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

THE SPECIFIC HEAT OF HYDROGEN GAS AT LOW TEMPERATURES FROM THE VELOCITY OF SOUND; AND A PRECISION METHOD OF MEASURING THE FREQUENCY OF AN OSCILLATING CIRCUIT

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At room temperature the specific heat of hydrogen gas is but slightly less than the classical value for a diatomic gas without vibrational energy. This theoretical value is $5/2\ R$ for specific heat at constant volume, where R is the gas constant expressed in the same units as the specific heat. It was found by Eucken,[1] who filled a calorimeter with hydrogen gas under pressure, that below room temperature the specific heat of hydrogen becomes less and approaches the value $3/2\ R$ at a temperature a little below the boiling point of liquid air. A number of specific heat equations, based on quantum theory, have been proposed[2] and accordingly it seemed advisable to make, if possible, a more accurate experimental determination of the specific heat of hydrogen over this range of temperature. Since the moment of inertia of the unresonated hydrogen molecule is not known, it is an undertermined constant in the specific heat equations. However, apparently no theories fit our data. (See end of this paper.)

The experimental method chosen for the specific heat measurements was to determine the velocity of sound by Thiesen's[3] method of closed cylindrical resonators. This method was much improved by Grüneisen and Merkel,[4] who used oscillating circuits and a telephone in place of the siren used by Thiesen for the excitation of the sound in the gas. Grüneisen and Merkel worked at 0°, using both air and hydrogen. The most important further apparatus used by us was a means of obtaining the required constant low temperatures in a resonance tube 150 cm. long, and a means of measuring the frequency of an oscillating circuit (of constant frequency) with an accuracy of $^1/_{30,000}$. If the suitable number of comparison circuits (each with suitable frequency) are set up, the method can be used for measuring the frequency of *any* oscillating circuit which can be excited by radio tubes; the mean frequency over a period of fifteen minutes could (if desired) be measured with an accuracy of $^1/_{1,000,000}$, even

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[1] (a) Eucken, *Sitzb. preuss. Akad. Wiss.*, **1912**, p. 128; (b) Scheel and Heuse, *ibid.*, **1913**, p. 44; (c) *Ann. Physik*, **40**, 473 (1913).

[2] (a) Einstein, *Ann. Physik*, [4] **22**, 180 (1907); (b) Reiche, *ibid.*, **58**, 657 (1919); (c) Tolman, *Phys. Rev.*, [2] **22**, 470 (1923); (d) Kemble and Van Vleck, *Phys. Rev.*, [2] **21**, 381, 653 (1923); (e) Dieke, *Physika, Nederlandsch Tijdschrift voor Natuurkunde*, **5e**, 412 (1925).

[3] Thiesen, *Ann. Physik*, **24**, 401 (1907); **25**, 506 (1907).

[4] (a) Grüneisen and Merkel, *Z. Physik*, **2**, 277 (1920); (b) *Ann. Physik*, [4] **66**, 344 (1921).

if the circuit oscillates only once per second. The only limitation of accuracy is due to the clock used to send the time signals, and to the constancy of the oscillating circuit.

Because of the low density of hydrogen gas, one must use resonance tubes of large diameter, to cut down damping. Because of the relatively long wave length of even the highest easily audible pitches (for example, 10,000 cycles per second) in a light gas, a longer resonance tube is required than with a heavier gas. An apparatus sufficient for determining the velocity of sound in hydrogen would give extremely accurate results with a heavier gas. In the latter case, however, the corrections for "imperfections" in the gas become larger, so that good data of state become necessary.

Calibration of Thermocouples.—For calculating specific heats from the velocity of sound, an error of 0.1°K. at 80°K. produces an error of 0.01 *R* in the specific heat. Accordingly, two separate thermocouples (C, Fig. 1) were used in all work, to detect any electrical defect appearing in the temperature element. For calibration, a hydrogen thermometer bulb was placed in the inner Dewar (D_2, Fig. 1) in place of the resonance tube. The pressure of the hydrogen was read to about 0.03 mm. by a Gaertner standard steel meter scale, using a cathetometer for interpolation. The bulb of the thermometer connected with the manometer by a capillary tube, and the dead space volume of hydrogen in the manometer was less than 3 cc. The hydrogen was made as for the velocity of sound work, taking special precautions to remove water vapor. Before filling, the thermometer bulb was evacuated for a week by a Cummings mercury vapor pump, using a McLeod gage. The gas pressure at the ice point was about 100.0 cm.

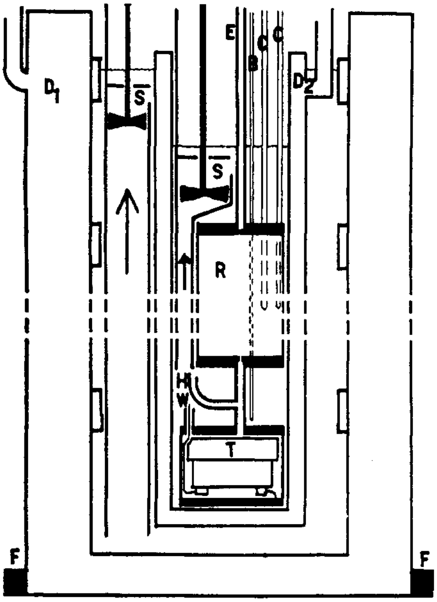

Fig. 1.—Resonator, showing temperature control.

The absolute temperature is not strictly proportional to the height of the mercury column; the necessary corrections are:

First, the imperfections of the thermometer gas (see Equation 18).

Second, by combining the volume expansion of mercury with the linear expansion of steel for a 100cm. column at a temperature of 1° above the reference temperature (arbitrarily taken as 20°), a correction of 0.17 mm. in the mercury height (representing about 0.05° in temperature) is needed. The temperature of the mercury column was found by hanging calibrated mercury thermometers along it. The manometer was encased in a wooden box, and read through a plate-glass door.

THIRD, the pressure coefficient of the thermometer bulb was measured by filling with water, changing the pressure, and noting the rising and sinking of the water level in an end tube of known diameter. About two-thirds of the observed compression was accounted for by the known compressibility of water. The calculated correction is of course 0.000° at 273°K., and below that point the Charles' law temperature must be decreased by 0.001° at 250°K., and by 0.002° at 200°K. or any lower temperature down to 50°K.

FOURTH, the dead space and gradient space. To make these corrections small a large bulb (2410 cc.) of hydrogen was used. Volumes were measured by weighing mercury (water for the bulb). The gradient length of capillary was very short, but three thermocouples were firmly mounted on it, and their readings were considered. A thread of black glass was sealed into the top of the dead space of the manometer, and the volume of the dead space measured to the lower tip of the thread. During runs the top of the lower meniscus could be adjusted to *below* the tip of the black glass thread, since the diameter of the manometer tube was accurately known.

FIFTH, variations in capillary depression of mercury menisci. This affects both the observed pressure and the dead space volume; the latter variation is negligible in our apparatus. The diameters of the manometer columns were 1.65 cm. From a rough extrapolation of a table given by Guyot[5] with the help of some measurements by Palacios,[6] one finds that a change of 0.4 mm. in the height of a meniscus affects the pressure reading by 0.01 mm.

SIXTH, the thermal contraction of the Pyrex thermometer bulb gives a considerable correction, which has been calculated by Dr. R. M. Buffington from the measurements of Buffington and Latimer.[7] We copy Buffington's table as Table I; from a plot the correction at any temperature can be read.

During measurements a vacuum of 0.0001 mm. or better was maintained over the upper meniscus.

In some of the work one thermocouple read as much as 2 microvolts different from the other. This is not serious, since our four-junction

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[5] Guyot, 4th edition of Smithsonian Physical Tables.

[6] Palacios, *Physik. Z.*, **24**, 154 (1923).

[7] Buffington and Latimer, THIS JOURNAL, **48**, 2305 (1926).

TABLE I

CORRECTION TO CONSTANT VOLUME HYDROGEN THERMOMETER DUE TO THERMAL EXPANSION OF PYREX GLASS, ACCORDING TO BUFFINGTON

To be *subtracted* from Charles' Law temperature below the ice-point; *added* above the ice-point.

Abs. temp., °K.	Correction, °K.	Abs. temp., °K.	Correction, °K.
315.9	+0.159	185.1	−0.150
298.0	+ .088	130.4	− .155
273.1	+ .000	118.2	− .152
248.9	− .053	88.7	− .118
218.3	− .110		

couple gives from 180 to 75 microvolts per degree over the range used in this work. The true e.m.f. was taken as the mean of the readings of the two couples; it was assumed that the temperature was 273.1°K. when this mean reading was zero.

From the equations given by Eastman and Rodebush[8] for the e.m.f. of a certain four-junction copper-constantan thermocouple, the e.m.f. was calculated for the various temperatures at which we used the hydrogen thermometer. These values were larger than our measured values and the ratios were calculated. The results are in Table II, in the order taken. All points represent from 3 to 6 determinations, any one of these series of 3 to 6 determinations being taken at one time, over a period of about half an hour. During this time the temperature of the apparatus drifted from 0.05 to 0.5°, but the results were calculated for the mean temperature by using d (e.m.f.)/d T. In all but two determinations the temperature difference between the top and bottom of the apparatus was 0.02° or less. In the series at 158.61° the difference became 0.05° and in the one at 134.87° the difference became 0.25°. This temperature difference was noted by differential thermocouple "B" (Fig. 1), and was due to heat leak at the top of the inner Dewar, since the inner bath was warming up although the outer bath was several degrees colder. At 135°K. the viscosity of the petroleum ether becomes large enough so that the stirring propellor cannot effectively equalize the temperature. This effect was avoided in the next measurement at 135°K. by filling the outer Dewar with liquid air. There is very little radiation at these temperatures and the cold air boiling off from the outer bath keeps the top of the inner Dewar cold. Even so, it was necessary to stir for three hours to obtain a uniformity of 0.02° at 133°K.

The lower temperatures for the velocity of sound measurements were calculated from the Eastman and Rodebush equations, applying the factors given in Table II.

For temperatures above 0° the boiling point of water was checked against our thermocouples a number of times. The e.m.f. was 1.01360 times

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[8] Eastman and Rodebush, THIS JOURNAL, **40**, 489 (1918).

TABLE II

CALIBRATION OF THERMOCOUPLES

Abs. temp., °K.	E.m.f. (E. and R.)/e.m.f. (obs.)	Abs. temp., °K.	E.m.f. (E. and R.)/e.m.f. (obs.)
284.98	1.0484	134.87	1.04679
273.09	"Ice point"	273.10	"Ice point"
234.04	1.0460	81.27	1.04836
203.36	1.0467	152.53	1.0469
185.97	1.0473	133.17	1.04694
158.61	1.0470	273.13	"Ice point"

that calculated from the table of L. H. Adams.[9] All our temperatures above 0° were calculated from Adams' table, using this same factor. This sort of procedure has been used before in this Laboratory for temperatures not below the boiling point of liquid air.[7]

We have four checks on our scale. The freezing point of mercury was measured as 234.24°K. while the accepted value is 234.22°. The transition point of sodium sulfate was measured as 305.51°, instead of 305.5°K. Finally, we placed together, in a liquid air-bath, the old Laboratory standard of Eastman and Rodebush,[8] our thermocouples and thermocouple "No. 17" of Giauque, Buffington and Schulze.[10] The three temperatures obtained are, respectively, 81.75, 81.77 and 81.92°K. The same comparison a year earlier of ours with the Eastman and Rodebush couple gave a difference of 0.00°.

The Resonator Tubes for the Gas (see Fig. 1).—Four different resonance tubes, 168 cm. or less in length, were used. They were made from brass tubing, the ends being closed with brass plates. The plates were soldered in place, after measuring the thicknesses and drilling central 1mm. holes. These holes were each 1 mm. long, and led into $^3/_{16}$-inch thin walled brass tubing. The tubing was fastened with silver solder and served to carry the sound in and out of the various resonators. Larger sized tubing was not used in order to damp out or broaden resonance maxima due to vibrating gas in these end fittings. Smaller tubing ($^1/_8$-inch diameter) was tried, but did not transmit sound well enough when filled with hydrogen, although it was satisfactory for air.

The lengths of the resonators were determined by comparison with a Gaertner steel meter scale, using a cathetometer as intermediate. Temperature corrections were made, assuming the steel scale to be exactly 1 meter long at 20° as stated by the makers and using expansion coefficients of 0.18×10^{-4} per degree for brass and 0.11×10^{-4} per degree for steel. The end thicknesses were subtracted from the lengths as determined by the cathetometer (Table III).

TABLE III

DIMENSIONS OF RESONATORS AT 0° (NO. 168 AT 20°)

Number	Length inside, cm.	Diam. inside, cm.	Wall thickness, in.	Total end thickness, cm.
150 A	149.969	4.790	$^1/_{16}$	1.318
150 B	150.291	2.400	$^1/_{32}$	1.323
100 A	99.978	4.785	$^1/_{16}$	1.316
168	168.173	9.87	$^3/_{64}$	1.295

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[9] "International Critical Tables," 1, 58 (1926).

[10] Giauque, Buffington and Schulze, THIS JOURNAL, **49**, 2343 (1927).

The accuracy of the lengths is 0.01 cm. or better. As the end surfaces of the resonators were not exactly perpendicular to the long axes, determinations 90 degrees apart were made of each length, and the average was taken. As much as 0.04 cm. difference in the length as measured along two opposite sides was found in one resonator (No. 150 A).

Sound in the resonators was heard through the $^3/_{16}$-inch tubing E, 30 cm. or more in length, with the ear pieces from a stethoscope fastened to the free end of the $^3/_{16}$-inch tube by a short piece of rubber tubing. During measurements, hydrogen gas was flowing out through the stethoscope into the ear of the observer. The stethoscope was most sensitive when not clamped tightly in the observer's ear, but held loosely. This effect was later avoided by by-passing the escaping hydrogen so it did not build up a pressure in the observer's ear. The only setting made while listening is a variable condenser, which is adjusted to give a maximum of sound (see below).

A too rapid flow of hydrogen through the apparatus produced uncertainty. The noise of vacuum pumps or talking was troublesome; these distractions were eliminated during all the velocity measurements. Stirring motors were shut off during actual setting of the resonant frequency.

At one time while working at low temperatures, a very baffling difficulty was found to be due to atmospheric air being drawn into the apparatus through tube "W," due to gravitation; this was later prevented by proper precautions.

As the resonators were mounted vertically in a thermostat, the telephone "T" was encased in a copper can, fastened at the bottom of the resonator (Fig. 1). The telephone was activated by an amplifier, the lead wire W (broken off in Fig. 1) being insulated by a small-sized rubber tube, encased in a steel tube. Tests showed a large fraction of the energy from the amplifier to be lost, due to the capacity between the lead wire and the encasing tube, for the return from telephone to amplifier was made by grounding to the apparatus. This loss was worst with frequencies of 10,000 per second or higher. The hydrogen was led into the short tube connecting the telephone and resonator by means of a copper tube H running from top to bottom of the thermostat. A very slow stream of the gas flowed around the telephone, and out through the steel current conduit so that gas in the telephone could not flow through the resonator. The main quantity of hydrogen flowed out through the stethoscope.

The "Impure" Hydrogen (for Tables VIII and X).—The hydrogen was made by the 500-ampere electrolytic generator which is used in this Laboratory for preparing hydrogen for the liquefaction cycle. According to Latimer, Buffington and Hoenshel,[11] the hydrogen contains about 1% by volume of oxygen as it comes from the generator, but this oxygen changed to steam by passage through the nickel catalyst of those authors. Using their method, analyses were run for oxygen both before this research was begun, and after it was finished. In both cases about 0.01% by volume of oxygen was found, and part might well be due to imperfect removal of dissolved air from the solutions necessary. The hydrogen was passed through 100 cm. of glass tubing cooled with liquid air and through a plug of glass wool also kept at liquid air temperature. From this the hydrogen was kept flowing continuously through the resonance tube during measurements, and in fact for at least six hours before beginning them. When

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[11] Latimer, Buffington and Hoenshel, THIS JOURNAL, **47**, 1571 (1925).

soldering had been done on the resonance apparatus, this was evacuated for at least twelve hours to evaporate the water from the soldering flux. It sometimes required six hours to pump out even most of this water, as indicated by a small manometer. Whatever parts of the system must be immersed in a liquid were carefully tested for leaks, using air pressure and immersing in water.

The "Pure" Hydrogen (for Table XI).—The purity of the above hydrogen cannot be guaranteed to better than 0.01% by volume. Because of the form of the relation between specific heat and velocity of sound, and because of the low density of hydrogen relative to air, an impurity of 0.01% by volume of oxygen or nitrogen amounts to 0.5% error in the specific heat, or to 0.0125 R. Accordingly, it was decided to repeat the measurements with hydrogen purified by passing through a glass spiral which was immersed in liquid hydrogen (using also the other glass spiral in liquid air as a preliminary). This new spiral contained a glass wool plug to collect air or other dust. The spiral was mounted in a hydrogen liquefier designed by Dr. W. F. Giauque of this Laboratory. The liquefier holds about 2 liters of liquid hydrogen, which permits measurements to be safely made for twelve hours. Some liquid is present even after twenty hours. The hydrogen used in the resonator was presumably never liquefied, but was certainly cooled to the condensing point since in the trap it was under slightly greater pressure than the liquid hydrogen in the surrounding container. As shown in Fig. 3, the specific heat results obtained below room temperature are only very slightly lower than those with hydrogen direct from the generator. In this new series the resonator was carefully evacuated for several days at a temperature higher than that used in the next run, using a Cummings mercury diffusion pump. In this way a few small leaks (otherwise practically undetectable) in the telephone chamber were detected and repaired from time to time, as they appeared, these being detected by the McLeod gage on removing the liquid from the thermostat. As previously explained, gas from the telephone cannot get into the resonator during specific heat runs; but it was found that, especially when the resonator was heated, a considerable amount of adsorbed gas (probably water) was given off, enough to account for the high results obtained above room temperature with "impure" hydrogen. We then check the statement of Latimer, Buffington and Hoenshel[11] that their nickel catalyst gives hydrogen better than 99.99% pure by volume. In this second series the resonator was never filled with hydrogen until measurements with the McLeod gage showed a rate of de-adsorption of gas which would not contaminate the hydrogen to as much as 0.001% by volume (taking into account the rate of flow of the hydrogen through the apparatus); at 100° this required several days of pumping.

The Air (for Table XII).—Runs were made with air at room temperature, to verify the Kirchhoff-Helmholtz tube correction. To avoid variation from day to day, *all* the air to be used was pumped into a gas cylinder by our liquid air plant compressor, first blowing out the compressor for some time to avoid fractionation due to the air liquefier. As used, the air was bubbled through several towers of concentrated potassium hydroxide solution, through towers of concentrated sulfuric acid and finally through a 100cm. glass spiral cooled with solid carbon dioxide. Several feet of glass wool were installed in appropriate places in the line, and especially more than enough to eliminate the smell of sulfuric acid spray.

Air cannot be purified safely by passing through a liquid air trap. Fresh liquid air contains about 20% oxygen, but the gas evaporating from it contains about 5% oxygen.[12] Obviously if ordinary air is passed very slowly through a trap cooled by *fresh*

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[12] Dodge and Dunbar, THIS JOURNAL, 49, 607 (1927).

liquid air, the gas emerging will contain 5% oxygen. This explains the supposedly surprising statement of Stock and Ritter[13] that the density of dried air varies from day to day over a range of 0.13%. Some measurements of ours (not given in this paper) on the velocity of sound in air purified by a liquid air trap indicated an even greater concentration of nitrogen than was found by Stock and Ritter. Moreover, Dr. M. Tamele of this Laboratory has found that carbon dioxide is not completely removed by passing air through a liquid air trap containing copper gauze unless at least some of the air is condensed, presumably thus wetting the carbon dioxide dust enough to allow it to stick to the gauze.

Oscillating Circuits.—The sound was produced by exciting the telephone ("T," Fig. 1) by radio apparatus. The telephone diaphragm must be tightly clamped to work at high frequencies without enormous distortion. In this telephone the hard rubber clamp was replaced by one of brass, as the rubber one becomes loose with large temperature changes. Presumably, using diaphragms of smaller diameter than ours of 1.75 inches, results could be obtained with frequencies higher than 12,000 cycles per second. This was not advisable, because the ear is not very sensitive to frequencies above 15,000 cycles, especially in recognizing changes in intensity. Also the ear shows a very great fatigue effect at such frequencies after listening for a few seconds.[14]

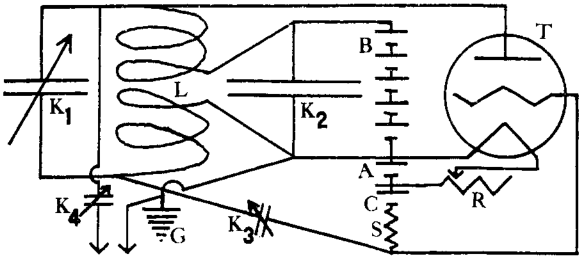

Fig. 2.—Oscillating circuit.

Two independent oscillating circuits are used, as should always be done when a constant frequency is desired; if the frequency of the circuit should begin to vary erratically, that is most easily noted by setting up beats between the two circuits.

The double inductances used in the two circuits for most of the measurements (L in Fig. 2) were of about 0.025 and 0.10 henries, respectively. Inductances were made from No. 21 wire, or wire larger in diameter, giving a low damping coefficient. Each inductance was in two approximately equal sections, for the "Hartley Circuit."

Small 3-electrode radio tubes were used for excitation. For constancy of frequency tungsten filaments were preferable to oxide filaments for the oscillator (not necessarily for the amplifier); the real requirement is probably a good vacuum in the tubes. A filament voltage of 2 to 5 volts heated the filament, battery "A" with rheostat "R" being used. The grid was coupled through a small 3-plate variable condenser "K_3." Its capacity, and the filament voltage, should be somewhat, but not a great deal, larger than the minimum necessary; the plate voltage should not be excessive. Below 1000 cycles "K_3" was short-circuited by a switch. The negative grid "bias" was maintained by battery "C" and resistance "S" (500,000 ohms).

Except for occasional replacing of inductances, the frequency was controlled by capacity "K_1," which could be varied continuously from 3 to almost 0 μF.

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[13] Stock and Ritter, *Z. angew. Chem.*, **39**, 1463 (1926).

[14] See, however, a method by which the velocity of sound was measured at frequencies as high as 1,500,000 cycles per second, Pierce, *Proc. Am. Acad. Arts Sci.*, **60**, 271 (1924–1925).

K_2 was a 15 μF by-pass condenser for the B battery. K_2 was often disconnected altogether, as usually it did not affect the constancy or ease of production of oscillations.

The output energy was very small, passing through a 3-plate condenser K_4 similar to K_3. This lead, together with the battery ground, excited the amplifiers.

It is important that all electrical connections be tight. Switches were avoided except for filament rheostats. Trouble was often produced by screws in the 3-plate condensers or in the tube supports working loose. Also the spring clips in the tube supports must sometimes be sandpapered.

With precautions noted above, the "instantaneous" frequency of the circuits did not usually change by more than 1 part in 30,000 in half an hour, as shown by heat measurements. This was sometimes true even only an hour after charging the batteries, and applies to the range 200 to 12,000 cycles per second. Frequencies below 300 were sensitive to changes in battery voltage.

Except for Murdock variable air condensers for the fine adjustment, of total range 0.001 or 0.0005 μF each (sometimes filled with oil to double the range), the condensers K_1 have mica for dielectric. Some are ordinary radio condensers, each of capacity 0.005 μF or less, connected in parallel by binding posts. The layers of the radio condensers were tightly clamped with nuts and bolts. After clamping it was necessary to measure the capacities of the small radio condensers, using a Wheatstone Bridge. For each inductance a plot of frequency against capacity was made to hasten the adjusting of capacities. By using logarithmic plotting paper a straight line is obtained.

Measurement of the Frequency.—The frequency of the oscillating circuits was measured by comparison with a siren, using a beat method. It is not necessary for the siren to run at constant speed, as long as the beats do not come too fast to be counted. The siren disk had 80 or 20 holes in the rim. Through these air was blown by a jet operated at a pressure of 50 lb. per sq. inch or less. The disk was mounted on a motor with a maximum speed of 50 revolutions per second. It was hard to make comparisons with the siren at frequencies higher than 6000 cycles, due to the preponderance of the noise of the driving motor over the high frequency. Accordingly, the main oscillating circuit is compared with the auxiliary one, whose frequency is almost $^1/_2$, $^1/_8$ or $^1/_4$ as great, by a beat method described below. Later the auxiliary circuit was kept at about the resonant frequency of the hydrogen (or at about twice the resonant frequency), which enormously speeded up the measurements, as only a few measurements on the siren were needed at each temperature, even when a large number of overtones was measured. The auxiliary oscillator operates a telephone near the siren, a radio tube providing amplification. This telephone was in a tight glass compartment from which a short glass tube led to an open end within 2 inches of the siren jet. The open end may be stuffed with cotton waste, the siren motor also being supported on rubber stoppers to drown out the noise of the motor. The siren note may be heard, for a cotton plug transmits more sound than can enter through the entire wall of the glass tubing.

Sound within the short glass tube is heard through a T-connection, using the ear pieces from a stethoscope. Thus any beats are easily heard and counted.

Besides the siren disk a 10-lb. flywheel is mounted on the motor. This shunt-wound, 0.5 horsepower D. C. motor was operated by a storage battery. After starting the motor, all resistance was cut out of the armature circuit. To obtain changes in speed, the armature voltage could be varied at will from 20 to 105 volts, in approximately 2-volt steps, by adding storage cells. The field was excited by the entire 105-volt battery, and fine adjustments of speed were obtained by a rheostat in series with the field coil. These precautions were necessary to obtain the required constancy and reliability in speed.

A second shaft is direct-connected to that of the motor by a short piece of rubber tubing, the rubber being prevented from slipping by wires through holes in the shafts. Thus, using a worm and gear, a disk is driven at a rate $^1/_{192}$ as fast as the siren disk.

For recording time on the two disks, we had two short, pointed No. 12 copper wires, one held near each disk. Either of the pointed wires could be connected at will to the secondary of an induction coil. The two disks are smoked by holding them in the flame of burning camphor, so that a spark mark made while the disks are moving may be located as a pinhole in the soot.[15]

A telegraph relay was actuated once a second by means of a chronometer in the Department of Astronomy. Tests showed the relay, together with our sparking system, to give two-second intervals to $^1/_{1000}$ second. The platinum contacts of the relay were in the primary circuit of the induction coil, which circuit could be finally completed by a knife switch so that sparks are not necessarily made whenever the relay moves. The relay had a set of contacts on each side of the moving arm, the second set operating a machine for counting seconds.

An actual comparison is made as follows:

Listening with the stethoscope, and with the proper armature voltage, the operator adjusts the field rheostat until the frequency of the siren is slightly above (or below) that of the telephone. This is noted by the slow beating between the two pitches of sound. The beats are then counted for a 120-second interval, there being between 200 and 600 beats during that time. At the start of the 120-second interval, that is, on the zero second, a spark mark is allowed to be made by the chronometer on the high speed siren disk. The sparking point near the disk is then shifted by means of a small electromagnet, and another spark mark is allowed to be made on the 120th second. On the No. 2 and No. 122 seconds, spark marks are made on the slow-moving disk. Here again an electromagnet allows the two spark marks to fall on circles of different radius, so that they may be distinguished from each other. The machine is stopped, and the spark positions measured. From the four positions, from the number of beats counted and from the whole number of revolutions of the slow-moving disk in 120 seconds (determined separately, usually between 5 and 25), the frequency of the telephone is calculated. If everything is working properly, a second comparison checks this to 0.10 cycle per second for frequencies around 3000 cycles per second. Frequencies less than 500 are checked to 0.01 cycle per second. The comparison must be made twice, because of the many chances for mistakes. The beats were occasionally double or triple, but measurements with the siren first above and then below the frequency of the auxiliary circuit eliminate any such uncertainty.

The "clock-fork" invented by Koenig many years ago gives frequencies as accurately as our siren; Miller[16] claims a possible accuracy of 1/650,000 for the frequency of his 60 to 70 cycle per second clock fork. However, for our purposes the siren has certain advantages of variability of pitch, ruggedness and quick operation.

Amplifiers.—Three amplifiers are used. The first is the radio tube which operates the telephone for comparison of the auxiliary oscillating circuit with the siren. The second amplifier was excited by the main oscillating circuit and consisted of two 7.5-watt stages, with two transformers. The output energy was regulated by the filament voltages. The output of this amplifier operates the telephone at the end of the hydrogen chamber, by which means stationary sound waves are set up in the hydrogen gas. A resistance repeating amplifier with 800 volts on plate[17] was tried in place of the transformer repeater but it did not increase the range of possible measurements to more than 14,000 cycles per second, while 12,000 cycles per second could be used with the trans-

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[15] See Encyclopædia Britannica, 11th ed., **6**, 303, for work of Sir Andrew Noble on bullet velocity.

[16] Miller, "Science of Musical Sounds," Macmillan Co., New York, **1916**, p. 40.

[17] Morecroft, "Principles of Radio Communication," John Wiley and Sons, Inc., **1921**.

former repeater. Because of the erratic character of the 3 determinations of velocity made using the resistance repeater (3 highest frequencies with tube No. 100A at 0°, see Table VIII), further work with it was abandoned.

The third amplifier was used for comparing the main and auxiliary oscillating circuits with each other. Three radio tubes were used. One was excited by the auxiliary circuit, one by the main circuit (through the output of the second amplifier) and both of these tubes induce into the third tube by means of a transformer. (Where the frequency of the main circuit is many times that of the comparison circuit, this third tube must be replaced by a 3-tube amplifier.) The last tube operates a pair of headphones, so that any beats may be heard. The auxiliary oscillator had approximately $^1/_2$ or $^1/_3$, etc. (the numerator of the fraction being 1 or occasionally 2), the frequency of the main oscillator. Calling this fraction x/n (where x/n is reduced to its lowest terms), the auxiliary frequency v and the main frequency $nv/x \pm d$, xd beats per second are usually heard in the headphones of the third amplifier, due to "distortion."[4a] A suitably small, variable condenser formed part of K_1 in the auxiliary oscillator and, by moving this, it could be found whether d was positive or negative. This condenser was fitted with a stop so that it could be brought to either end of its range but have a reproducible capacity at those two positions. From the measured difference of capacity between the ends of this range, together with the approximate frequencies of the two oscillating circuits and the value of K_1 in the auxiliary circuit, we may calculate the change in d when the small variable condenser is moved from one end of its range to the other. If now we measured the difference in the number of beats per second in the headphones for the two positions of this condenser, this was found almost always to agree with the calculated value. In a *very* few cases, however, this number of beats was exactly half (not twice) the calculated number; also, both types of beats were sometimes heard at once.

When the *difference* in the numbers of beats was a *multiple* of the calculated difference, or if the *total* number of beats was very large, a spurious maximum was being used. Obviously these tests are most reliable if the auxiliary circuit is kept at the resonant frequency of the hydrogen.

Accordingly, the auxiliary and main circuits were compared by counting the number of beats produced by the third amplifier in a definite time (25 sec.), with the above condenser at one end of its range, and by determining the sign of this beat difference, from the effect of moving the condenser.

Maintenance of Temperatures (see Fig. 1).—The resonator and its telephone were immersed in a stirred liquid-bath contained in a 180cm. long Dewar tube (D_2). The stirrer propellor was so efficient that when this Dewar was filled with water and a 5cm. layer of crushed ice was maintained at the top, the temperature difference between top and bottom dropped to 0.003° in about thirty minutes; but the behavior of this thermostat was discussed in the section on "calibration of thermocouples." For work at lower or higher temperatures than that of the room, a liquid bath was maintained in a larger Dewar (D_1) outside the first one.

The larger Dewar was made from a steel tube 9 inches in diameter and 220 cm. long, and an inner tube of sheet Monel Metal 6 inches in diameter. The space between the walls and between the bottoms was filled with silk floss and a vacuum of about 0.003 mm. or better maintained by continuous pumping with a Cummings mercury vapor pump and a liquid air trap. A leak prevented a better vacuum. (This was later remedied by replacing the Monel Metal tube by a brass tube.) The pressure sometimes rose to between 0.01 mm. and 0.02 mm., due to various causes, and this increased the heat leak into the outer bath by a factor of 3 or 4. The 6 inch sheet Monel tube was made by folding and riveting a flat sheet of the metal and soldering. Considerable trouble was found due to vacuum leaks around the soldered rivets. Dr. W. F. Giauque of this Laboratory found that this trouble could be avoided by using Monel Metal rivets in place of rivets of galvanized iron. At the lower temperatures the outer bath warmed about 2° per hour.

The lower end of the outer tube was threaded so that an ordinary 9-inch pipe cap could be screwed on (see "F" in figure). Gas leakage past the threads was prevented by de Khotinsky cement.

The smaller Dewar was made from brass tubing. For about 20 cm. from the top, the inner piece of brass tubing was replaced by a German silver tube (thickness 0.01 inch) for reducing heat leak. The diameters of the walls were 3.5 and 2.75 inches. A vacuum of 10^{-5} mm., or better, was maintained by continuous pumping, using a liquid air trap as well.

At first a 180cm. silvered Pyrex glass Dewar was used in place of the brass one, many of the measurements being made with it. However, two such Dewars were lost by breakage, due in at least one case to the giving way of strains and not to mechanical shock. The metal Dewar gave a somewhat greater heat leak at the top than the glass one but the vacuum in the metal Dewar could always be read.

For all work where water or liquid air or oil (heated electrically) were not used for the baths, petroleum ether was used. This was cooled by immersing in it large test tubes (with a 2-liter baffle at the top), to hold liquid air.

Thermal Expansion of Brass.—In velocity of sound determinations other than at room temperature, it is necessary to know the thermal expansion of the apparatus. Buffington and Latimer[7] measured the coefficients of expansion of copper and aluminum over the required temperature range and, accordingly, the coefficient of expansion of the brass sound tube No. 150A was measured relative to both copper and aluminum. For this purpose, three aluminum rods 0.25 inch in diameter barely projected out of the smaller Dewar, which was nearly filled with an appropriate stirred liquid bath, with a thermocouple for measuring the temperature. A scratch was made on each of the three aluminum rods and the heights of these scratches measured at various temperatures, by means of a cathetometer, after scraping off the atmospheric ice. One of the aluminum rods was short and was soldered to the top of the brass resonance tube. Another much longer aluminum rod was soldered near the bottom of the brass tube. The third aluminum rod was short and was soldered to a long copper rod, the other end of the copper rod being soldered to the bottom of the brass tube. The relative motion of the scratches gave the relative thermal expansions of brass, copper and aluminum, for bending of the rods was prevented. In Table IV are given the results; either series is probably accurate to 0.1 mm. A graph was used for the velocity of sound calculations. The uncertainties which are evident are due to us and not to Buffington and Latimer.

TABLE IV

LENGTH OF A 100CM. BRASS TUBE RELATIVE TO ITS LENGTH AT 273.1°K.

Abs. temp., °K.	From copper data, mm.	From aluminum data, mm.	Average
273.1	0.00	0.00	0.00
254.1	− .32	− .39	− .36
236.3	− .57	− .68	− .63
218.3	− .93	− .95	− .94
196.3	−1.31	−1.35	−1.33
174.4	−1.67	−1.71	−1.69
157.2	−1.93	−1.97	−1.95
151.6	−2.00	−2.06	−2.03
81.7	−3.05	−2.92	−2.98

For work above 0°, the coefficient of expansion of brass was obtained from tables.[18]

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[18] *Scientific Papers*, U. S. Bureau of Standards, **17**, 110 (1922).

Calculation of Specific Heat from Velocity of Sound at a Given Temperature

In this section all quantities except pressure are taken in absolute, C. G. S. units.

R = Gas constant (ergs per degree per mole).
P = Pressure (dynes per sq. cm.).
p = Pressure (atmospheres).
V = Volume of 1 mole of substance (cc.).
M = Molecular weight of substance and number of grams in 1 mole.
T = Absolute temperature.
C_p = Specific heat at constant pressure (ergs per degree per mole).
C_v = Specific heat at constant volume (ergs per degree per mole).
W = Velocity of sound (cm. per sec.).
S = Entropy of substance (ergs per degree per mole).

Other quantities are defined as needed.

Many years ago Sir Isaac Newton showed that

$$W = \sqrt{-\frac{V^2}{M}\cdot\frac{\partial P}{\partial V}} \tag{1}$$

for a gas or liquid or for longitudinal waves in a solid. Assuming the process to be reversible and adiabatic, the entropy of any part of the gas is constant, or

$$W = \sqrt{-\frac{V^2}{M}\left(\frac{\partial P}{\partial V}\right)_S} \tag{2}$$

As[19]

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_P \text{ and } C_v = T\left(\frac{\partial S}{\partial T}\right)_V$$

$$W = \sqrt{-\frac{V^2}{M}\left(\frac{\partial P}{\partial V}\right)_T\frac{C_p}{C_v}} \tag{3}$$

Also[20]

$$C_p - C_v = -T\left(\frac{\partial V}{\partial T}\right)_P^2\left(\frac{\partial P}{\partial V}\right)_T \tag{4}$$

As the equation of state of hydrogen at low pressure, we will take

$$PV = RT + \frac{a}{V} \tag{5}$$

where a is a function of T, but not of P or V. This equation, or one equivalent to it, was used by Kamerlingh Onnes and his staff for calculating the relation between the hydrogen and thermodynamic temperature scales.[21]

Solving (5) for P, and differentiating

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{1}{V^2}\left[RT + \frac{2a}{V}\right] \tag{6}$$

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[19] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, p. 132.

[20] Ref. 19, p. 136.

[21] See, for example, Onnes and Braak, *Comm. Phys. Lab. Univ. Leiden*, No. 97 b, p. 34, where it is shown that the form of this equation of state introduces an error not larger than 0.0003° in the hydrogen scale at as low a temperature as 56°K., although his total correction to change to the thermodynamic scale amounts to 0.076° at this temperature.

Also, dividing (5) by P, and differentiating

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{P}\left[R + \frac{1}{V}\frac{\mathrm{d}a}{\mathrm{d}T} - \frac{a}{V^2}\left(\frac{\partial V}{\partial T}\right)_P\right]$$

Solving this for $\left(\frac{\partial V}{\partial T}\right)_P$, and substituting for P its value from (5)

$$\left(\frac{\partial V}{\partial T}\right)_P = V\frac{R + \frac{1}{V}\frac{\mathrm{d}a}{\mathrm{d}T}}{RT + \frac{2a}{V}} \qquad (7)$$

If, now, we eliminate C_p between (3) and (4), solving for C_v, and substitute for the partial derivatives their values given by (6) and (7)

$$C_v = T\frac{\left[R + \frac{1}{V}\frac{\mathrm{d}a}{\mathrm{d}T}\right]^2}{MW^2 - \left[RT + \frac{2a}{V}\right]} \qquad (8)$$

This equation gives C_v at p atmospheres if the velocity of sound is measured at that pressure. Supposing the experiment to be carried out at a pressure of p atmospheres and writing C_{v_0} for the specific heat of the substance at zero pressure, we have first[22]

$$\left(\frac{\partial C_v}{\partial V}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V \qquad (9)$$

Now by dividing (5) by V and then differentiating twice, we have

$$\left(\frac{\partial^2 P}{\partial T^2}\right)_V = \frac{1}{V^2}\frac{\mathrm{d}^2 a}{\mathrm{d}T^2}$$

Substituting this value for the second derivative in (9), we may integrate

$$C_v - C_{v_0} = \int_{P=0}^{P=p\text{ atm.}} \frac{T}{V^2}\frac{\mathrm{d}^2 a}{\mathrm{d}T^2}(\partial V)_T = T\frac{\mathrm{d}^2 a}{\mathrm{d}T^2}\int_{P=0}^{P=p\text{ atm.}}\frac{(\partial V)_T}{V^2} = \frac{-T\,\mathrm{d}^2 a}{V\,\mathrm{d}T^2} \qquad (10)$$

Now the terms involving a in (8) and (10) are so small that we may write $1/V = P/RT$ in them without appreciable error for pressures of 1 atmosphere or less. We also expand the square in the numerator of (8) and neglect the second order term involving $(1/V)^2$. Then, if (8) and (10) are combined, eliminating C_v, and solving for C_{v_0}, we obtain finally

$$\frac{C_{v_0}}{R} = \frac{R\left[T + \frac{2P}{R^2}\frac{\mathrm{d}a}{\mathrm{d}T}\right]}{MW^2 - R\left[T + \frac{2aP}{R^2T}\right]} + \frac{P}{R^2}\frac{\mathrm{d}^2 a}{\mathrm{d}T^2} \qquad (11)$$

We may remark that the R on the left-hand side of equation (11) may be taken in any units in which we wish to have C_{v_0} expressed; the R's on the right side of the equation must be in absolute c.g.s. units.

The data of state for hydrogen gas at pressures of 1 atmosphere or less are expressed by Onnes and Braak as values of B'_T at various temperatures.[23]

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[22] Ref. 19, p. 141.

[23] Onnes and Braak, *Comm. Phys. Lab. Univ. Leiden*, No. **101b**, p. **16**; *Verslag. Akad. Wetenschappen Amsterdam*, **1907**, p. 427.

B'_T is defined by the equation[24]

$$pv = A_T\left[1 + \frac{B'_T}{v}\right]$$

Here p is the pressure in atmospheres and we will write $P = bp$, b being the number of dynes per sq. cm. in 1 atmosphere. A_T is defined as $T/273.10$ and v is the volume divided by the "theoretical normal volume." As the latter volume is, for 1 mole, $273.1\ R/b$ cc., we have $v = bV/273.1\ R$. The Leiden equation of state may then be written in c.g.s. units as

$$PV = RT + \frac{273.1\ B'_T\ R^2T}{bV} \tag{12}$$

Comparing this with equation (5), we see that

$$a = \frac{273.1\ R^2T\ B'_T}{b} \tag{13}$$

Considering again equation (11), we see that it involves three correction terms, each involving P to the first power. Expressing now the pressure in atmospheres, (11) may be written

$$\frac{C_{v0}}{R} = \frac{R(T + Yp)}{MW^2 - R(T + Xp)} + Zp \tag{14}$$

and it follows that

$$\begin{aligned} X &= \frac{2ab}{R^2T} = 546.2\ B'_T \\ Y &= \frac{2b}{R^2}\frac{\mathrm{d}a}{\mathrm{d}T} = 546.2\ \frac{\mathrm{d}(T\ B'_T)}{\mathrm{d}T} \\ Z &= \frac{b}{R^2}\frac{\mathrm{d}^2a}{\mathrm{d}T^2} = 273.1\ \frac{\mathrm{d}^2(T\ B'_T)}{\mathrm{d}T^2} \end{aligned} \tag{15}$$

Merely for convenience, we define a new quantity Δ such that

$$B'_T\ 10^3 = 1 - \frac{110}{T} + \Delta \tag{16}$$

In Table V are given values of Δ at the temperatures of the measurements of Onnes and Braak,[23,24] as well as their values of B'_T.

TABLE V

HYDROGEN DATA OF STATE

Abs. temp., °K.	$1 - \frac{110}{T}$	$B'_T\ 10^3$	$\Delta \cdot 10^3$
373.10	+0.705	+0.6321	−0.073
293.10	+ .625	+ .622	− .003
273.10	+ .597	+ .5807	− .016
169.55	+ .351	+ .394	+ .043
133.25	+ .174	+ .229	+ .055
109.00	− .009	+ .018	+ .027
90.34	− .218	− .241	− .023
77.89	− .412	− .432	− .020
68.47	− .606	− .692	− .086
60.36	− .822	−1.009	− .187
55.77	− .972	−1.203	− .231

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[24] Onnes and Braak, *Comm. Phys. Lab. Univ. Leiden*, No. 97b, p. 33; *Verslag. Akad. Wetenschappen Amsterdam*, **1907**, p. 668.

Equations (15) may now be written in the form

$$\begin{aligned} X &= 0.5462\left(1 - \frac{110}{T} + \Delta\right) \\ Y &= 0.5462\left(1 + \frac{\mathrm{d}(T\Delta)}{\mathrm{d}T}\right) \\ Z &= 0.2731\left(\frac{\mathrm{d}^2(T\Delta)}{\mathrm{d}T^2}\right) \end{aligned} \tag{17}$$

We have plotted Δ from Table V, drawing the best curve. From this curve values of Δ and hence of X may be obtained at 10° intervals, from which Y could be obtained. Similarly, by again differentiating these slopes, we may obtain Z. The slopes found were smoothed out by plotting them directly against T (see Table VI).

For comparison we give Table VII, calculated from Berthelot's equation of state, using a critical pressure of 12.8 atmospheres and a critical temperature of 33.1°K. Use of the actual critical volume in this equation gives poorer agreement with Table VI.

TABLE VI

VALUES OF CORRECTION TERMS IN EQUATIONS (14), (18) AND (21), FOR HYDROGEN, FROM DATA OF ONNES AND BRAAK

Abs. temp., °K.	X, °/atm.	Y, °/atm.	Z, per atm.	$t°$, °/atm.
373	+0.345	+0.41	?	−0.019
300	+ .332	+ .427	−0.00022	− .008
270	+ .318	+ .440	30	+ .000
250	+ .307	+ .455	36	+ .006
200	+ .262	+ .496	53	+ .021
150	+ .175	+ .561	77	+ .039
100	− .049	+ .659	107	+ .067
90	− .121	+ .683	112	+ .073
80	− .227	+ .710	118	+ .080
70	− .356	+ .741	...	+ .087
60	− .497	...	...	+ .096

TABLE VII

SAME AS TABLE VI, CALCULATED FROM BERTHELOT'S EQUATION

Abs. temp., °K.	X, °/atm.	Y, °/atm.
Infinite	0.364	0.364
300	.327	.391
200	.304	.424
100	.125	.603
70	− .123	.851
60	− .289	1.017

An equation of state of Keyes[25] requires that $Z = 0$, and hence that C_v is independent of pressure. But Table V shows that Δ has a second derivative different from zero; in any case, the Z term is less than the experimental errors of this research.

In Table VI we give $t°$, the correction for giving the temperature scale

[25] Keyes, Townshend and Young, *J. Math. Phys., Mass. Inst. Tech.*, **1**, 251 (1922).

in terms of the absolute scale. In the constant volume hydrogen thermometer, if T be any temperature, J the corresponding pressure of the hydrogen in atmospheres and J_0 the pressure when $T = 273.1$°K., we define t° as follows

$$T = 273.10 \frac{J}{J_0} + t^\circ J_0 \tag{18}$$

We may calculate t° from equation (12). In the correction term of that equation we may write

$$V = \frac{P_0}{273.1\ R} = \frac{b\ J_0}{273.1\ R}$$

which gives for the equation of state of the thermometer gas

$$PV = RT\,(1 - B'_T\,J_0)$$

Equating the hydrogen volume at T with that at 273.1°, we obtain, neglecting second order corrections

$$T = 273.1 \frac{J_0}{J} + T(B'_{273.1} - B'_T)\ J_0$$

that is

$$t^\circ = T\,(0.5807 \cdot 10^{-3} - B'_T) \tag{19}$$

We may put Keyes' hydrogen scale correction in the form[26]

$$t^\circ = 0.055^\circ \left(1 - \frac{T}{273.1}\right) . \tag{20}$$

This agrees with Table VI at 273.1°K. Also, at 373.1°K., Equations (20) and (19) differ by only 0.001°, for Keyes, Townshend and Young picked the 0.055° with that very purpose in mind. However, (20) requires that t° should not become greater than 0.055° at low temperatures, but the values of t° in Table VI become considerably greater.

Referring to Equation (14) for our measurements we take $p = 1$ atmosphere, not bothering to read the barometer at any time. We have also $R = 8.316 \times 10^7$ ergs per degree,[27] and for the molecular weight of hydrogen $M = 2.01554$ g. per mole.[28] Our final equation for the calculation of the specific heats of hydrogen is, then, from (14)

$$\frac{C_{v_0}}{R} = \frac{T + Y}{2.42369 \times 10^{-8} W^2 - T - X} + Z \tag{21}$$

T being the absolute temperature of the measurement and W being in cm. per mean solar second.

Effect of the Tube on the Velocity of Sound

When hydrogen is confined in a tube, the velocity of sound is less than in the free gas. This decrease in velocity is almost entirely due to the walls of the tube, rather than the ends, if the tube is very long. The effect of the walls is given by the formula of Kirchhoff and Helmholtz[29]

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[26] Keyes, Townshend and Young, ref. 25, p. 295, and equation 11, p. 251.

[27] Ref. 19, p. 60.

[28] Moles, *Z. physik. Chem.*, **115**, 61 (1925); **117**, 157 (1925); *Anales españ. fís. quím.*, **23**, 39 (1925); THIS JOURNAL, **48**, 552 (1926).

[29] Kirchhoff, *Pogg. Ann.*, **134**, 177 (1868).

(Equation 22). Many observers have said that this formula gives too small a correction,[30] but their work involves tubes containing a large amount of dust. The correction affects our specific heats by about 2%, but in some work of Partington and Shilling[31] an incorrect application of this correction makes their gas specific heats at high temperatures too low by about 13%. This is because they use a tube correction 9 times too great. These observers claim an accuracy of 1%. The only plausible explanation of their high results seems to be that they did not carefully measure their frequency, for they used a "standard wave meter." Making that explanation, a recalculation of Partington and Shilling's data for air at 1073°K. gives C_p as 7.87 cal. per mole per degree, while Lewis and Randall[32] estimate 7.57, and Partington and Shilling give 7.222. Assuming Partington and Shilling to have the correct frequency, we obtain 8.17. These calculations were only made roughly.

The holes in the ends of our resonators were 1 mm. in diameter as with Grüneisen and Merkel; however, ours were 1 mm. long as well. The careful work of Grüneisen and Merkel[4b] indicated that with air at 0°, the end openings have very little effect. With hydrogen, the end openings might be much greater, because of the ability of hydrogen to be easily blown through small openings. In the case of regular, viscous flow, we find that since the viscosity of hydrogen is about half that of air,[33] only twice as much energy will be lost through the end openings with hydrogen as with air. If then the flow is not at all turbulent, the end correction amounts to about twice the percentage of the velocity of sound with hydrogen as with air (for the same frequency); accordingly we ignore any end correction. The purpose of using tubes of different lengths was to measure the end correction, but it was found, as also noted by Grüneisen and Merkel, that with hydrogen the end correction is less than the error of experiment.

Because of the importance of the wall correction, a large number of measurements (Table VIII) were made at 0° (although with "impure" hydrogen), so that a more or less reliable estimate of that correction could be made. Each value of Table VIII represents the mean of six determinations. The Kirchhoff-Helmholtz relation requires that the tube correction be inversely proportional to the square root of the frequency, but the range of frequency over which the velocity of sound can be measured accurately in hydrogen is not sufficient to test that (see Equation 22). Moreover, our source of sound was probably not a pure sine vibration.

[30] (a) Stürm, *Ann. Physik.*, **14**, 822 (1904); (b) Seebek, *ibid.*, **139**, 104 (1870); (c) Kayser, *ibid.*, **2**, 218 (1877); (d) Muller, *ibid.*, **11**, 331 (1903).

[31] Partington and Shilling, *Trans. Faraday Soc.*, **18**, 386 (1923).

[32] Ref. 19, p. 80.

[33] Landolt-Börnstein, "Physikalisch-Chemische Tabellen," Julius Springer, Berlin, **1923**, Vol. I, p. 171; **1923**, Vol. II, p. 1274, 1277, 1304.

TABLE VIII

VELOCITY OF SOUND IN HYDROGEN IN VARIOUS RESONATORS AT 0° (273.1°K.)

In meters per second (equations in this paper refer to cm. per sec.). Fundamental counted as first overtone. "Impure" hydrogen. Not corrected for effect of tube.

Tone no.	Tube 150A	Tube 150B	Tube 100A
8	....	....	1256.6
9	....	....	1257.6
			1256.9
10	1256.2	....	1256.9
11	1256.8	....	....
12	1256.4	1254.0	1258.1
13	1256.7	1257.4	1257.9
	1257.5		
14	1257.1	1254.9	1257.8
15	1256.8	1255.3	1257.4
16	1256.6	....	1258.0
	1256.9		
17	1257.4	1254.2	1257.5
18	1257.3	1255.7	1258.4
19	1257.6	1253.8	1257.8
			1258.2
20	....	1255.1	1258.3
21	1256.7	1253.2	1258.3
		1254.7	
22	1256.7	1253.2	....
23	1257.0	....	....
24	1258.4	1256.2	....
25	....	1255.3	....
26	1256.1	1256.1	....
	1256.1		
27	1256.6	....	....
28	1257.0	1252.0	....
Mean	1256.95	1255.0	1257.8 (Certain values not considered)

Grüneisen and Merkel found, by taking average results of the 8th to the 16th or 17th overtones, a velocity of sound of 1258.9 m. per sec. for a 5cm. diameter tube, and 1256.5 m. per sec. for one of 2.6 cm. diameter. Assuming an inverse diameter law, this gives a correction of about 2.6 m. per second for the 5cm. tube, and a corrected velocity of 1261.5 m. per sec. Their wider tube was about 95 cm. long and the narrower one about 79 cm. The range of frequency is from about 5000 cycles per sec. to 12,000. For our own data, this same method of calculation was tried; from our 150cm. tubes (Table VIII) we obtain 1258.9 meters per sec. (Later results with "pure" hydrogen give 1260.75 m. per sec.) Grüneisen and Merkel believe their best value to be 1260.2, but their method of calculation consists in making a rather doubtful comparison with the tube correction for air.

In Table VIII it was not considered necessary to give the frequencies, these being converted into velocity by dividing by the number of the overtone and multiplying by twice the inside length of the tube in question. The three highest frequencies used for tube 100A were amplified with the resistance repeater and not considered in the average. The overtones below No. 11 in the longer tubes, or below No. 8 in the shorter tube, were not sharp or well defined. The dashes in the table are overtones which could not be measured accurately because some other maximum, due to the brass apparatus or perhaps to hydrogen in the telephone chamber, was close to the overtone wanted. In some cases disturbing maxima could be eliminated by using a lower intensity of sound in the telephone. If an unnecessarily large current was fed into the telephone, disturbing maxima appeared, or the true maximum became less well defined.

We need the tube correction for a 4.8cm. diameter tube at all temperatures used. From Table VIII we obtain 1256.95–1255.0, or 1.95 meters per second for 0°. Combining with the 2.5 m. per sec. of Grüneisen and Merkel for 0°, an average of 2.2 meters per second is to be used for 0°. If we write W for the velocity of sound, S for the density of the gas, n for the coefficient of viscosity, j for the heat conductivity, v for the frequency and D for the diameter of the tube, then the Kirchhoff-Helmholtz value for the tube correction ΔW is, using absolute c.g.s. units (except that any consistent energy unit may be used for C_p, C_v and j),[29]

$$\frac{\Delta W}{W} = \frac{1}{D\sqrt{\pi v S}}\left\{\sqrt{n} + \left[\sqrt{\frac{C_p}{C_v}} - \sqrt{\frac{C_v}{C_p}}\right]\frac{j}{C_v}\right\} \qquad (22)$$

For 0°, we take $D = 4.8$ cm., v as 7000 cycles per second as a rough mean value of the frequencies used, and obtain from equation (22) $\Delta W/W = 0.00185$. About three-fourths of the correction is due to viscosity and the other one-fourth to heat interchange between the walls and the gas. The experimental value of the correction, quoted above, gives $\Delta W/W = 2.2/1259.3 = 0.00175$. The agreement is close, and it was decided to use theoretical values for the Kirchhoff-Helmholtz correction.

TABLE IX

KIRCHHOFF-HELMHOLTZ CORRECTION FOR HYDROGEN IN A TUBE OF 4.8 CM. DIAMETER

Observed velocity of sound is too low by percentage in table, at frequency of 10,000 cycles per second.

Abs. temp., °K.	Correction, %	Abs. temp., °K.	Correction, %
373.1	0.191	100	0.075
273.1	.155	50	.063
250	.144	SAME FOR AIR	
200	.122	298	0.0476
150	.0995		

In Table IX are given the values of $\Delta W/W$ for various temperatures. The values of heat conductivity, viscosity and C_v were taken from Landolt-Börnstein.[33] A curve was plotted to make interpolation easy.

The values are for 10,000 cycles per second but the correction varies inversely as the square root of the frequency.

To settle finally the correctness of the Kirchhoff-Helmholtz correction, a wide tube 9.87 cm. in diameter was made (No. 168, Table III). Measurements at room temperature (Table XI, at 294.27°K.) were made with "pure" hydrogen and the specific heat was calculated. As seen in Fig. 3, this point falls nearly on the curve. The effect of the correction is to lower the specific heat by about $0.017R$ while results in Tube 150A at about the same temperature are lowered by about $0.035R$, a difference of $0.018R$; but Fig. 3 shows a deviation of much less than $0.018R$. This is more obvious if the specific heats of Table XI near room temperature are plotted on a larger scale. The total evidence for the correctness of Kirchhoff and Helmholtz is overwhelming.

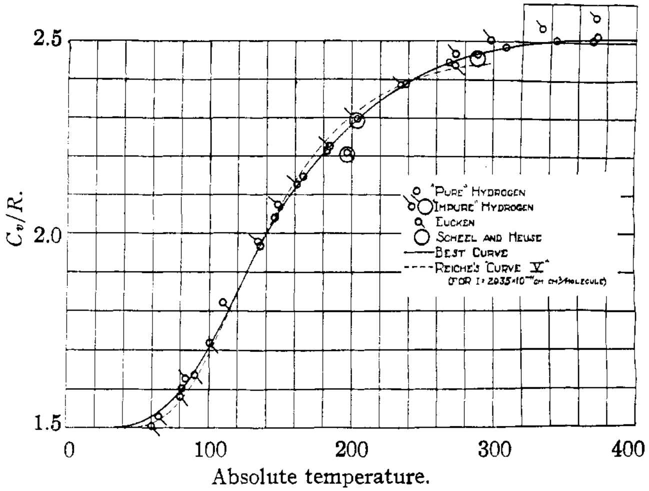

Fig. 3.—Specific heat of hydrogen.

Grüneisen and Merkel concluded from their own data that the Kirchhoff-Helmholtz formula holds for air, but we also made runs with air at room temperature (purified as already stated). The difference between the tube corrections is not much more than the experimental error, and the results of Table XII check the Kirchhoff-Helmholtz formula to a fortuitous degree, although the three runs of the table each represent the mean of about 50 determinations. For reducing the air results to the same temperature, it was assumed that the velocity of sound is proportional to $\sqrt{T}$ over the small temperature range in question. For 24°, we obtain 34,566 cm. per sec. as the velocity of sound in free air.

Determination of Velocity of Sound and Specific Heat

For the Grüneisen and Merkel data at 0°, it is best to ignore their narrow tubes. Applying the theoretical tube correction to the data from their largest tube, we obtain 126,115 cm. per sec. while our best curve (Fig. 3) gives 126,075. Either of these values is preferable to the value 126,020 cm. per sec. which Grüneisen and Merkel estimate from their own data. A mean of 126,090 cm. per sec. is probably the best value.

The measurements of velocity of sound at each temperature other than 0° consisted, both with "impure" and with "pure" hydrogen, of five or more different overtones, each overtone being measured at a slightly different temperature due to temperature drift of the thermostat. For each overtone the variable condenser of the main oscillating circuit was set at the maximum of sound about 6 times successively. The frequency was noted each time by beat comparison (for 25 seconds) with the very constant auxiliary oscillating circuit. Accordingly, for every temperature in the tables, from 30 to 60 independent measurements are averaged together.

The data are fairly consistent. For each of the temperatures used the values of the fundamental resonant frequency are usually the same, as given by the various overtones, within 0.1% or less. Moreover, the various measurements of a given overtone usually agreed among themselves to 0.1% or less. With air the agreement was to about 0.03% or less. For brevity the actual data are omitted. To take account of temperature drift during the various series, a single plot of e.m.f. of thermocouple against frequency was made and the slopes were read off the curve for each temperature in question. We thus may obtain the several values for the fundamental, reduced to the same mean temperature. While this method of calculation obviously gives the same result as a simple average (even if the wrong slope is read from the curve), yet it makes possible the elimination of a few slightly displaced maxima. These displacements and their cause are discussed above.

TABLE X

SPECIFIC HEAT OF HYDROGEN AT CONSTANT VOLUME IN TERMS OF THE GAS CONSTANT. VELOCITY OF SOUND IN UNCONFINED HYDROGEN

("Impure" hydrogen, Tube 150A)

Abs. temp., °K.	Velocity of sound, cm./sec.	C_v/R	From tones	Fundamental, per sec.
371.55	146,040	2.564	No. 13 to 17	484.96
333.51	138,590	2.536	14 to 18	460.62
297.79	131,200	2.505	16 to 19	436.41
273.10	125,920	2.467	10 to 28	419.07
234.77	117,210	2.387	19 to 23	390.50
203.63	109,830	2.294	19 to 24	366.10
184.57	105,040	2.228	16 to 21	350.23
161.58	99,030	2.128	22 to 27	330.39
148.00	95,210	2.076	18 to 23	317.70
133.89	91,280	1.979	21 to 25	304.70
83.52	74,640	1.628	18 to 22	249.36

TABLE XI

SPECIFIC HEAT OF HYDROGEN AT CONSTANT VOLUME IN TERMS OF THE GAS CONSTANT. VELOCITY OF SOUND IN UNCONFINED HYDROGEN

(Pure hydrogen, Tube 150A)

Abs. temp., °K.	Velocity of sound, cm./sec.	C_v/R	From tones	Fundamental, per sec.
372.52	146,630	2.516	No. 10 to 20	486.84
369.40	146,110	2.504	10 to 19	485.12
333.31	138,930	2.505	13 to 17	461.36
308.96	133,770	2.486	13 to 18	444.80
294.27	130,710	2.466	10 to 25	388.23[a]
269.02	125,150	2.444	10 to 20	486.84
238.23	118,170	2.390	16 to 26	393.61
203.63	109,900	2.298	14 to 24	366.30
182.41	104,630	2.213	14 to 23	348.87
165.58	100,160	2.147	18 to 27	334.12
145.64	94,715	2.041	15 to 20	316.03
135.71	92,000	1.967	15 to 23	307.05
81.12	73,800	1.6015	17 to 23	246.55

[a] Tube 168 used.

In Tables X and XI are given the velocity of sound and the specific heat. The velocity was found by multiplying the fundamental frequency by twice the length of the tube, applying the corrections for thermal expansion (Table IV) and the Kirchhoff-Helmholtz correction (Table IX). The specific heat was then calculated from Equation (21), using Table VI.

The results of Table XI for the velocity of sound and for the specific heat are believed to be correct to about 0.1 and 0.5%, respectively, but an extra decimal place is added. The result of Table XII for the velocity of sound in air at room temperature is believed to be good to 0.01%. All values are for 1 atmosphere pressure, but the specific heats at zero pressure may be found by merely adding algebraically the Z of Table VI; this effect is never more than 0.001.

TABLE XII

VELOCITY OF SOUND IN DRY CARBON DIOXIDE-FREE AIR AT ROOM TEMPERATURE

Series	Tube	Overtones	Abs. temp., °K.	Velocity (in tube), m./sec.	Velocity at 296.324 °K., m./sec.
1	150A	No. 37 to 44	298.60	346.276	344.959
2	150A	45 to 56	296.324	345.009	345.009
3	168	30 to 40	296.237	345.019	345.070

Series	Mean Kirch.-Helm. corr., m./sec.	Velocity of sound in free air, m./sec.
1	0.242	345.201
2	.216	345.225
3	.137	345.207
		Av., 345.21

Velocity at 24° in dry, carbon dioxide-free air = 345.66 meters per sec.

For the purpose of comparison, the results of some other observers are plotted in Fig. 3, as well as our own results. Also, Reiche's[2b] "curve V" is given, assuming a moment of inertia 2.035×10^{-41} gm. cm.^{2} per molecule.

Relation of Results to Quantum Theory

All quantum theories of rotational specific heat assume various states in which the number of molecules is proportional to $Pe^{-E/RT}$, where P is the "probability" of the state, e the base of the natural system of logarithms, E the energy of the state and RT the gas constant times the absolute temperature.

G. N. Lewis suggests the following graphical method of attacking the data. At low temperatures only the first two states have appreciable weight. Hence, writing now E for the energy *difference* between these two states, we have for the rotational heat content, H_r

$$H_r = PEe^{-E/RT}$$

as the limiting law for low temperatures. Differentiating, and writing $\mathrm{d}H_r/\mathrm{d}T = C_r$, we may easily show (using common logarithms)

$$\log (T^2C_r/R) = \log (PE^2/R^2) - E/2.303\, RT \tag{23}$$

Accordingly, by plotting $\log (T^2C_r/R)$ against $1/T$, the equation of the limiting straight line for low temperatures gives us both E and P. This was done, and from the "impure" hydrogen we obtain $E = 1003$ cal./mole and $P = 1.48$. The "pure" hydrogen gives $E = 1035$ cal./mole and $P = 1.51$ (see below, however).

These values for P are less than 2. Most theoretical equations proposed previously make P 2 or more. One of the best of such equations is curve V of Reiche, which gives $E = 1160$ cal./mole and $P = 2$, and which is shown for comparison in Fig. 3 (assuming moment of inertia 2.035×10^{-41} gm.cm.^{2}/molecule). E independently of P determines the moment of inertia; we obtain for the moment of inertia 0.742×10^{-41} $(n_2^2 - n_1^2)$ gm.cm.^{2}/molecule, assuming quantum numbers n_1 and n_2 for the first two states, and E as 1060. cal./mole. We may remark that all theoretical equations *must* lead to about the same value for the first energy jump; differing moments of inertia are due to use of different quantum numbers.

A recent specific heat equation due to Dennison[34] fits our data extremely closely below 250°K. It gives lower values than ours above 250°K., as might be expected if stretching of the molecule at high rotational speeds is ignored. He assumes a moment of inertia, 4.64×10^{-41}, but the fit is better with 4.75×10^{-41}. At this moment of inertia we find $n_2^2 - n_1^2 = 4.75/0.742 = 6.4$. To get such a large value theoretically Dennison could assume a large quantum number for the zero state, but he rather assumes two independent series of quantum numbers $^1/_2$, $^5/_2$, $^9/_2$, $^{13}/_2$, ... and $^3/_2$, $^7/_2$, $^{11}/_2$, $^{15}/_2$, etc., three-fourths of the molecules

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[34] Dennison, *Proc. Roy. Soc.* (*London*), **115A**, 483 (1927).

being in the latter series. For the first series (the only one effective at the lowest temperatures) $n_2^2 - n_1^2 = {}^{25}/_4 - {}^1/_4 = 6$. The second series gives ${}^{49}/_4 - {}^9/_4$ or 10. It would seem that under certain conditions Dennison's mixture would evolve up to 100 cal. per mole when passed over a palladium catalyst. Although the first energy jump is a part of the specific heat curve that must be fitted, we do not imply that it is the only requirement; any theory whatever can be made to give this energy jump by adjusting the moment of inertia.

At 145°K. the rotational heat content is estimated from Fig. 3 to be around 35 cal./mole (by graphical integration), and this is small compared to 1035 cal. Accordingly, since also the amount of gas in the 2nd resonated state is here around 0.01%, Lewis' assumptions are nearly justified at temperatures as high as 150°K. Making allowance for about $3^1/_2$% of the gas not in the lowest state at 145°K. we find an increase in the value of E of 25 cal., so that finally $E = 1060$ cal. and $P = 1.69$. It is possible that these values for E and P may be found a little high (that is, they should be closer to the values 1035 and 1.51, respectively) when allowance is made for the molecules in the second activated state. This will be considered in a subsequent paper.

As this work was made possible by the loan of valuable clocks and condensers by the Departments of Physics and Astronomy, we take this opportunity of expressing hearty appreciation, especially to Professors L. B. Loeb and R. T. Crawford of those Departments. We must acknowledge our indebtedness to Dr. R. M. Buffington for suggestions in connection with calibrating the thermocouples, and to Dr. W. F. Giauque for many of the points in our quantum theory discussion.

Summary

A rapid precision method, capable of an accuracy of $^1/_{1,000,000}$, is described for measuring the frequency of any regularly oscillating circuit, and the properties of certain "audio-frequency" oscillators are discussed. Details are given of rigorous calculation of the specific heats of hydrogen from the velocity of sound. The thermal expansion of a sample of brass at low temperatures is measured and the hydrogen thermometer is briefly discussed. Details are given of the construction and operation of a thermostat 180 cm. long for low or moderately high temperatures. The claim by Stock and Ritter of large variations in the composition of atmospheric air is shown to be baseless. Measurements of the velocity of sound in hydrogen gas, and the corresponding calculated specific heats, are given for the range 80 to 373°K. The energy difference between the first two rotational states of the hydrogen molecule is shown, by a method of calculation due to G. N. Lewis, to be 1060 cal. per mole, and the relative "probabilities" of the first two states are found to be 1:1.69 (Reiche's best

equation giving 1160 and 1:2, respectively). The effect of a confining tube on the velocity of sound in a gas is found to be accurately given by the formula of Kirchhoff and Helmholtz. Neglect of that fact caused errors of over 10% in the sound velocity specific heat measurements of Partington and Shilling, making their work worthless unless recalculated. The velocity of sound in unconfined, dry, carbon dioxide-free air at 24° is found to be 345.66 meters per second and the velocity of sound in free hydrogen at 0° is found to be 1260.9 meters per second.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF STANFORD UNIVERSITY]

DISPLACEMENT OF METALS FROM SOLUTIONS OF THEIR SALTS BY LESS ELECTROPOSITIVE ELEMENTS

IV. POTASSIUM AMMONO BERYLLATE AND SODIUM AMMONO BERYLLATE

BY F. W. BERGSTROM

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In attempting to prepare aluminum amide by the action of ammonium bromide—an acid in liquid ammonia—upon a solution of sodium ammono aluminate in accordance with the equation, $Al(NH_2)_2NHNa + NH_4Br = NaBr + NH_3 + Al(NH_2)_3$,[1] the author obtained precipitates which varied in composition approximately between the limits of $Al(NH)NH_2$ and $Al_2(NH)_3$. In explanation of this behavior it is suggested that these precipitates be regarded as indefinite compounds resembling the hydrous oxides in constitution, and therefore appropriately called ammonous aluminum nitrides, $AlN + xNH_3$. In view of the chemical similarity between aluminum and beryllium one might expect that beryllium amide would likewise prove to be an ammonous beryllium nitride. The present investigation was then undertaken primarily for the purpose of preparing beryllium amide or an ammonous beryllium nitride. As the potassium ammono beryllate required in the expected reaction, $Be(NHK)_2 + 2NH_4Br = Be(NH_2)_2 + 2NH_3 + 2KBr$, is unknown, the first experiments were directed toward the preparation of this compound.

Potassium Ammono Beryllate.—Since potassium hydroxide dissolves metallic beryllium to form potassium aquo beryllate, we should expect the analogous base of the ammonia system, potassium amide, to dissolve beryllium to form a potassium ammono beryllate. N. C. Jones and P. F. Frohring, at Western Reserve University in the summer of 1926, found that beryllium dissolves in solutions of sodium and potassium amides in liquid ammonia to form extremely soluble ammono beryllates

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[1] Bergstrom, *J. Phys. Chem.*, March, 1928. This reaction resembles the precipitation of aluminum hydroxide by the addition of an acid to a solution of an aquo aluminate in water.