

Sound Speed in Liquid-Gas Mixtures: Water-Air and Water-Steam

SUSAN WERNER KIEFFER

Department of Geology, University of California, Los Angeles, California 90024

The sound speed of a two-phase fluid, such as a magma-gas, water-air, or water-steam mixture, is dramatically different from the sound speed of either pure component. In numerous geologic situations the sound speed of such two-phase systems may be of interest: in the search for magma reservoirs, in seismic exploration of geothermal areas, in prediction of *P* wave velocity decreases prior to earthquakes, and in inversion of crustal and upper mantle seismic records. Probably most dramatically, fluid flow characteristics during eruptions of volcanoes and geysers are strongly dependent on the sound speed of erupting two-phase (or multiphase) fluids. In this paper the sound speeds of water, air, steam, water-air mixtures, and water-steam mixtures are calculated. It is demonstrated that sound speeds calculated from classical acoustic and fluid dynamics analyses agree with results obtained from finite amplitude 'vaporization wave' theory. To the extent that air and steam are represented as perfect gases with an adiabatic exponent γ , independent of temperature, their sound speeds vary in a simple manner directly with the square root of the absolute temperature. The sound speed of pure liquid water is a complex function of pressure and temperature and is given here to 8 kbar, 900°C. In pure water at all pressures the sound speed attains a maximum value near 100°C and decreases at higher temperatures; at high pressures the decrease is continuous, but at pressures below 1 kbar the sound speed reaches a minimum value in the vicinity of 500°–600°C, above which it again increases. The sound speed of a water-air mixture depends on the pressure, the void or mass fraction of air, the frequency of the sound wave, and, if surface tension effects are included, on bubble radius. The admixture of small volume fractions of air causes a dramatic lowering of the sound speed by nearly 3 orders of magnitude. The sound speeds of the pure liquid and gas end-members are nearly independent of pressure, but the sound speed of a mixture is highly dependent on pressure. Calculated values for water-air mixtures are in good agreement with measured values. The sound speed in a single-component two-phase system, such as a water-steam mixture, depends on whether or not equilibrium between the phases on the saturation curve is maintained. Heat and mass transfer which occur when equilibrium is maintained cause the sound speed to be much lower than under non-equilibrium conditions in which heat and mass transfer are absent. The sound speed in a water-steam mixture may be as low as 1 m s^{-1} .

INTRODUCTION

The presence of gas or vapor bubbles in a liquid dramatically reduces the sound speed in the liquid [Mallock, 1910; Karplus, 1958, 1961; Barclay *et al.*, 1969; McWilliam and Duggins, 1969]. In particular, the sound speed is much lower in a liquid-gas mixture than in either the gas or the liquid components. For example, it is about $1440\text{--}1480 \text{ m s}^{-1}$ in water and about 340 m s^{-1} in air, but in an air-water mixture falls to about 20 m s^{-1} [McWilliam and Duggins, 1969]. Even very small concentrations of gas dramatically reduce the sound speed: 1% by volume of air in water lowers the velocity by 95% to 100 m s^{-1} [McWilliam and Duggins, 1969]. This dramatic phenomenon occurs because the two-phase system has the density of a liquid but the compressibility of a gas. The sound speed is even less in a water-steam mixture than in a water-air mixture, as low as a few meters per second [Barclay *et al.*, 1969]. The liquid-gas and liquid-vapor cases differ because of mass transfer and latent heat exchanges which may accompany passage of a sound wave in a liquid-vapor system but which are absent in a liquid-gas system.

There are numerous geologic situations in which the sound speed properties of two-phase liquid-gas systems may be important. On the surface of the earth at ambient pressure and temperature the propagation of acoustic signals through bodies of water depends on air content [Carstensen and Foldy, 1947; Hsieh and Plesset, 1961; Grouse and Brown, 1964; Laird and Kendig, 1952; MacPherson, 1957]. White [1976] has suggested that gas bubbles which come out of solution in connate water during dilatation may cause *P* wave decreases prior to earthquakes. In geothermal areas, hot water and admixed gases may be present to fairly great depths in the crust. Re-

cently, 'hot spot' seismic techniques have been developed to locate geothermal energy sources. A detailed model for the sound speed of water and magma, both of which may contain vapor phases, is required for proper inversion of seismic data for use of these techniques. Volatile elements and compounds (CO_2 , H_2O , and S) are thought to be present in the lower crust and mantle in numerous possible forms [Irving and Wyllie, 1973]: as free vapors [Wyllie and Huang, 1975; Eggler, 1976], as vapor dissolved in silicate magma [Green, 1972; Eggler, 1976], in crystalline compounds [Newton and Sharp, 1975; Eggler, 1976], as interstitial immiscible liquids [McGetchin *et al.*, 1973], and as proxying complexes or structurally bound complexes. Knowledge of the sound speed of these possible forms is required to test for their presence by seismic methods. However, perhaps the most dramatic manifestation of the effect of sound speed in liquid-gas systems is the control which the sound speed exerts on fluid flow during volcanic and geyser eruptions. The role of two-phase flow in volcanic eruptions has been developed qualitatively by Bennett [1971, 1974]. His considerations of flow processes in two-phase systems lead to different conclusions about mechanisms of vesiculation and volcanic ash formation than are arrived at from petrographic considerations [Verhoogen, 1951; McBirney, 1963; McBirney and Murase, 1970]. Models of eruption mechanics of volcanoes [McGetchin, 1974; Sanford *et al.*, 1975] and geysers [Kieffer, 1975] show a strong dependence of the eruption manifestations on the sound speed of the fluid in the column. For example, the height to which a geyser rises during an eruption depends strongly on the sound speed of the fluid in the geyser conduit. Since the sound speed depends on the temperature and condition of the water in the conduit, it is possible to infer the conditions of the geyser fluid from observations of its surface behavior [Kieffer, 1975, also manuscript in prepara-

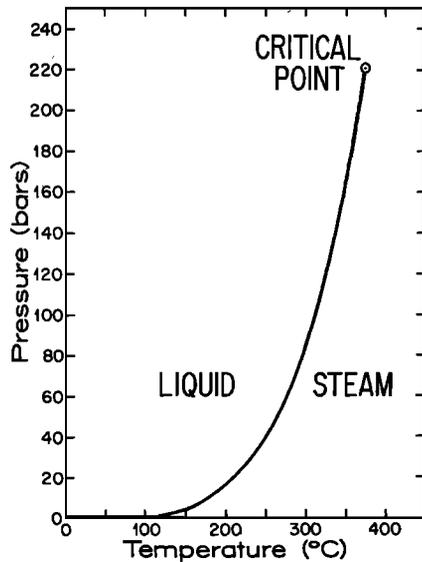


Fig. 1. Pressure and temperature of water at saturation.

tion, 1977]. It is apparent that much remains to be learned about the relationship between flow during eruptions and the properties of material during the flow. The calculations presented here of sound speed in a two-phase medium represent the initial phase of an attempt to develop a quantitative model for volcanic eruption phenomena and to relate the thermodynamic parameters of water-steam and magma-gas systems to the flow parameters observed during an eruption.

Although only a few theories for sound speed in liquid-gas mixtures exist, they are more abundant than the extremely sparse experimental data. Much of the theory was developed in studies of containment of water-moderated nuclear reactors. It is the purpose of this paper to review and synthesize the concepts required for calculations of the sound speed in liquid-gas and liquid-vapor mixtures and to examine the effect of volatile content on the sound speed for water-air and water-steam systems. This work is being extended to magma-gas mixtures.

EQUATIONS OF STATE AND SOUND SPEEDS OF WATER, AIR, AND STEAM

A simplified phase diagram of water and its saturation curve are shown in Figure 1. Because of the great volume differences between the liquid and vapor phases and because of the critical phenomenon it is difficult to express the equation of state of water in analytical form over a wide range of pressures and temperatures (e.g., see discussions by *Burnham et al.* [1969] and *Helgeson and Kirkham* [1974]). Because of these complexities the sound speed of water and water-gas mixtures cannot be calculated at all pressures and temperatures from a single equation of state. Therefore in this paper several different expressions for the equation of state of the water, air, and steam components are used, each of which is an appropriate and relatively simple expression for the pressure and temperature conditions for which it is used.

1. For liquid water at 25°C an adiabatic equation of state is used:

$$\rho_L = \rho_{LA} \exp [(P - P_A)/K] \quad (1)$$

where ρ_L is the density of the liquid phase, ρ_{LA} is the density of the liquid phase in a reference state (1.0 g cm^{-3} at 1 bar), P is the pressure, P_A is a reference pressure (1 bar), and K is the

bulk modulus of water (2.2×10^9 bars). The sound speed appropriate to this expression is

$$c = (K/\rho)^{1/2} \quad (2)$$

2. For water on the saturation curve and to pressures of 8 kbar and temperatures between 25° and 900°C, internally consistent tabulated data of *Helgeson and Kirkham* [1974] are used. The tabulated isothermal compressibilities κ_T were converted to adiabatic compressibilities κ_S , and the sound speed was calculated from $c = (\kappa_S \rho)^{-1/2}$.

3. For water on the saturation curve an equation of state of the form $P(T)$ is required by the theory developed in this paper. Two expressions are used [*Keenan et al.*, 1969; *Helgeson and Kirkham*, 1974, p. 1102]:

$$P_{\text{sat}} = P_c \exp \left[10^{-5} \tau (t_c - t) \sum_{i=1}^{\infty} F_i (0.65 - 0.01t)^{i-1} \right] \quad (3a)$$

In this equation, P_c is the critical pressure (220.38 bars), T is the temperature (in degrees Kelvin), τ is $1000/T$, t is the temperature in degrees Celsius, t_c is the critical temperature (374.136°C), and the F_i are coefficients used: $F_1 = -741.9242$, $F_2 = -29.7210$, $F_3 = -11.5529$, $F_4 = -0.8686$, $F_5 = 0.1094$, $F_6 = 0.4400$, $F_7 = 0.2521$, and $F_8 = 0.0522$. The second, and simpler, assumption is that

$$P_{\text{sat}} = AT^\alpha \exp (-\Delta H/RT) \quad (3b)$$

(A common assumption is that $\alpha = 0$.) This simpler form is commonly used for vaporization curves and is directly related to the Clausius-Clapeyron equation with the simplifying assumptions that the gas phase obeys the perfect gas law, the volume of the gas phase is much greater than that of the liquid phase, and the heat of vaporization is constant. For water the coefficient A is $2.6 \times 10^{11} \text{ dyn cm}^{-2}$, and the ratio $\Delta H/R$ is $4.6 \times 10^3 \text{ }^\circ\text{K}$.

4. For steam an ideal gas equation of state is used:

$$PV^\gamma = \text{const} = G_{\text{st}} \quad (4)$$

where $G_{\text{st}} = T_0 R_0 / M \rho_0^{\gamma-1}$, T_0 is a reference temperature (100°C at 1 bar), V is the volume, R_0 is the gas constant ($8.32 \times 10^7 \text{ ergs } ^\circ\text{C}^{-1} \text{ mol}^{-1}$), M is the molecular weight (18.02 for steam), ρ_0 is the density in the reference state (0.96 g cm^{-3}), and γ is the isentropic exponent (1.31 for steam). For an ideal gas,

$$c = (\gamma RT)^{1/2} \quad (5)$$

where $R = R_0/M$.

5. For air an ideal gas equation of state is used:

$$PV^\gamma = \text{const} = G_{\text{air}} \quad (6)$$

where $G_{\text{air}} = T_0 R_0 / M \rho_0^{\gamma-1}$, $M = 28.98$ for air, and $\gamma = 1.40$ for an adiabatic process.

To the extent that air and steam are represented as perfect gases with γ independent of temperature, the sound speed varies directly with the square root of the absolute temperature (Figure 2). The sound speed of a perfect gas is independent of pressure for a fixed temperature. Measured data for air show a slight dependence on pressure [*Hilsenrath et al.*, 1955], but this dependence can be ignored here. Because the specific gas constant R depends on the molecular weight, the sound speed of steam is higher than that of air ($c \propto M^{-1/2}$).

The behavior of the sound speed of water is much more complex and depends on both pressure and temperature (Figure 2). Values of sound speed calculated from the static compressibility data increase systematically with pressure but be-

cause of the anomalous compressibility are a complicated function of temperature. The high-pressure and high-temperature values for water obtained from the static compressibility data are systematically 5–10% lower than those obtained experimentally from dynamic ultrasonic experiments [Smith and Lawson, 1954] but show the same trend. The sound speed initially increases with temperature in the range 25°–100°C. A maximum value is attained near 100°C, and with further temperature increase the sound speed decreases rapidly. The maximum in sound speed is always attained at temperatures somewhat larger than the minimum in compressibility. (Compare Figure 2 of this work with Figure 7 of Helgeson and Kirkham [1974].) Sound speeds obtained from the compressibility data show that the temperature at which the maximum is attained increases with increasing pressure. The direction in which this maximum moves when temperature is increased has been the subject of controversy. Experimental results are contradictory. The most recent, and apparently most reliable, data of Smith and Lawson [1954] show the same trend as the static data, but earlier data [Holton, 1951] show the opposite trend: the temperature at which the maximum is attained decreases with increasing pressure.

Besides these low-temperature inflection points there are high-temperature inflections in the velocities at 0.5 and 1 kbar. The minima in the 0.5- and 1-kbar sound velocity curves correspond to minima in 0.5- and 1-kbar compressibility curves of Helgeson and Kirkham [1974, p. 1112]. There do not appear to be any experimental high-pressure high-temperature ultrasonic data to compare with the calculated curves.

SOUND SPEED IN A TWO-COMPONENT SYSTEM

In this section the word 'gas' refers to a gas phase of different composition than the liquid phase. The most obvious geologic systems involving water-gas mixtures are at low pressure and low temperature, e.g., surface water systems with admixed air bubbles or shallow crustal water with admixed gas. In order to avoid tedious algebraic complexities (associated with the water equation of state) which do not provide much additional insight, the general properties of the sound speed in such systems are illustrated by considering a water-air system at 25°C and pressures from 1 to 500 bars.

The first quantitative analysis of the effect of gas bubbles on the sound speed in a liquid was published by Mallock [1910] in an investigation of the damping of sound by frothy liquids. A more elegant calculation has been given by McWilliam and Duggins [1969], and their treatment is followed here. The assumptions inherent in their model are as follows. (1) The liquid and gas phases are in equilibrium, and there is negligible mass transfer between the phases owing to gas becoming dissolved or liquefied; (2) There is no slip between the liquid and gas phases; (3) The wavelength of the sound wave is much larger than the average dimension of nonuniformity of the mixture; and (4) The gas is compressible and obeys the perfect gas law (equation (6)), and the liquid is elastic with a constant bulk modulus.

Two cases are considered:

1. The gas bubbles are sufficiently large that surface tension effects can be neglected.

2. The gas bubbles are small, so that surface tension is appreciable. It is assumed that the bubbles are spherical and of uniform size and that classical surface tension theory applies.

Although case 1 is a limiting case of 2, it is instructive to consider it first and separately in order to illustrate the dependence of sound speed on pressure and vapor fraction.

Case 1: surface tension effects neglected. In the absence of

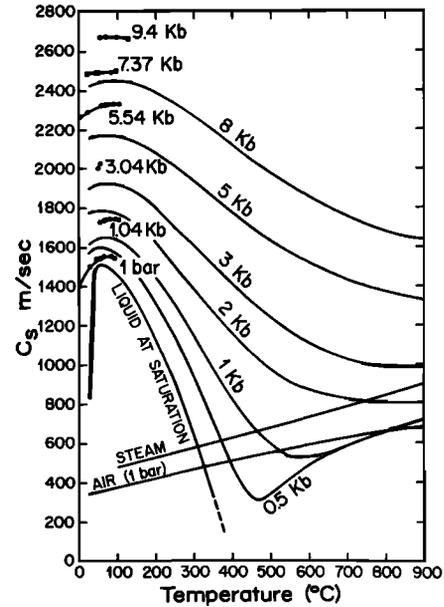


Fig. 2. Sound speed of the pure phases discussed in this paper, water, steam, and air. Heavy curves for water were calculated from compressibility and volume data tabulated by Helgeson and Kirkham [1974]. Isothermal compressibilities were converted to adiabatic compressibilities by using their tabulated thermal expansion and specific heat data. Dotted curves of measured sound speeds of water [Smith and Lawson, 1954] are shown for comparison. Data for air are from Hilsenrath et al. [1955], and data for steam are from Hodgman et al. [1958, p. 2320].

surface tension (i.e., with the assumption that the bubbles have radii greater than $\sim 10^{-4}$ cm) the pressure within the gas bubbles P_G in a liquid is the same as the pressure in the liquid P_L :

$$P_G = P_L \equiv P \quad (7)$$

As given by (1) and (6), the densities of the liquid ρ_L and gas ρ_G , respectively, are given by

$$\rho_L = \rho_{LA} \exp[(P - P_A)/K] \quad (8)$$

and

$$\rho_G = (P/G_{\text{air}})^{1/\gamma} \quad (9)$$

The density ρ of a two-phase mixture which has gas mass fraction $\eta = M_G/M_L$ is given implicitly by

$$(1 + \eta)/\rho = (\eta/\rho_G) + (1/\rho_L) \quad (10)$$

The void fraction x is simply related to the mass fraction η through

$$x = (1 + \rho_G/\eta\rho_L)^{-1} \quad (11)$$

Substitution for ρ_L and ρ_G in terms of P gives the adiabatic equation of state of the mixture:

$$\rho = (1 + \eta)\rho_{LA} \left[\frac{\eta\rho_{LA}G_{\text{air}}^{1/\gamma}}{P^{1/\gamma}} + \exp\left(\frac{P_A - P}{K}\right) \right]^{-1} \quad (12)$$

from which the sound speed $c = (dP/d\rho)^{1/2}$ is

$$c = \eta\rho_{LA} \left(\frac{G_{\text{air}}}{P}\right)^{1/\gamma} + \exp\left(\frac{P_A - P}{K}\right) \left\{ \left[(1 + \eta)\rho_{LA} \right]^{1/2} \cdot \left[\frac{\eta\rho_{LA}G_{\text{air}}^{1/\gamma}}{\gamma P^{\gamma+1/\gamma}} + \frac{1}{K} \exp\left(\frac{P_A - P}{K}\right) \right]^{1/2} \right\}^{-1} \quad (13)$$

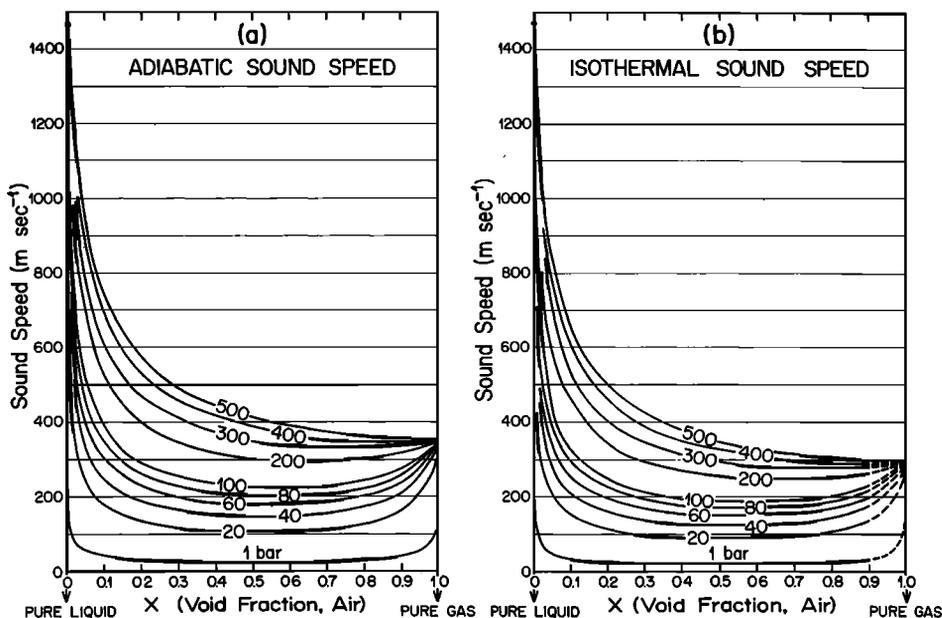


Fig. 3. Calculated dependence of (a) adiabatic and (b) isothermal sound speed of water-air mixture on volume content of gas and on pressure. Surface tension is neglected.

Values of the sound speed according to this model are shown in Figures 3 and 4, where the sound speed is plotted against void fraction and mass fraction, respectively. Consider first only Figure 3a, which shows the dependence of the adiabatic sound speed $c = (\partial P / \partial \rho)_s^{1/2}$ on a void fraction. The most dramatic effect of the admixture of small-volume fractions of air is the lowering of the sound speed; e.g., at 1-bar pressure with one part in 10^4 by volume of air the sound speed is lowered from that of pure water, 1470 m s^{-1} , to 900 m s^{-1} . The decrease is most dramatic at low pressures. At 1-bar pressure a minimum value of the sound velocity is attained at void fraction $x = 0.5$. At higher pressures the minimum is shifted to larger values of x , and at 500-bar pressure the minimum vanishes, and the sound speed decreases monotonically to that of pure air. At very large values of the void fraction ($x > 0.9$) the sound speed approaches that of the gas. The sound speed of the mixture is highly pressure dependent, whereas the sound speeds of the pure end-members are independent of pressure.

The variation of sound speed with mass fraction is shown in Figure 4 on a semilogarithmic graph to emphasize the magnitude of the effect for small mass fractions of air. Consider first the dotted curves, which show the adiabatic sound speed. At 1-bar pressure, 1 ppm air causes the sound speed to drop to one quarter of the value for pure water. At higher pressures, larger mass fractions of air are required to cause the same decrease. The minimum value attained at 1 bar is 24 m s^{-1} .

Measured data [Karplus, 1958] are compared with calculated values in Figure 5. At mass fraction $\eta = 10^{-6}$ the sound speed is approximately 100 m s^{-1} , and at mass fraction $\eta = 10^{-3}$ it decreases to 24 m s^{-1} . There is a definite dependence of sound speed on frequency (considered below), but in general the data confirm the theoretical prediction of a large decrease with admixture of gas into the liquid.

The propagation of a sound wave through a two-phase liquid-gas mixture may be an isothermal rather than an adiabatic process. Heat may be conducted between the gas and liquid phases, and because of the large heat capacity of water

the temperature variation within the water may be small enough to be ignored [Karplus, 1958]. The sound speed of the mixture may therefore depend on the frequency or, equivalently, the period of the sound waves. If the period of the waves is less than the time in which heat can be conducted from the gas bubbles into or away from the surrounding liquid, the compressions and rarefactions accompanying the passage of the sound wave will be adiabatic, and the behavior of the gas will be given by the adiabatic polytropic exponent ($\gamma = 1.4$ for air). If, however, the period of the sound waves is greater than the time required for conductive heat flow from the bubbles into the liquid, the process will be nearly isothermal, and the behavior of the gas will be given by the isothermal

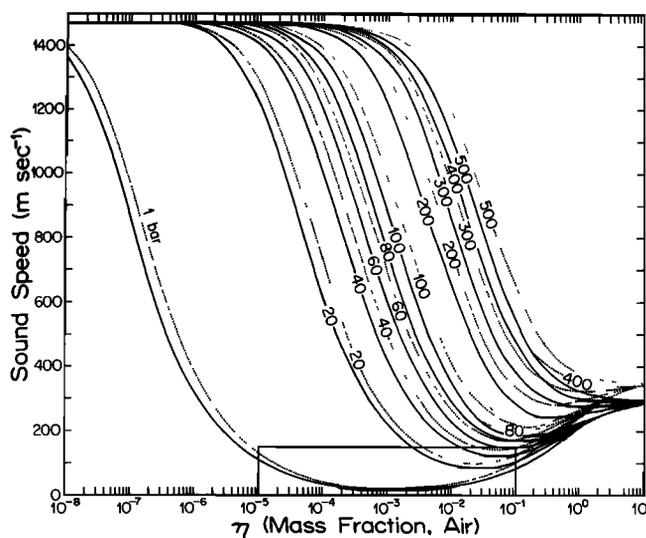


Fig. 4. Calculated dependence of sound speed of water-air mixture on mass fraction of gas and on pressure, plotted on semilogarithmic paper to show the effect of small volume fractions of air. Surface tension is neglected. Solid curves indicate isothermal sound speed, and dotted curves indicate adiabatic sound speed. Inset region at bottom is shown enlarged in Figure 5.

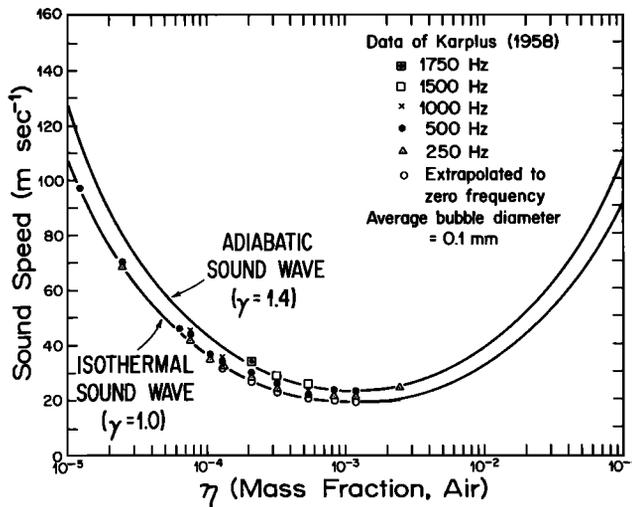


Fig. 5. Comparison of calculated sound speeds with data of Karplus [1958].

polytropic exponent ($\gamma = 1$ for air). Correspondingly, the isothermal bulk modulus for the liquid should be used.

The isothermal sound speed of a two-phase mixture decreases with the admixture of small amounts of air, as does the adiabatic sound speed (Figure 3b and Figure 4, solid curves). However, the sound speed of air compressed isothermally is less than that of air compressed adiabatically by the factor $\gamma^{1/2}$, so that isothermal sound speeds of a two-phase mixture are lower than adiabatic sound speeds. The assumption of isothermal propagation must break down at large void fractions of air, since propagation in pure air must be adiabatic. For this reason the isothermal sound speed curves shown in Figure 3b are dashed for large void fractions.

The frequency at which thermal conductivity effects may become significant can be estimated as follows. A characteristic time constant for thermal cooling of small spheres is $t = 0.05D^2/\kappa$, where D is the diameter of the sphere and κ is its thermal diffusivity (see Karplus, 1961, p. H-1 or Carslaw and Jaeger, 1959, chapter 9). For a 0.1-mm sphere of air with diffusivity $0.187 \text{ cm}^2 \text{ s}^{-1}$ [Carslaw and Jaeger, 1959, p. 497] the characteristic time is $2.5 \times 10^{-5} \text{ s}$. The reciprocal of this time constant gives a value of frequency below which the isothermal approximation should be approached and above which the adiabatic approximation should be approached. For air bubbles of diameter 0.1 mm the characteristic frequency for conductive heat transfer is 40,000 Hz. Karplus [1958, p. 11] obtained experimental values of sound speeds in water-air mixtures which had bubbles of this diameter. The data were measured at frequencies from 250 to 1750 Hz and the bubble mass fractions from 1.2×10^{-5} to 2.4×10^{-3} . All of the data were obtained at frequencies low in comparison to the characteristic frequency of 40,000 Hz. The lowest frequency data lie near the calculated isothermal curve (Figure 5), supporting the idea that low-frequency sound propagation in a water-air system is an isothermal process. There is an increase in the sound speed with increasing frequency, as would be expected from the above discussion, but the adiabatic curve is approached (and even exceeded by a few data points) at frequencies much less than the calculated value of 40,000 Hz. Karplus himself attributed the frequency dependence to the presence of a detergent in the experimental mixture, but his experiments designed to test this hypothesis were inconclusive. Thus although the

frequency dependence of the sound speed due to this effect has not been experimentally proven, it is important to keep in mind that at low frequencies the sound speed of a water-air mixture appears to be isothermal and that the sound speed of a two-phase mixture is sensitive to frequency. Entirely different results should be expected in laboratory experiments at, say, 1 MHz and field experiments at, say, 1–10 Hz.

The variation of sound speed with void fraction is given in Figures 3a and 3b because void fraction is the natural variable of mixing theory and previous investigators generally have followed this convention. For many engineering purposes it is preferable to specify mass fraction as a measure of gas content, rather than void fraction, because mass fraction is invariant with surface tension and pressure [McWilliam and Duggins, 1969, p. 105]. There are many geologic situations in which it is also preferable to specify mass fraction. One such situation is the passage of a gas-liquid mixture up a geyser conduit or a volcanic neck. During the expansion of the mixture the void fraction may vary greatly as the fluid rises, but the mass fraction will not if gas is neither condensing nor dissolving. In the remaining calculations, mass fraction will be specified.

In the following section the effect of small bubbles which have appreciable surface tension is examined. McWilliam and Duggins developed this model for the specific case of isothermal compression. Generalization to the case of adiabatic compression requires considerable algebraic complexity which is not warranted at this time because of the paucity of experimental data.

Case 2: surface tension effects considered. When the surface tension becomes significant, the pressure in a gas bubble exceeds the pressure in the surrounding liquid:

$$P_G = P_L + (2\sigma/r) \quad (14)$$

where r is the bubble radius. For the case of isothermal compression of the gas bubbles the same procedure used in the previous section gives the following sound velocity [McWilliam and Duggins, 1969, p. 104]:

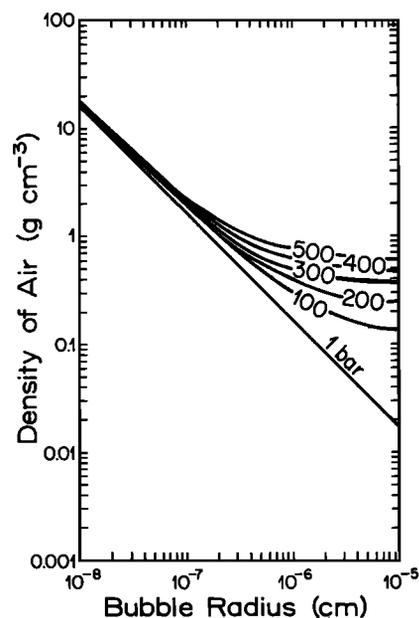


Fig. 6. Density of air in bubbles in water mixture as a function of bubble radius and pressure.

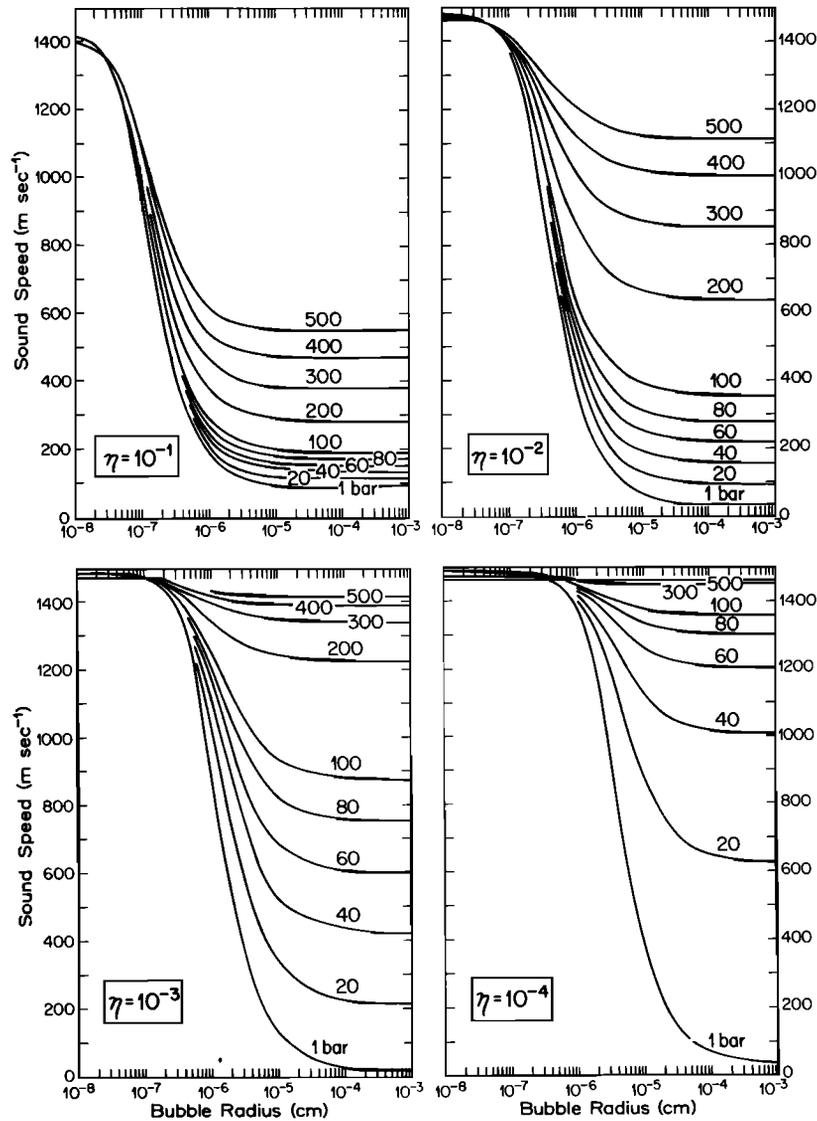


Fig. 7. Calculated sound speed of water-air mixture as a function of bubble radius and pressure for four mass fractions, $\eta = 10^{-1}, 10^{-2}, 10^{-3},$ and 10^{-4} .

$$c = \left(\frac{3\beta^2\gamma - \delta\epsilon}{3\beta^2\theta - \delta\lambda} \right)^{1/2} \quad (15)$$

in which

$$\begin{aligned} \beta &= 2\sigma/r \\ \gamma &= \frac{(1+\eta)}{\rho^2\eta G} \left(\frac{2\sigma}{r} + P_L \right)^2 \\ \delta &= 32\pi\eta\sigma^3/3m \\ \epsilon &= \gamma/\eta G \\ \theta - 1 &= \frac{\exp[(P_A - P_L)/K][(2\sigma/r) + P_L]^2}{K\rho_L\eta G} \\ \lambda &= (\theta - 1)/\eta G \end{aligned} \quad (16)$$

A value of 72.2 dyn cm^{-1} was used for the surface tension of an air-water interface.

The density of the air depends on the bubble size as well as on the pressure, as is shown in Figure 6. The gas density is insensitive to radius if the bubbles are large and becomes equal to the value obtained in the absence of surface tension. The gas density increases because of surface tension as the bubble size decreases. At radii of $1-5 \times 10^{-7} \text{ cm}$ ($10-50 \text{ \AA}$) the gas density would become as large as the liquid density; presumably at smaller radii, bubbles are unstable.

When surface tension is taken into account, both pressure and bubble size affect the sound speed of a two-phase mixture, as is shown in Figure 7: Consider first the case $\eta = 10^{-1}$, shown in the upper left of this figure. At 1-bar pressure the sound speed is close to that of the pure liquid if the bubble radius is smaller than about $3 \times 10^{-8} \text{ cm}$ (3 \AA). The sound speed decreases rapidly in the range 3×10^{-8} to about 10^{-6} cm . It is nearly constant, equal to the value obtained in the model in which surface tension is ignored, for bubble radii greater than about 10^{-6} cm . With increasing pressure the decrease in sound speed occurs over approximately the same range of bubble sizes, but the magnitude of the drop is smaller.

Three distinct regions of behavior are recognizable: (1) a

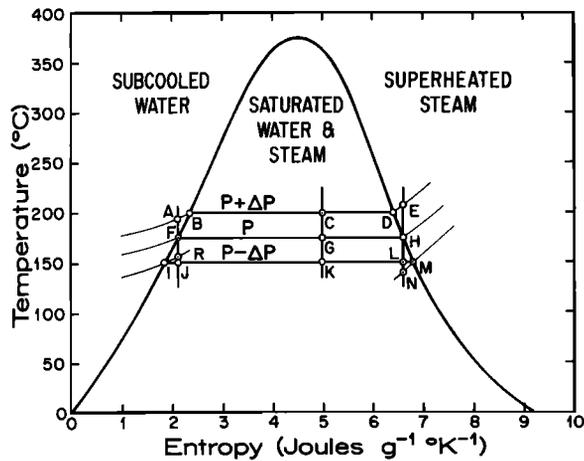


Fig. 8. Temperature-entropy diagram for H_2O (data from Keenan *et al.* [1969]). The thermodynamic paths which illustrate the effect of adiabatic compression and decompression on the mixture [after Davies, 1965] are discussed in the text. Vertical scale of paths is exaggerated. Thin lines extending into the single phase regions from A, F, and I and from E, H, and M are constant pressure lines.

region at small bubble radii where the sound speed is approximately independent of both bubble size and pressure, (2) a region at intermediate bubble radii where the sound speed depends sensitively on both pressure and bubble radius, and (3) a region at larger bubble radii where the sound speed is independent of bubble radius but sensitive to pressure.

For smaller mass fractions ($\eta = 10^{-2}$, 10^{-3} , and 10^{-4} in Figure 7) these regions shift in a systematic manner. The region at small bubble radius where the sound speed is independent of both pressure and bubble size is enlarged. The region where both effects are important moves progressively to larger bubble radii with decreasing mass fraction. Finally, the magnitude of the sound speed drop decreases with decreasing mass fraction.

SOUND SPEED OF SINGLE-COMPONENT TWO-PHASE SYSTEM

General considerations. Calculation of the sound speed of a two-component two-phase system is an easy procedure if adiabatic equation of state data are available, because pressure and temperature may be considered to be independent variables in such a system. Calculation of the sound speed in a one-component two-phase system is a more difficult matter because pressure and temperature are not independent variables but are related by the Gibbs equation for equilibrium between the phases.

The physical processes which occur during propagation of a sound wave through a two-phase mixture are much more complex than for a single-phase mixture [e.g., Davies, 1965]. Consider the temperature-entropy (TS) diagram of water shown in Figure 8. A mixture of saturated water and steam is represented as point G, where the chord ratio FG/FH is the mass fraction η of steam in the mixture. Isentropic pressure changes, such as the compressions and rarefactions which occur during propagation of a sound wave, are represented by movement up and down the constant entropy line CGK. If steam and water remain in thermal equilibrium on the saturation line, there must be mass transfer between the phases, since the fraction of steam in the mixture changes ($BC/BD \neq FG/FH \neq IK/IM$). This requires that condensation or evaporation take place.

An isentropic pressure increase from P to $P + \Delta P$ corresponds to movement of the mixture from G to C in the temperature-entropy diagram of Figure 8. The pressure increase in the water phase corresponds to movement from F to A; as a result, the water phase becomes subcooled. The pressure increase in the steam phase corresponds to movement from H to E as the steam becomes superheated. The induced temperature difference between the steam and the water leads to heat transfer from the superheated steam to the subcooled water. If the original composition of the mixture G lies to the right of the peak of the two-phase loop, as is shown in Figure 8, some water will be vaporized, and the mass fraction of steam in the mixture will increase during adiabatic compression ($BC/BD > FG/FH$). (This phenomenon occurs during meteorological conditions when saturated air is adiabatically compressed during descent and a decrease in relative humidity is induced.) If the original composition lies to the left of the top of the two-phase loop (assumed to be symmetric), some steam will condense, and the mass fraction of steam in the mixture will decrease during adiabatic compression. Thus by heat and mass transfer both the water and the steam are restored to the saturation line, the water by the path A to B, and the steam by the path E to D.

An isentropic pressure reduction from P to $P - \Delta P$ corresponds to movement from G to K in the TS diagram. The pressure decrease in the water phase corresponds to movement from F to R; as a result, the water becomes superheated above its saturation temperature, point I (IR is a continuation of a constant pressure line from the water region). The pressure decrease in the steam phase alone corresponds to movement from H to N in the TS diagram, and the steam becomes subcooled or supersaturated with respect to its saturation temperature, point M (MN is a continuation of a constant pressure line from the superheated region). If the original composition of the mixture G lies to the right of the peak of the two-phase loop, some vapor will condense to form a mixture of saturated water and steam (point L), and thus the subcooled steam may move toward the stable state M. The mass fraction of steam in such a mixture will decrease ($IK/IM < FG/FH$) (a direct application of this phenomenon is found in the Wilson cloud chamber). If the original composition lies to the left of the two-phase loop (assumed to be symmetric), cavitation, and some vaporization, of the subcooled liquid will be the dominant process, and the mass fraction of steam in the mixture will increase. Cavitation of the water creates a local mixture with the composition of point J, and the superheated water at point R thus moves toward the stable state I, a mixture of water and steam.

In general, condensation and evaporation cannot take place instantaneously, since the transportation of heat and mass can only occur at a finite speed. The time lag in flashing water to steam or condensing steam to water is important in determining the degree of equilibrium obtained in the sound wave. Since condensation and evaporation generally proceed at different rates, it should be expected that compression and rarefaction waves behave differently. Experiments have confirmed that finite amplitude rarefaction waves in water-steam mixtures have lower velocities than compression waves because rarefaction waves tend to maintain continuous thermal equilibrium [Barclay *et al.*, 1969].

In summary, a mixture of liquid and its vapor may respond to pressure disturbances by (1) nonequilibrium response (in which there is no mass transfer between the phases; i.e., the liquid and the vapor are independently isentropic, and both

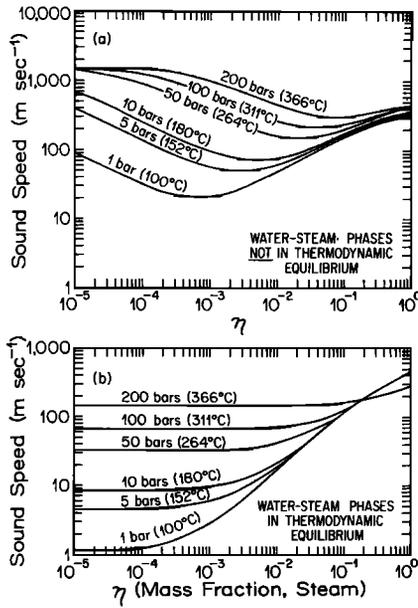


Fig. 9. Calculated sound speed of water-steam mixture (a) not in equilibrium and (b) in equilibrium as a function of mass fraction and pressure.

depart from the saturation line) and (2) equilibrium response (in which there is mass transfer between the phases and the liquid and vapor remain on the saturation line). Real systems will probably show behavior between these two extremes.

Case 1: nonequilibrium response. If there is no mass transfer between the liquid and vapor phases, the sound speed will be given by the theory of the previous section. Surface tension effects should not be important for a liquid-vapor system on the saturation curve, and the sound speed is therefore independent of bubble size. The adiabatic sound speed in this case is given by (13). This would most nearly be the case for high-frequency waves; the case of low-frequency nonequilibrium propagation, which would be more nearly isothermal, is not considered here because mass transfer effects may become important (case 2, discussed below).

The sound speed of a water-steam system in which the phases are not in thermodynamic equilibrium is shown in Figure 9a. At 1-bar pressure (100°C) the sound speed decreases steadily with the addition of small amounts of steam to 24 m s⁻¹ at $\eta = 10^{-3}$ and then increases to 446 m s⁻¹, the sound speed of pure steam at 100°C. At higher pressures the decrease is less pronounced, and the minimum value is attained at higher mass fractions of steam.

Case 2: equilibrium response. Equilibrium between the liquid and vapor phases can be maintained if mass transfer between the liquid and vapor phases occurs in a time short in comparison to the acoustic wave period. The sound speed can be calculated from the equation of state of the system in the form $V(P, S, x)$ [Davies, 1965]. A differential change in volume of the two-phase system is given by

$$dV = \left(\frac{\partial V}{\partial P}\right)_{S,\eta} dP + \left(\frac{\partial V}{\partial S}\right)_{P,\eta} dS + \left(\frac{\partial V}{\partial X}\right)_{P,S} d\eta \quad (17)$$

For adiabatic propagation of sound, $dS = 0$:

$$dV = \left(\frac{\partial V}{\partial P}\right)_{S,\eta} dP + \left(\frac{\partial V}{\partial X}\right)_{P,S} d\eta \quad (18)$$

giving

$$\left(\frac{\partial V}{\partial P}\right)_S = \left(\frac{\partial V}{\partial P}\right)_{S,\eta} + \left(\frac{\partial V}{\partial \eta}\right)_{P,S} \frac{d\eta}{dP} \quad (19)$$

In the limiting case of $P \rightarrow 0$, dx/dP becomes $V_g - V_l$. The system derivative $(\partial V/\partial P)_{S,\eta}$ can be written as the sum of component derivatives $(1 - \eta)(\partial V_l/\partial P) + \eta(\partial V_g/\partial P)$. Hence (18) becomes

$$\left(\frac{\partial V}{\partial P}\right)_S = (1 - \eta) \left(\frac{dV_l}{dP}\right)_{\text{sat}} + \eta \left(\frac{dV_g}{dP}\right)_{\text{sat}} + (V_g - V_l) \left(\frac{\partial \eta}{\partial P}\right)_S \quad (20)$$

The derivative $(\partial \eta/\partial P)_S$ can be determined from the first law of thermodynamics:

$$\delta Q = \delta E + P\delta V \quad (21)$$

For an adiabatic change, $\delta Q = 0$. The differential internal energy in this equation is more meaningfully expressed in terms of the enthalpy of reaction

$$\delta H = \delta E + P\delta V + V\delta P$$

so the first law becomes

$$\delta H - V\delta P = 0 \quad (22)$$

For the liquid-vapor mixture,

$$H = (1 - \eta)H_l + \eta H_g = H_l + \eta L \quad (23)$$

where L is the latent heat of transformation. For this,

$$\delta H = \delta H_l + \eta \delta L + L \delta \eta \quad (24)$$

and substituting into (22) gives

$$\delta H_l + \eta \delta L + L \delta \eta - V \delta P = 0 \quad (25)$$

Rearranging terms gives

$$L \delta \eta = V \delta P - \delta H_l - L \delta \eta \quad (26a)$$

or

$$\left(\frac{\delta \eta}{\delta P}\right)_S \approx \left(\frac{\partial \eta}{\partial P}\right)_S = \frac{V}{L} - \frac{1}{L} \left(\frac{dH_l}{dP}\right)_{\text{sat}} - \frac{\eta}{L} \left(\frac{dL}{dP}\right) \quad (26b)$$

Finally, then, the sound speed obtained from

$$c^2 = -V^2(dV/dP)_S \quad (27)$$

is

$$\frac{-c^2}{V^2} = (1 - \eta) \left(\frac{dV_l}{dP}\right)_{\text{sat}} + \eta \left(\frac{dV_g}{dP}\right)_{\text{sat}} + (V_g - V_l) \left[\frac{V}{L} - \frac{1}{L} \left(\frac{dH_l}{dP}\right)_{\text{sat}} - \frac{\eta}{L} \left(\frac{dL}{dP}\right) \right] \quad (28)$$

The four derivatives required in this equation can be obtained from tables of thermodynamic data if the data exist for the liquid-gas systems in question. For this study, data were obtained from Keenan *et al.* [1969].

The sound speed of a water-steam mixture in which thermodynamic equilibrium between the phases is maintained is shown in Figure 9b. The behavior is quite different from the nonequilibrium case shown in Figure 9a. At 1-bar pressure the velocity drops discontinuously to 1 m s⁻¹ with the addition of a finite amount of steam and remains at this low value for mass fractions η less than 10^{-4} . With the formation of larger

amounts of steam in the mixture the velocity rises slowly toward, but does not attain, the value for the pure steam phase. At higher pressures the velocity decrease is less dramatic but is maintained to higher mass fractions. The most pronounced effect of equilibrium behavior in contrast to nonequilibrium behavior is the magnitude of the decrease: at 1-bar pressure it drops to approximately 1 m s^{-1} , much lower than the minimum velocity of 24 m s^{-1} obtained for the nonequilibrium case.

The sound speed of a two-phase liquid-vapor mixture does not smoothly approach the component velocities at $\eta = 0$ and $\eta = 1$, as may be seen by writing (28) in the form [Davies, 1965, p. 5]:

$$-\frac{c^2}{V^2} = (1 - \eta) \left(\frac{\partial V_l}{\partial P} \right)_s + \eta \left(\frac{\partial V_g}{\partial P} \right)_s + \left[(1 - \eta) \left(\frac{\partial V_l}{\partial S} \right)_p \left(\frac{\partial S_l}{\partial P} \right)_{\text{sat}} + \eta \left(\frac{\partial V_g}{\partial S} \right)_p \left(\frac{\partial S_g}{\partial P} \right)_{\text{sat}} + (V_g - V_l) \left(\frac{\partial \eta}{\partial P} \right)_s \right] \quad (29)$$

The term in brackets represents the difference between the nonequilibrium case and the equilibrium case. The nonequilibrium case correctly converges to the liquid and gas sound velocities at $\eta = 0$ and $\eta = 1$. Since the term in brackets does not reduce to zero at $\eta = 0$ and $\eta = 1$, there are mathematical discontinuities with the formation of an infinitesimally small amount of vapor in liquid or droplets in vapor.

Approximations to (29) can be made for very small ($\eta \ll 1$) and very large ($1 - \eta \ll 1$) mass fractions of gas [Landau and Lifshitz, 1959, p. 249]. For $\eta \ll 1$ (a liquid containing some bubbles of vapor) the velocity of sound is

$$c \approx LMPV_l/RT(C_p T)^{1/2} \quad (30)$$

This velocity is very small (approximately 1 m s^{-1} for water). For $(1 - \eta) \ll 1$ (a vapor containing some droplets of liquid) the velocity of sound is given by

$$\frac{1}{c^2} \approx \frac{M}{RT} - \frac{2}{L} + \frac{C_p T}{L^2} \quad (31)$$

This velocity is lower than the velocity of sound in the pure gas (390 m s^{-1} for steam with droplets of water in comparison to 446 m s^{-1} for pure water vapor). The discontinuity in sound speed of a vapor to which a few droplets of liquid have been added is not nearly as pronounced as that of a liquid in which a few bubbles have formed.

Bennett *et al.* [1964] obtained similar results with a quite different model and assumptions. In an analysis of the speed with which 'vaporization waves' (expansion waves across which a liquid is converted to a vapor) propagate into exploding wires they analyzed the problem of the sound speed of a liquid-vapor system. The sound speed of a wave moving into the liquid at the saturation curve (corresponding to $\eta \ll 1$ above) is

$$c = (1/\rho)(dP/dT)(T/(C_p T)^{1/2}) \quad (32)$$

At the saturation curve the pressure P is just the vapor pressure $P(T)$, independent of density. Bennett *et al.* [1964, p. 84] used (3b) for the vapor pressure:

$$P_{\text{sat}} = AT^n \exp(-\Delta H/RT) \quad (33)$$

When the derivative of this equation of state is combined with (32), the sound speed is found to be

$$c = \frac{1}{\rho_L} \left(\frac{T}{C_{V_l}} \right)^{1/2} \left[\frac{A \Delta H \exp(-\Delta H/RT)}{RT^2} \right] \quad (34)$$

This equation gives values in good agreement with those of the Landau and Lifshitz [1959] approximation (equation (30)) and the rigorous equation (28).

CONCLUSIONS

The theory for sound speed in two-phase fluids demonstrates that several variables in addition to the equation of state may affect the sound speed of such systems. The sound speed of the simplest system considered, water-air, depends on the amount of gas present, on the pressure and temperature, on the frequency of the sound wave, and, for small bubbles, on bubble radius. Calculated sound speeds are in good agreement with the sparse data which exist. The sound speed of a liquid initially in equilibrium with its vapor depends on whether or not the equilibrium is maintained during passage of the sound wave. In order to maintain equilibrium, steam must condense, and bubbles must nucleate or increase in mass to transfer mass and energy from one phase to the other. The sound speed depends on the amount of gas present and on the pressure on the saturation curve but not on bubble size because surface tension effects should be unimportant in saturated liquids. The sound speed of a liquid-vapor system is appreciably less than the sound speed of a liquid-gas system if heat and mass transfer occur between the phases to maintain thermal equilibrium.

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