when the interferometer and finally one in which no rotation of the piston rod was allowed. The driving mechanism in Fig. (11) fulfills the above requirements and has worked quite satisfactorily at all times.

Any unbalanced thrust is taken up by the two thrust bearings located on the top and bottom of the central cylinder. The end of the piston rod which extends below the middle horizontal plate is milled flat and rests against two roller bearings placed on opposite sides of the piston rod which prevents any rotation of the rod but still allows a vertical movement of the rod. The portion of the rod inside the central section of the assembly is provided with a single pitch square thread which fits into a similar female thread. As the small hand wheel attached to the worm drive is rotated, the wheel transmits it to the cylinder, the wheel being rigidly fastened to the cylinder, thereby causing the cylinder to rotate
Fig. 10. Sectional Drawing of Driving Mechanism

- to piston
- thrust bearing
- nut
- driving knob
- worm wheel
- worm
- ball bearing
- milled flat
Fig. 11. The Driving Mechanism
between the two thrust bearings. Since the cylinder is prevented from moving in a vertical direction by the bearings the piston rod will move instead, and it in turn being prevented from rotation by the two roller bearings at the bottom of the shaft as previously mentioned. With the present worm and wheel arrangement, one complete revolution of the worm produces only two thousandths of an inch vertical travel of the shaft or piston rod. Other combinations of worm and wheel arrangements can be easily substituted for any desired shaft displacement.

(c) Electrical Apparatus

An electrical circuit diagram is shown in Fig. (12) of the driving oscillator. It is of the electron-coupled type used in previous work. Two stages of amplification are used, the output being inductively coupled to the external circuit containing the quartz crystal. A small tubular type vernier condenser is used in parallel with the main condenser in the tank circuit for fine adjustment of driving frequency. At present, power supplies are used both for the driving oscillator and crystal controlled calibrated frequency meter from a 110 volt source for filament and plate voltages. An electron voltage stabilizer is used on the input side of the power supply in order to provide a stable voltage.

Fig. (3) shows a schematic diagram of the quartz crystal resonant circuit which contains a variable condenser, fixed inductance and the quartz crystal. It is loosely coupled to the output of the driving oscillator. A vacuum tube thermocouple is attached to the circuit and in turn to a sensitive galvanometer. Any variation in current to the crystal therefore being indicated by the galvanometer. A vacuum tube voltmeter can be attached across the surfaces of the crystal to measure any
voltage change. It was found that when the piston was moved in the acoustic chamber the thermal characteristics of the vacuum tube thermocouple produced an appreciable time lag. However, by using the vacuum tube voltmeter the time lag was considerably reduced almost to zero.
FIG. 12. SCHEMATIC DIAGRAM OF POWER SUPPLY, AMPLIFIER, OSCILLATOR AND INTERFEROMETER CIRCUITS.
EXPERIMENTAL PROCEDURE

Before assembling the various parts of the interferometer, valves, gages, piping, etc., all parts were thoroughly cleaned and free of oil or grease. Extreme care was used in cleaning all parts in order that the gas sample would not be contaminated. The interferometer when assembled was placed inside the tank or heating jacket and leveled by the three leveling screws at the base of the interferometer on the spider or platform which was approximately six inches above and parallel to the bottom of the tank. The interferometer was then bolted to the spider on platform in order to prevent any lateral movement of the piston rod which extended through the base of the tank. Any lateral movement would cause the piston rod to bind in the conventional packing gland through which the rod moved at the base of the tank. The driving mechanism below the tank was accurately aligned with the end of the piston rod which protruded through the base of the tank.

All gas connections, valves, gages, and fittings were then assembled and the quartz crystal placed in position in the interferometer leaving the cap removed. The electrode to the quartz crystal was assembled and the driving oscillator turned on to see if the crystal would function properly. That is, the crystal crevasse was obtained by slowly tuning the main condenser to the driving frequency or frequency of the crystal. The piston was then moved in order to indicate the sound peaks in air by means of the variation in voltage across the quartz crystal as indicated by the vacuum tube voltmeter.
When the crystal showed signs of operating properly, the interferometer cap was bolted down tightly, the system pressurized with nitrogen, and the heating jacket filled with water up to the bolted joint in order to test for leaks. All external joints and valve stems were tested for leaks with a soap solution. If, after a period of five or six hours, the manometer indicated no reduction in pressure, the system was considered as satisfactory. The flanged lid was then bolted to the top of the tank and the thermocouples placed in their respective welds and the thermocouple circuits checked at room temperature. The system was then evacuated for several hours, usually overnight or longer, to prepare for admission of the heptane sample.

The steam was then turned on and the system allowed to heat up slowly, measurements of the temperature being taken at half-hour intervals for several hours. When a steady state condition existed, the heptane was poured into a small vessel and heated to boiling in order to degass the heptane. The liquid was then allowed to enter the interferometer under atmospheric pressure, the valve being closed after the system was full. In a matter of minutes the heptane inside the interferometer attained the temperature of the bath. When a difference of 0.5 degrees Fah. or less existed between the gas inside the interferometer and the steam bath outside the interferometer, conditions were suitable to take measurements.

The driving oscillator and calibrated frequency meter were usually turned on thirty to forty minutes previous to the above conditions in order that voltage variations were at a minimum. The driving oscillator was then slowly tuned to the natural frequency of the crystal, the small vernier condenser of the driving oscillator being used for final adjustments. In this way the crystal crevasse was obtained. The
driving mechanism was then slowly turned and the distance the piston moved through an interval of ten successive sound peaks was noted and recorded. At least five such readings were obtained at each particular temperature.

Since one experimental run could only be obtained during the day due to the eight to ten hour heating period, the vacuum pump was turned on after the completion of test run and the system evacuated overnight. The heptane was collected by a conventional dry ice and ether cold trap. Such a procedure required a fresh gas sample for each run and at least two runs at the same conditions on different days were completed in order that check tests on the measurements were obtained. Also, after a test run, the steam inlet and outlet valves were closed and the system allowed to cool down slowly, thereby avoiding any seizing or galling between the close fitting piston and cylinder, due to unequal temperature variations.

The driving-oscillator was checked against the crystal controlled standard frequency meter by the conventional audible beat method, and by which the frequency was determined.
NORMAL HEPTANE

50 mm Hg 273.5°F

Frequency 575,700 cycles per second

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<th>Difference</th>
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<td>0.8136</td>
<td>0.7520</td>
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Each measurement is for 10 successive sound peaks.

Average 10 half wave-lengths = \((616 \pm 1.7) \times 10^{-4}\) inches

Average half wave-length = \((616 \pm 1.7) \times 10^{-5}\) inches

Acoustic velocity = \(0.00616 \times \frac{1}{6} \times 575,700\) ft/sec.

= 590.77 ± 1.6 ft/sec.
**NORMAL HEPTANE**

50 mm Hg  290.3°F

**Frequency**  569980 cycles per second

<table>
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<th>Initial Reading</th>
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<th>Difference</th>
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<td>Inches</td>
<td>Inches</td>
<td>Inches</td>
</tr>
<tr>
<td>0.8219</td>
<td>0.7584</td>
<td>0.0635</td>
</tr>
<tr>
<td>0.7681</td>
<td>0.8311</td>
<td>0.0630</td>
</tr>
<tr>
<td>0.7965</td>
<td>0.7330</td>
<td>0.0635</td>
</tr>
<tr>
<td>0.8152</td>
<td>0.7519</td>
<td>0.0633</td>
</tr>
<tr>
<td>0.8151</td>
<td>0.7516</td>
<td>0.0635</td>
</tr>
<tr>
<td>0.8280</td>
<td>0.7648</td>
<td>0.0632</td>
</tr>
<tr>
<td>0.8086</td>
<td>0.7456</td>
<td>0.0630</td>
</tr>
<tr>
<td>0.7963</td>
<td>0.7328</td>
<td>0.0635</td>
</tr>
<tr>
<td>0.7481</td>
<td>0.8115</td>
<td>0.0634</td>
</tr>
<tr>
<td>0.8090</td>
<td>0.7457</td>
<td>0.0633</td>
</tr>
<tr>
<td>0.7485</td>
<td>0.8118</td>
<td>0.0633</td>
</tr>
</tbody>
</table>

Average 10 half wave-lengths  \(= (633. \pm 1.8) \times 10^{-4} \text{ inches} \)

Average half wave-length  \(= (633. \pm 1.8) \times 10^{-5} \text{ inches} \)

Frequency  \(= 569980 \text{ cycles per second} \)

Acoustic velocity  \(= 0.00633 \times \frac{1}{6} \times 569980 \)

\(= 601.14 \pm 1.7 \text{ ft/sec} \)
NORMAL HEPTANE

30 mm Hg 327.2°F

Frequency 569,560 cycles per second

<table>
<thead>
<tr>
<th>Initial Reading Inches</th>
<th>Final Reading Inches</th>
<th>Difference Inches</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.7458</td>
<td>0.8123</td>
<td>0.0665</td>
</tr>
<tr>
<td>0.7665</td>
<td>0.8320</td>
<td>0.0655</td>
</tr>
<tr>
<td>0.7598</td>
<td>0.8267</td>
<td>0.0669</td>
</tr>
<tr>
<td>0.7737</td>
<td>0.8401</td>
<td>0.0664</td>
</tr>
<tr>
<td>0.8374</td>
<td>0.7718</td>
<td>0.0656</td>
</tr>
</tbody>
</table>

Average 10 half wave-lengths = \((662 \pm 5.4) \times 10^{-4}\) inches

Average half wave-length = \((662 \pm 5.4) \times 10^{-5}\) inches

Frequency = 569,560 cycles per second

Acoustic velocity = \(0.00662 \times \frac{1}{6} \times 569,560\)

= 628.22 ± 5.1 ft/sec.
**NORMAL HEPTANE**

43 mm Hg  346.0°F

Frequency  569,220 cycles per second

<table>
<thead>
<tr>
<th>Initial Reading</th>
<th>Final Reading</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inches</td>
<td>Inches</td>
<td>Inches</td>
</tr>
<tr>
<td>0.7500</td>
<td>0.8178</td>
<td>0.0678</td>
</tr>
<tr>
<td>0.8273</td>
<td>0.7595</td>
<td>0.0678</td>
</tr>
<tr>
<td>0.7578</td>
<td>0.8251</td>
<td>0.0673</td>
</tr>
<tr>
<td>0.8087</td>
<td>0.7414</td>
<td>0.0673</td>
</tr>
<tr>
<td>0.7651</td>
<td>0.8324</td>
<td>0.0673</td>
</tr>
<tr>
<td>0.8221</td>
<td>0.7548</td>
<td>0.0673</td>
</tr>
<tr>
<td>0.7654</td>
<td>0.8331</td>
<td>0.0677</td>
</tr>
<tr>
<td>0.8225</td>
<td>0.7549</td>
<td>0.0676</td>
</tr>
<tr>
<td>0.7588</td>
<td>0.8261</td>
<td>0.0673</td>
</tr>
<tr>
<td>0.8161</td>
<td>0.7484</td>
<td>0.0677</td>
</tr>
</tbody>
</table>

Average 10 half wave-lengths = (675. ± 2.0) x 10^{-4} inches

Average half wave-length = (675. ± 2.0) x 10^{-5} inches

Frequency = 569,220 cycles per second

Acoustic velocity = 0.00675 x 1/6 x 569220

= 640.57 ± 1.9 ft/sec.
NORMAL HEPTANE

50 mm Hg 368.9°F

Frequency 568,570 cycles per second

<table>
<thead>
<tr>
<th>Initial</th>
<th>Final</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inches</td>
<td>Inches</td>
<td>Inches</td>
</tr>
<tr>
<td>0.8522</td>
<td>.7824</td>
<td>0.0698</td>
</tr>
<tr>
<td>0.9134</td>
<td>.8439</td>
<td>0.0695</td>
</tr>
<tr>
<td>.8856</td>
<td>.8163</td>
<td>0.0693</td>
</tr>
<tr>
<td>.8918</td>
<td>.8229</td>
<td>0.0689</td>
</tr>
</tbody>
</table>

Average 10 half wave-lengths = \((694 \pm 3.3) \times 10^{-4}\) inches

Average half wave-length = \((694 \pm 3.3) \times 10^{-5}\) inches

Frequency = 568,570 cycles per second

Acoustic velocity = \(0.00694 \times \frac{1}{6} \times 568570\)

= 657.46 ± 3.1 ft/sec.
**Results and Conclusions**

The operation of the interferometer and auxiliary apparatus pertinent to the present research functioned quite satisfactorily in all phases from this initial work the apparatus may be used for studying other hydrocarbons and hydrocarbon mixtures with very little rearrangement of apparatus. The normal heptane used during the experiments was obtained from Food Machinery and Chemical Corp., Westvaco Chemical Division, which had a certification from the Bureau of Standards in regard to its purity. The pertinent data obtained from the certificate is as follows:

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling Point, 760 mm. Hg., Dec. C</td>
<td>98.41</td>
</tr>
<tr>
<td>Freezing Point, deg. C.</td>
<td>-90.68</td>
</tr>
<tr>
<td>Density at 20 deg. C, g/ml.</td>
<td>0.68385</td>
</tr>
<tr>
<td>Refractive Index, n&lt;sub&gt;D&lt;/sub&gt;</td>
<td>1.38770</td>
</tr>
</tbody>
</table>

Engine Tests Meets ASTM Requirements

Several types of trouble occurred during the performance of the various experiments such as leakage in the system, improper gasket design, and variation in the supply line voltage to the power supplies which were connected to the frequency meter and driving oscillator. However, all these conditions were remedied in due course of time. The gaskets were redesigned and new fittings were obtained which prevented any leaks in the system. Also, an electron type voltage regulator was obtained from the Electrical Engineering Department for use during the experiments which eliminated the trouble of varying line voltage to the electrical apparatus as above mentioned.

By using the special vernier condenser on the driving for final
### TABLE II

**EXPERIMENTAL DATA**

<table>
<thead>
<tr>
<th>Temp °F</th>
<th>Half Wavelength (Inches)</th>
<th>Frequency c.p.s</th>
<th>Acoustic Velocity Ft/Sec</th>
<th>Acoustic Velocity Ft/Sec</th>
<th>Perfect Gas Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>273.5</td>
<td>0.00616</td>
<td>575,700</td>
<td>590.77</td>
<td>617.10</td>
<td></td>
</tr>
<tr>
<td>290.3</td>
<td>0.00633</td>
<td>569,980</td>
<td>601.14</td>
<td>624.90</td>
<td></td>
</tr>
<tr>
<td>327.2</td>
<td>0.00622</td>
<td>569,560</td>
<td>628.22</td>
<td>639.50</td>
<td></td>
</tr>
<tr>
<td>346.0</td>
<td>0.00675</td>
<td>569,220</td>
<td>640.57</td>
<td>648.20</td>
<td></td>
</tr>
<tr>
<td>368.9</td>
<td>0.00694</td>
<td>568,570</td>
<td>657.46</td>
<td>658.00</td>
<td></td>
</tr>
</tbody>
</table>

Pressure at above temperatures held at atmospheric pressure.
FIG. 13. SONIC VELOCITY VERSUS TEMPERATURE IN N-HEPTANE
adjustment to locate the bottom of the crevasse, approximately one-half to one volt was required to drive the crystal. If patience and care were exercised, it was possible to maintain an accuracy at the fundamental mode of vibration with only two to three-tenths of a volt applied across the crystal. With such a small voltage being used to drive the crystal any small change in supply line voltage to the oscillator gave serious trouble. Electrical machinery on the same power circuit when turned on and off would cause very large variations in the crystal voltage, throwing the crystal out of oscillation. It was found necessary to perform all of the experiments late at night, usually after midnight. In this way no other additional electrical apparatus was being served by the system which served the power supply to the oscillator. This greatly reduced the above trouble.

The superheater which was used to maintain a constant temperature suffered from a similar cause; that is variation in supply line gas pressure to the burners which in turn caused a variation in temperature of the steam to the heating jacket. A gas pressure regulator was installed ahead of the burners; however this was not completely satisfactory and for this reason it was necessary to perform the experiments after midnight because at such times the gas supply pressure to the burners was constant.

In regard to the actual measurements obtained, something quite interesting was observed. After the heptane was admitted to the system it was noticed that about one hour at the temperatures used, the acoustic velocity showed signs of slowly increasing with time. Usually decomposition of such a material at the temperature involved is not brought about. However, this happened in every experiment and it was found necessary to perform the experiments as quickly as possible. It is felt that additional exper-
ments should be obtained before any definite conclusions are reached in regard to the decomposition of the medium with temperature. In practice decomposition of the heptane occurs at much higher temperatures. It is well known in ultrasonics that slight traces of impurity in a gas may be detected by the change in acoustic velocity which is very sensitive to small amounts of impurities. This factor may be of interest to chemical engineers if it is proved to be correct when more information is obtained. It would mean that measurements would have to be made and extrapolated to zero time to obtain the desired acoustic velocity.

At present a high pressure pump of special design is being constructed to pressurize the system; that is, to be able to study the acoustic velocity of heptane as both a function of pressure and temperature. Provision has also been made in the present apparatus to study the effect of frequency with acoustic velocity in heptane and also for studying gas mixtures in hydrocarbons in the very near future.

The present piece of apparatus has shown itself to be suitable for determining the velocity of sound in hydrocarbon gases. However, due to insufficient time results could not be obtained over a range of pressures and temperatures. When the special type pump is used the equipment will be complete in order to determine the acoustic velocity of various hydrocarbons at pressures up to 400 psia and 700°Fah. When this information is obtained then it will be possible to calculate accurate information on the ratio of special heats of a gas. At present the effects of both pressures and temperatures in addition to the frequency of a sound source are not known. These factors have to be determined before any reliable information on the ratio of specific heats can be evaluated.
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7. J. Woodburn: "Experimental Determination of Velocity of Sound in Superheated Steam,"


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