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**Supplementary Material Available.** Table I will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JCED-74-268.

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# Velocity of Sound in Binary Mixtures of Benzene, Hexane, and Methanol at 0-65°C

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**Sound velocities and densities of liquid hexane, benzene, methanol, and a number of binary solutions were measured over the temperature range from 0° to 65°C. The sound velocities were scaled from photographic records provided by a pulse-echo instrument by using a 1-MHz quartz crystal. The sound velocity isotherms of the nonideal binary mixtures exhibited minima, whereas those for the ideal mixture were slightly curved. The densities varied linearly with temperature. Adiabatic compressibilities, ratio of heat capacities, and the heat capacity at constant volume were calculated. The results were in general agreement with available experimental and theoretical values in the literature.**

Considerable scientific and practical interest has been stimulated by the investigation of organic solutions with ultrasonic measurements. Important physicochemical properties of solutions, such as adiabatic and isothermal compressibilities, ratio of heat capacities ($C_p/C_v$), heat capacity at constant volume ($C_v$), coefficient of expansion, and critical temperature, may be determined from ultrasonic velocity and density data.

Most previous investigations, e.g., methyl and ethyl alcohol in carbon tetrachloride (*5*), n-hexane in methanol (*14*), fluorocarbons (*7*), alcohols (*8*), benzene in nitrobenzene (*16*), aniline in n-hexane and triethylamine–$H_2O$ (*2*), and aniline–cyclohexane (*1*), have been limited to narrow temperature ranges. Nozdrev's (*9*) investigation of benzene, toluene, and methylxylene in carbon tetrachloride and Marks' (*8*) investigation of alcohol mixtures initiated the systematic study of solutions based upon ultrasonic velocity data. Additional systematic investigations of solutions by ultrasonic velocity data are needed to elucidate the liquid state and correlate mixing rules.

This paper presents data from a systematic study of sound velocity as a function of composition for the binary mixtures of benzene, methanol, and hexane over a temperature range of 0–65°C.

## Experimental

Measurements of sound velocity were made at 1 MHz by the pulse echo method (*15*) by using an electronic pulser coupled to a high gain amplifier (*13*). The oscilloscope trace of the echoes was photographed, and the time between successive echoes was scaled to ±0.2 μ sec on a microscope equipped with a movable Lafayette mechanical stage. A standard time signal (Micro-Marker) was superimposed on the oscilloscope trace and used to correct for nonlinear amplification of the high gain amplifier and oscilloscope. Velocity data were calculated from the time between two successive echoes and the distance between the barium titanate transducer and the nickel reflector. Parallelism of the reflector and transducer was maintained by three adjustment screws on the reflector. The liquid sample chamber containing the reflector and transducer was immersed in a constant tempera-

**Table I. Least-Squares Coefficients for Pure Component Relations**

Polynomial coefficients of density in g/cm³ for $\rho = A + Bt$ with $t$ = °C

| Polynomial degree | Component | $A \times 10^{+1}$ | $B \times 10^{+3}$ | SD | No of points |
|---|---|---|---|---|---|
| | | Density–temperature | | | |
| 1 | Benzene | 9.0000 | −1.0597 | $2.96 \times 10^{-4}$ | 15 |
| 1 | Methanol | 8.104229 | −0.93779 | $2.38 \times 10^{-3}$ | 14 |
| 1 | Hexane | 6.799439 | −0.90556 | $1.14 \times 10^{-3}$ | 14 |

Polynomial coefficients of sound velocity in m/sec for $C = A + Bt$ with $t$ = °C

| Polynomial degree | Component | $A \times 10^{-3}$ | $A \times 10^{0}$ | SD | No. of points |
|---|---|---|---|---|---|
| | | Sound velocity–temperature | | | |
| 1 | Benzene | 1.37798 | −4.4490 | 4.67 | 30 |
| 1 | Methanol | 1.14909 | −2.9223 | 4.73 | 14 |
| 1 | Hexane | 1.15818 | −4.31796 | 2.32 | 36 |

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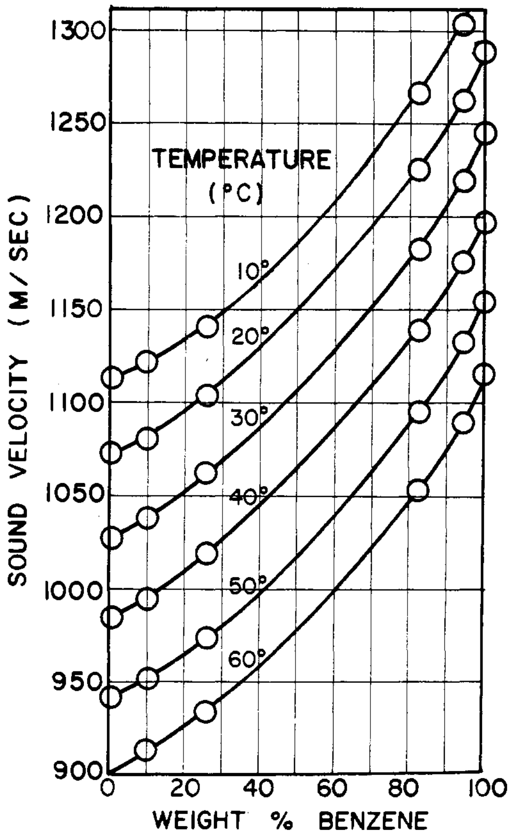

**Figure 1.** Isotherms of sound velocity as a function of composition for benzene in hexane

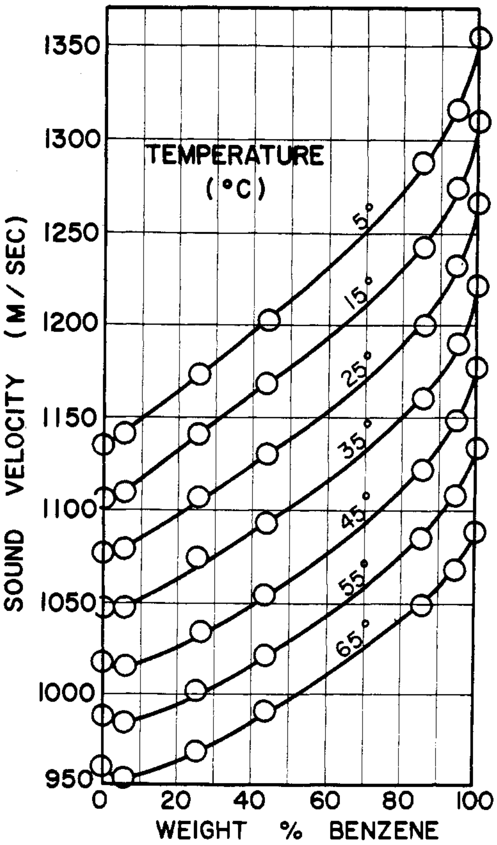

**Figure 2.** Isotherms of sound velocity as a function of composition for benzene in methanol

ture bath and controlled to ±0.05°C. Thermocouples calibrated with a platinum resistance thermometer were used for temperature measurement.

Spectral grade materials supplied by Matheson Coleman & Bell, with a purity of 99.9% determined by gas chromatography, were used. To minimize contamination during storage and transfer, the system was constructed entirely of glass, teflon, and stainless steel. The transfer of liquids was made through stainless-steel adapters fitted to the reagent bottles. The reagent bottles were only opened under a nitrogen atmosphere to insert the dispensers. The liquid sample cell was filled by vacuum transfer.

Constituents for solutions were transferred by syringe to a Teflon-stoppered glass flask (equipped with stainless-steel hypodermic tubing), frozen, and weighed on an analytical balance.

Densities reproducible to ±0.00020 g/ml were determined within the range of 0–65°C by using a Lipkin pycnometer and a cathetometer. The error in sound velocity replication was less than ±1%.

## Results and Discussions

To determine thermodynamic properties of mixtures, reliable data for the pure components are required. Thus, the sound velocity and density were determined for spectral quality hexane, benzene, and methanol at atmospheric pressure and from 0° to 65°C. The variations of density with temperature for the pure components were linear

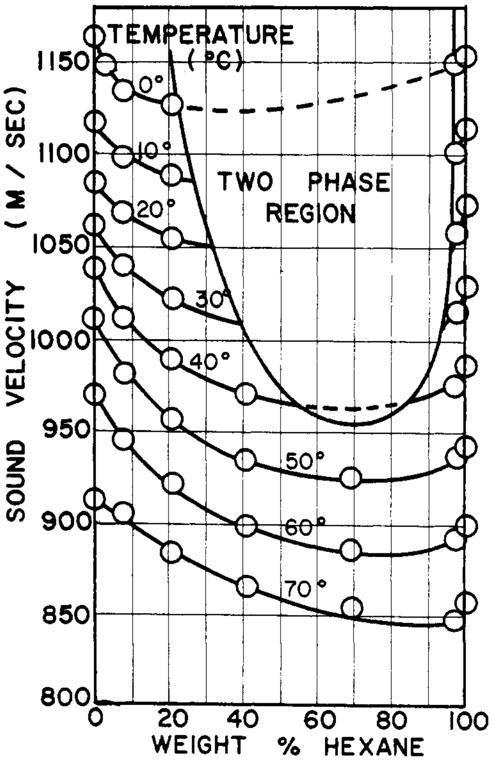

**Figure 3.** Isotherms of sound velocity as a function of composition for hexane in methanol

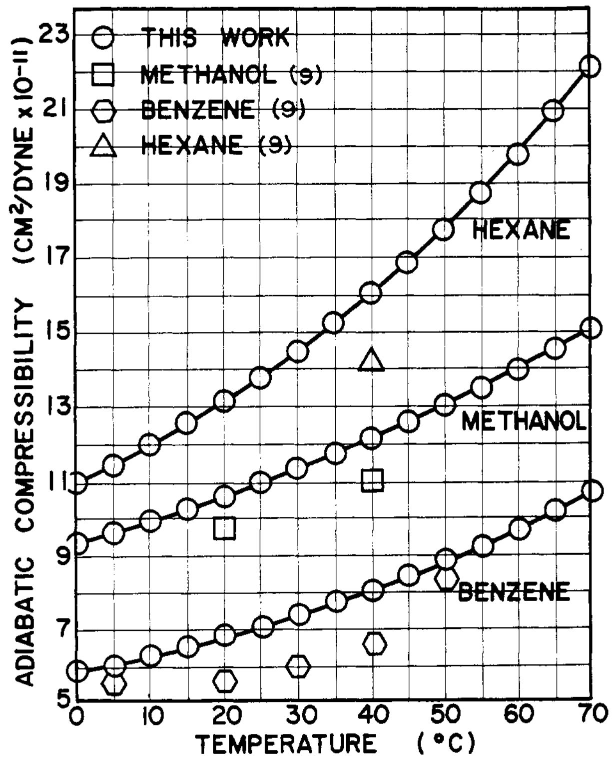

**Figure 4.** Adiabatic compressibility of benzene, hexane, and methanol

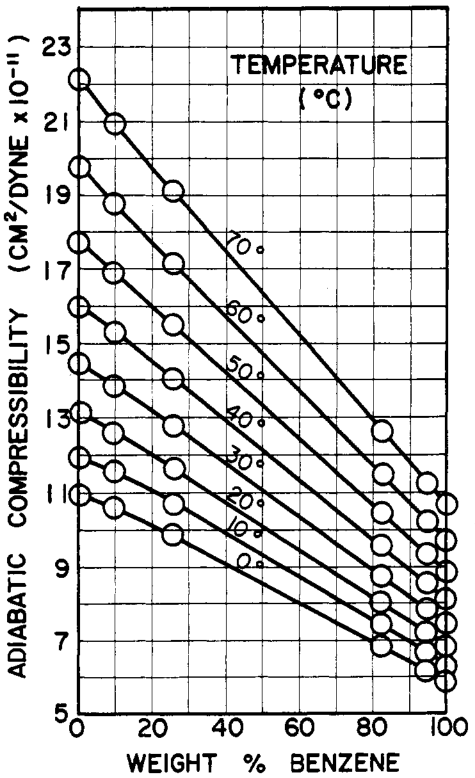

**Figure 5.** Isotherms of adiabatic compressibility for benzene in hexane

(within experimental error), although some curvature occurred at the higher temperatures. The coefficients of a least-squares correlation are shown in Table I.

Three binary systems were chosen for study: benzene-hexane, benzene-methanol, and hexane-methanol. The benzene-hexane system according to solution theory should exhibit near ideal behavior. The benzene-methanol (*3*) system is reported to have a critical solution temperature (CST at 29°C) which would indicate nonideal solution behavior. The CST at 29°C is dubious. The hexane-methanol (*16*) system is nonideal since two liquid phases exist in equilibrium at temperatures below 36.6°C. Thus, the object of this study was to investigate the solutions of these three systems by determining sound velocities and densities.

***Benzene-hexane system.*** Sound velocity and density were determined as a function of temperature for solutions of 9.64, 25.54, 82.33, and 94.78 wt % benzene in hexane. From these data, isotherms of sound velocity were plotted in Figure 1. Using solution theory, one would expect mixtures of benzene and hexane to be almost ideal solutions allowing for some small interaction of the $\pi$ electron structure of benzene with hexane. However, the isotherms show significant curvature and hence deviation from ideal behavior. As the temperature increases, the deviation tends to remain constant. Either there is extreme particle interaction or the planar benzene rings radically disturb the equilibrium distribution of hexane. Further investigation is required to elucidate this phenomenon.

***Benzene-methanol system.*** In examining the isotherms of Figure 2 obtained from data on the sound velocity-temperature relationships for compositions of 5.68, 25.02, 43.59, 85.45, and 94.74 wt % benzene in methanol, three interesting points occur.

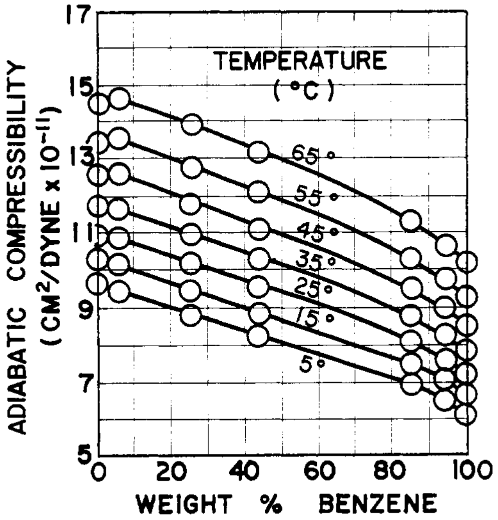

**Figure 6.** Isotherms of adiabatic compressibility of benzene in methanol

First, the curvature for low concentrations of benzene increases as the temperature increases until a minimum is obtained. The formation of a minimum in sound velocity has also been observed in alcohol water systems by Giacomini and Derenzini (*5*). As the temperature increases, the minimum becomes more pronounced and shifts to higher concentrations of benzene. This phenomenon indicates that increased thermal motion affects the formation of the minimum in sound velocity.

Secondly, the isotherms at 25-30°C show no discontinuity or radical curvature indicating the absence of a CST at 29°C. This absence of a CST was also confirmed by

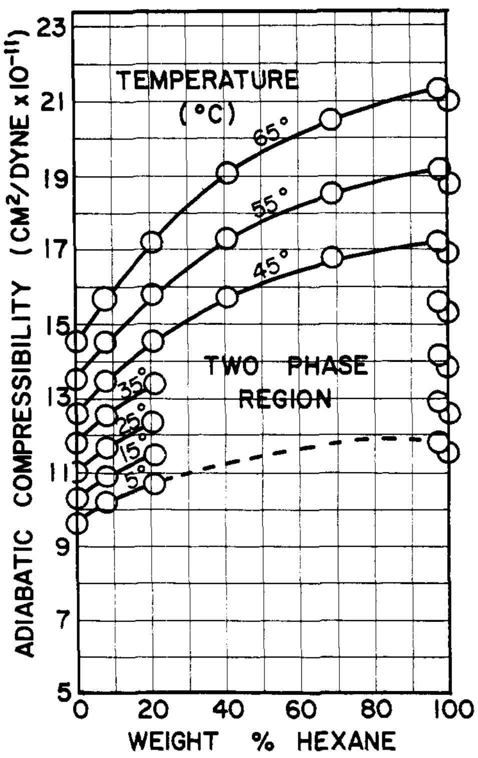

**Figure 7.** Isotherms of adiabatic compressibility of hexane in methanol

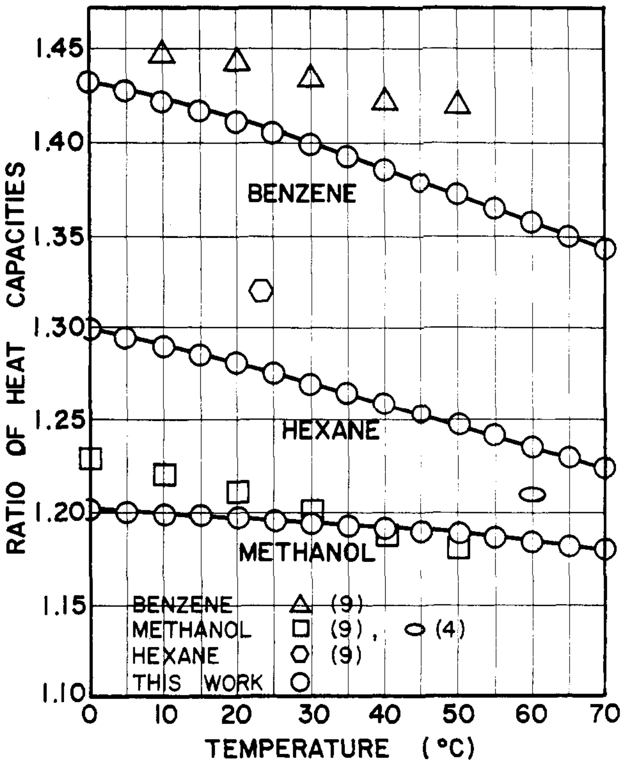

**Figure 8.** Comparison of calculated and experimental ratio of heat capacities

visual observation of a single homogeneous phase. If a CST does exist, it occurs at temperatures below 5°C.

Thirdly, even though the system does not exhibit a CST, it is more nonideal than the benzene-hexane system. This increase in nonideality is expected because of the polar hydroxyl group in methanol making methanol a dipole. Increasing the alcohol concentration decreases the dipoles because of agglomeration, and the sound velocity should decrease with concentration. An alternate explanation is that the addition of benzene to methanol changes the equilibrium complex particle distribution which, in turn, causes a deviation in the linearity in sound velocity.

***Hexane-methanol system.*** For hexane-methanol mixtures which have a reported CST between 35° to 42.6°C, the curvature in the sound velocity vs. composition plots should be relatively great. Figure 3 shows the isotherms of sound velocity obtained for compositions of 7.89, 20.93, 40.86, 68.92, and 97.62 wt % hexane. These results are in good agreement with work done previously by Smirnov and Predvoditelev (*14*). However, their results indicate a CST of 36.6°C compared to 42.5°C from Figure 3. Other literature indicate a CST determined by meniscus disappearance as high as 42.6°C (*5*) and as low as 35.0°C (*6*). Although the CST is very sensitive to impurities, the values determined by independent ultrasonic methods are in good agreement compared to values determined by visual observation. This agreement can be attributed to the nonhysteresis of the ultrasonic wave propagation (*11*).

***Adiabatic Compressibility.*** With least-squares correlated polynomials for density and sound velocity, the adiabatic compressibility was calculated for hexane, methanol, benzene, and various mixtures by the relation:

$$B_s = \frac{1}{c^2 \rho}$$

(Tabular compressibility data appear in Appendix A which has been deposited with the ACS Microfilm Depository Service.)

The adiabatic compressibility for hexane, benzene, and methanol increases with increasing temperature (Figure 4). However, the increase in adiabatic compressibility with temperature is not linear, even though sound velocity and density are approximately linear functions of temperature. The general agreement with literature values is good. A typical discrepancy is on the order of 6-18%. This discrepancy derives from the disagreement of sound velocity with literature values. For benzene, hexane, and methanol, the author's sound velocity data are less than the literature values by 1-3%.

The isotherms of the adiabatic compressibility for benzene-hexane mixtures (Figure 5) are linear functions of composition except at low concentrations of benzene. In contrast, the isotherms for the adiabatic compressibility of the benzene-methanol mixtures (Figure 6) show significant curvature with composition, especially at low concentrations of benzene in methanol. The rapid increase in adiabatic compressibility as a small amount of solute is added to solvent is probably due to the change in the equilibrium distribution of the associated states in the solvent and solute. The adiabatic compressibility of the benzene-methanol mixtures reaches a maximum greater than either of the pure components.

The isotherms of the adiabatic compressibility for the hexane-methanol system (Figure 7) show extreme curvature. For temperatures below the CST, the adiabatic compressibility of the light phase and heavy phase in-

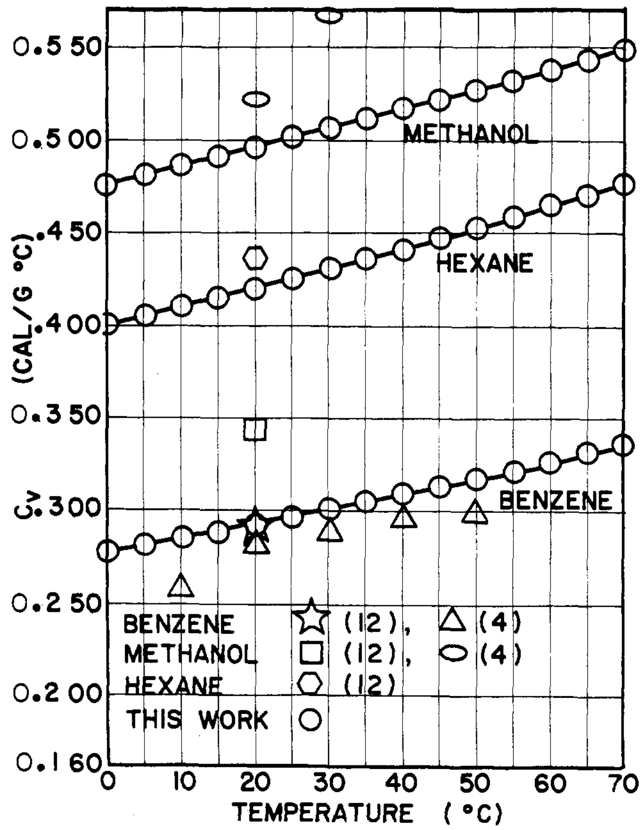

**Figure 9.** Comparison of calculated and experimental heat capacity at constant volume

creases with increasing solute concentration. At the CST, the adiabatic compressibility for both phases merges. The adiabatic compressibility for the homogeneous system (above the CST) passes through a maxima. It appears that no discontinuity exists at the CST, although additional data are needed to confirm this observation.

***Ratio of heat capacities.*** The ratio of the heat capacity at constant pressure ($C_p$) and the adiabatic compressibility. For mixtures the heat capacities were assumed to be at constant pressure ($C_p$) and the adiabatic compressibility. For mixtures the heat capacities were assumed to be additive. The ratio of heat capacities ($\gamma$) for hexane, benzene, and methanol decreases with increasing temperature (Figure 8).

***Heat capacity at constant volume.*** Constant volume calorimetry is tedious and difficult: therefore, the heat capacity at constant volume ($C_v$) is thus obtained more reliably by indirect calculation. $C_v$ can be determined easily and accurately from sound velocity, density, and $C_p$ data by using the relations:

$$c^2 = \frac{\gamma}{B_T \rho}$$

$$C_v = \frac{C_p^2}{C_p + T\alpha^2 c^2}$$

Figure 9 shows that $C_v$ increases with an increase in temperature as one would expect, although not necessarily in a linear manner. The agreement of the calculated values of $C_v$ with the literature values is good. For benzene the maximum deviation of 15.5% occurs at 50°C, whereas the minimum deviation of 1.4% occurs at 10°C. The deviations from literature values for hexane and methanol are 3.81 and 5.26%, respectively.

### Nomenclature

$B_T$ = isothermal compressibility, atm$^{-1}$
$B_S$ = adiabatic compressibility, atm$^{-1}$
$C_p$ = heat capacity at constant volume, cal/g °C
$C_v$ = heat capacity at constant volume, cal/g °C
$t$ = temperature, °C
$T$ = absolute temperature, K
$c$ = sound velocity, m/sec
$\rho$ = density, g/cm$^3$
$\alpha$ = thermal coefficient of expansion, °C$^{-1}$
$\gamma$ = ratio of heat capacities, $C_p/C_v$

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