P = pressure
P_c = critical pressure
P_c° = critical pressure in the classical (high-temperature) limit
P_{cM} = pseudocritical pressure of mixture
R = universal gas constant
T = absolute temperature
T_c = critical temperature
T_c° = critical temperature in the classical (high-temperature) limit
T_{cM} = pseudocritical temperature of mixture
V_c = critical volume
V_c° = critical volume in the classical (high-temperature) limit
V_{cM} = pseudocritical volume of mixture
c_1, c_2, c_3 = constants given by Equations 11, 12, and 13
d = density, moles per unit volume
m = molecular weight
y = mole fraction
z = compressibility factor
θ = reduced temperature
π = reduced pressure
ρ = reduced density
ω = acentric factor

Subscripts

c = critical
i = component i
M = mixture

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Isothermal Compressibility of Liquid Water at 1 Atm.

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Recent measurements of the velocity of sound in distilled ordinary water give the isothermal compressibility with a standard error of 0.002 × 10^{-6} bar^{-1}, one tenth that of direct determinations. At least at low temperatures, isothermal compressibilities from the velocity of sound should have fewer systematic errors than direct determinations. Interpolating equations represent the temperature dependence of the velocity of sound, u, of $1/u^2$, and of the isentropic and isothermal compressibilities. Acoustic and direct measurements together give an equation for the isothermal compressibility valid from 0° to 150° C. and to be considered a best estimate of the isothermal compressibility; a table is given to 110° C. The change of temperature of maximum density with pressure is −0.0200 ± 0.0003 deg. bar^{-1}.

THREE RELIABLE DETERMINATIONS of the velocity of sound in ordinary water (*1, 2, 8*) agree well and supersede previous measurements. The velocity of sound, u, is related to the isentropic compressibility, κ_S,

$$\kappa_S = -(\partial \ln V/\partial p)_S = (\partial \ln \rho/\partial p)_S$$

by the relation

$$\left(\frac{\partial \rho}{\partial p}\right)_S = \frac{1}{u^2} \tag{1}$$

where V is volume, ρ density, and p pressure, and the differentiation is made at constant entropy S. Equation 1 gives the static value of $(\partial\rho/\partial p)_S$, provided u is measured with waves of small amplitude at frequencies sufficiently below the region of dispersion that absorption is small. As absorption is proportional to the square of the frequency, f, in this range, the numerical requirement (*7*) is that $\alpha^2u^2/4\pi^2f^2 << 1$, where α is the attenuation coefficient, given for water at 25° C. by $\alpha/f^2 = 2.3 \times 10^{-16}$ neper sec.^{2} cm.$^{-1}$ (*10*). The measurements used were in the frequency range 10 to 70 MHz.; at 70 MHz. absorption was troublesome for the longest path length (*2*), but the value of u had not shifted.

The isothermal compressibility, κ_T,

$$\kappa_T = -(\partial \ln V/\partial p)_T = (\partial \ln \rho/\partial p)_T$$

may be calculated from κ_S by

$$\kappa_T = \kappa_S + \frac{T}{\rho^3 C_p}\left(\frac{\partial \rho}{\partial T}\right)_p^2 \tag{2}$$

and requires, in addition, a knowledge of the specific heat at constant pressure C_p, the absolute temperature, T, and the thermal expansivity.

ANALYSIS OF SOUND VELOCITIES

McSkimin (*8*) gave 37 values of the velocity of sound in water at atmospheric pressure from 20° to 75° C. Barlow and Yazgan (*1*) gave 43 values from 23° to 80° C. Carnvale, Bowen, Basileo, and Sprenke (*2*) gave values from 0° to 40° C.; their nine published values were the mean of 27 observations. This third set of data shows slightly less scatter than the other two. For least squares calculations, the sets were weighted in the ratio 37:43:27. The values of the compressibility calculated from McSkimin are systematically lower than those from Barlow and Yazgan by about 0.004×10^{-6} bar^{-1}; this is much less than the scatter in direct determinations of κ_T, yet this difference sets a lower limit to the standard error that can be obtained in a fit.

For the calculation of isothermal compressibilities the additional data were taken from the literature: specific heats from Stimson (*11*); the relation of practical and thermodynamic temperatures from Stimson (*12*); and densities and thermal expansivity from Kell (*4*). The practical temperature, t, used in the equations of this paper is that of the international practical temperature scale of 1948.

As the required data and numerical techniques were available, a study was also made of the temperature dependence of the velocity of sound, u, the isentropic compressibility, κ_S, and the quantity, $1/u^2$, which appears in Equation 1 and which is useful in the determination of change of density from measurements made under pressure. Rational functions were fitted to the data, as was done by Kell (*4*) in his investigation of the temperature dependence of the volume of water. A rational function is of the form

$$y(t) = R_{nm}(t) \equiv \frac{a_0 + a_1 t + a_2 t^2 + \cdots + a_n t^n}{1 + b_1 t + \cdots + b_m t^m} = \frac{\sum_{i=0}^{n} a_i t^i}{1 + \sum_{j=1}^{m} b_j t^j} \tag{3}$$

with $n + m + 1$ parameters to be determined. An ordinary polynomial is of the form R_{n0}. As the properties considered here are inherently positive, the relation $\ln y = R_{nm}(t)$ was also considered. While with small numbers of parameters the logarithmic form was occasionally better, when a good fit was obtained $y = R_{nm}$ was as good for the same number of parameters, and is reported as simpler for hand calculations.

The best functions found, the coefficients, and the standard errors of the fits are given in Table I. The analysis showed that κ_S, κ_T, and $1/u^2$ are best fitted by rational function R_{41} with 6 parameters. For u a polynomial was best.

DIRECT DETERMINATIONS OF ISOTHERMAL COMPRESSIBILITY

Kell and Whalley (*5*), whose direct determination—a direct determination is from *PVT* data—of the isothermal compressibility from 0° to 150° C. appears to be the most precise, gave 22 points from 0° to 150° C. with a standard error about ten times that of the acoustic ones. These values of Kell and Whalley were obtained by fitting polynomials to their compressions to 1000 bars. The suitability of such a power series has been examined by Macdonald (*6*), who finds that the use of different equations can produce variations of 0.1×10^{-6} bar^{-1} in the value of κ_T found for 1 atm. From his analysis, the particular polynomials used by Kell and Whalley seem unlikely to produce an error of more than 0.03×10^{-6} bar^{-1}, compared with the 0.02×10^{-6} bar^{-1} they claimed for each point, and compared with the standard error of 0.04×10^{-6} bar^{-1} of their 1-atm. values fitted by the quintic polynomial

$$10^6\,\kappa_T/\text{bar}^{-1} = 50.9804 - 0.374957t + 7.21324 \times 10^{-3}t^2 - 64.1785 \times 10^{-6}t^3 + 0.343024 \times 10^{-3}t^4 - 0.684212 \times 10^{-9}t^5 \tag{4}$$

A table calculated from Equation 4 has been published (*4*).

Two other direct determinations of the compressibility show relatively little internal scatter. Millero, Curry, and Drost-Hansen (*9*) made measurements at 14 temperatures from 2° to 55° C. at pressures to 18 bars; their deviation from the acoustic values, as seen from Figure 1, is about twice that of Kell and Whalley. Diaz-Pena and McGlashan (*3*) made eight measurements from 5° to 60° C. at pressures to 30 bars; at low temperatures their values are systematically high, and their temperature coefficient of the compressibility appears in error by -1×10^{-6} bar^{-1} per 50° C. Earlier work, which may be found through the references cited, is believed less reliable.

FUNCTION FOR EXTENDED RANGE

Figure 1 shows that direct determinations of κ_T and determinations from the velocity of sound determine the same property; however, the systematic errors differ. In the direct method, measurements are made relative to a vessel whose compressibility must then be determined in a separate experiment. Determinations from the velocity of sound do not involve this particular correction. With them, the compressibility of the vessel does not enter in measurements made at atmospheric pressure, and enters only as a second-order correction in measurements made under pressure. Hence, the acoustic method is to be preferred where the data needed to use Equation 2 are available.

In addition to fitting the four properties derived from acoustic properties as described above, a fit of the isothermal compressibility, including the 107 points from the velocity of sound as well as the direct determinations of Kell and Whalley (*5*), was made. The data of Kell and Whalley have ten times the standard error of those from acoustic measurements, so each value was given 1/100 the weight of the acoustic ones. They were included because: at sufficiently high temperatures the calculation of isothermal compressibilities from adiabatic ones involves a large correction and introduces errors, though significant errors seem unlikely here where the correction is 8% at 80° C., the highest temperature of these acoustic measurements; and the data of Kell and Whalley extend to 150° C., well above the range of the acoustic measurements. Accordingly, the function follows the more precise acoustic measurements at low temperatures and tends toward the values of Kell and Whalley at higher temperatures.

The function obtained was of the form $\kappa_T = R_{51}$. It was

$$10^6\kappa_T/\text{bar}^{-1} = (50.88630 + 0.7171582t + 0.7819867 \times 10^{-3}t^2 + 31.62214 \times 10^{-6}t^3 - 0.1323594 \times 10^{-6}t^4 + 0.6345750 \times 10^{-9}t^5)/(1 + 21.65928 \times 10^{-3}t) \tag{5}$$

with a standard error of 0.0021 × 10^{-6} bar^{-1}. The function representing κ_T from solely acoustic measurements in Table I has only positive signs; Equation 5 has only one negative sign—these functions are an efficient representation of κ_T in the sense that loss of significant figures through subtraction is unimportant. Table II gives compressibilities calculated from Equation 5. This agrees with the function for κ_T from Table I to the number of figures given over their common range. Between 0° and 150° C. the difference between Equation 4 and Equation 5 nowhere exceeds 0.11 × 10^{-6} bar^{-1}. Below −10° C. the two functions diverge rapidly, perhaps because of the denominator of Equation 5. In any event, below −10° C. the extrapolated compressibility must be considered uncertain to at least 1 × 10^{-6} bar^{-1}.

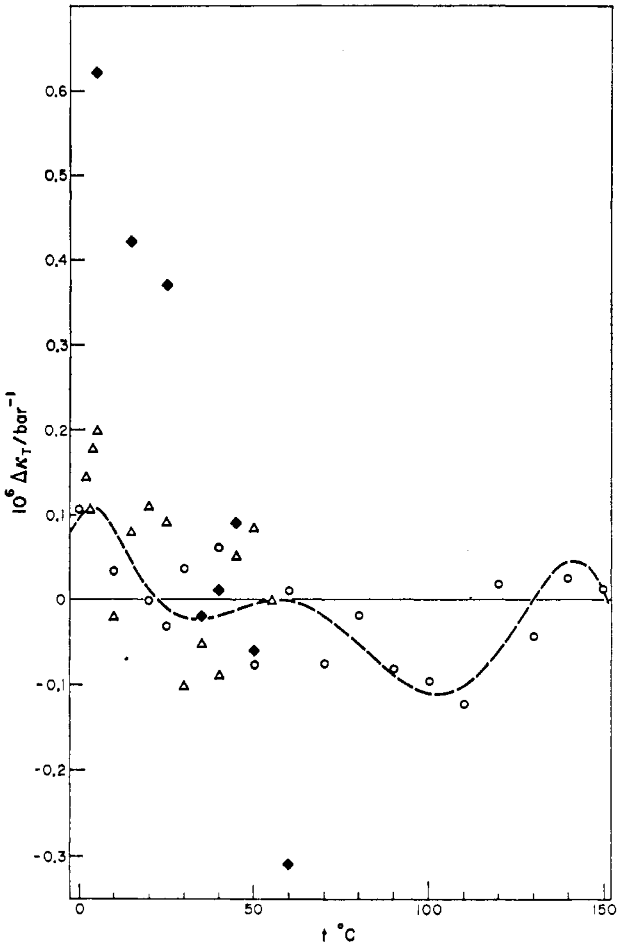

Figure 1. Differences between isothermal compressibility of water from Equation 5 and other sources

$\Delta\kappa_T = \kappa_T$ (other source) − κ_T (Equation 5)

Acoustic measurements from 0° to 80° C. give κ_T with standard error about twice width of central line

○ Kell and Whalley
△ Millero, Curry, and Drost-Hansen
◆ Diaz-Pena and McGlashan
— — — Equation 4

TEMPERATURE OF MAXIMUM DENSITY

The temperature of maximum density is the temperature at which

$$\left(\frac{\partial \rho}{\partial T}\right)_p = 0$$

Hence the change of temperature of maximum density with pressure is given by

$$\left(\frac{\partial T}{\partial p}\right)_{\text{max den}} = -\frac{\left(\frac{\partial}{\partial T}\left(\frac{\partial \rho}{\partial p}\right)_T\right)_p}{\left(\frac{\partial^2 \rho}{\partial T^2}\right)_p} \tag{6}$$

Taking the temperature dependence of the compressibility from Equation 5 and the thermal expansion from Kell (*4*) gives $(\partial T/\partial p)_{\text{max den}} = -0.01998$ deg. bar^{-1}, but the errors of curve fitting, aside from errors in the original data, make this uncertain to 1 or 2%. It should be taken as $(\partial T/\partial p)_{\text{max den}} = -0.0200 \pm 0.0003$ deg bar^{-1}.

Table II. Isothermal Compressibility of Water from Equation 5

T, ° C.	$10^6\kappa_T$, Bar^{-1}	T, ° C.	$10^6\kappa_T$, Bar^{-1}	T, ° C.	$10^6\kappa_T$, Bar^{-1}
−20	64.5	25	45.250	70	45.170
−15	59.5	30	44.774	75	45.621
−10	55.86	35	44.444	80	46.149
−5	53.06	40	44.243	85	46.751
0	50.886	45	44.158	90	47.428
5	49.171	50	44.179	95	48.18
10	47.811	55	44.296	100	49.01
15	46.736	60	44.504	105	49.91
20	45.895	65	44.796	110	50.90

Table I. Coefficients of Equation 3 to Represent Properties Determined from Acoustic Measurements (Temperature range 0° to 80° C.)

Coefficients	u, MSec.$^{-1}$	$10^6\kappa_S$, Bar^{-1}	$10^6\kappa_T$, Bar^{-1}	$10^{12}/u^2T$, Cm.$^{-2}$ Sec.^{2}
a_0	1402.385	50.85541	50.88539	50.84744
a_1	5.03522	0.2962265	0.5200294	0.2816838
10^3a_2	−58.3087	1.864987	2.140826	1.566732
10^6a_3	345.300	−1.71515	7.37010	−2.04020
10^9a_4	−1645.13	37.2105	44.0991	28.1355
10^9a_5	3.9625			
10^3b_1		13.07477	17.77306	12.72426
Standard error of function	0.038	0.0016	0.0014	0.0015
Temperature of extremum t,° C.	74	64	46.5	74

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Thermal Conductivity and Viscosity of Biphenyl and the Terphenyls

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The thermal conductivities and viscosities of liquid biphenyl and the three terphenyls were measured over a range of temperatures using the hot-wire and capillary viscometer methods. These properties were also calculated as a function of temperature in the vapor phase to provide data for calculation of the performance of these compounds in heat transfer and other applications. Equations for the thermal conductivity of vapors at low pressure were formulated directly from a general equation fitted to the tabulated data of Bromley and Wilke.

THE LIQUID AND VAPOR VISCOSITY and thermal conductivity values of biphenyl and the three isomeric terphenyls were determined to provide data for use in heat transfer calculations and engineering design of heat transfer equipment. Because of their good radiation and thermal stability, the polyphenyls are useful as nuclear reactor coolants and in other high temperature heat transfer applications.

The purity (*12, 13*) of the samples used in the viscosity and thermal conductivity measurements was:

Biphenyl	99.95%
o-Terphenyl	99.9%
m-Terphenyl	99.5%
p-Terphenyl	99.99%

The samples of biphenyl, *o*-, and *m*-terphenyl were prepared by an initial vacuum fractional distillation of commercial materials, and then these batches were refined further by repeated fractional freezing. The *p*-terphenyl was purified by recrystallization from benzene. The purity of these materials was checked by vapor phase chromatography with a flame ionization detector.

All experimental temperatures quoted were measured with platinum resistance thermometers which had been calibrated by the National Bureau of Standards.

VISCOSITY

Liquid Viscosity. The viscosities of liquid biphenyl, *o*-terphenyl, and *m*-terphenyl were measured on 1-ml. samples using a Cannon-Manning semimicroviscometer; with *p*-terphenyl a Cannon-Ubbelohde semimicroviscometer was used. Viscosity measurements were made using constant temperature baths controlled to ±0.006° C. at 98.9° C. and ±0.02° C. at higher temperatures. The viscometer calibration runs with water and the measurements on the polyphenyls were done in accordance with ASTM standard D 445-52T, and the observed kinematic viscosities are listed in Table I.

These data are fitted to the following Andrade equations:

Biphenyl $\log \eta = -1.7080 + 634.8/T$ for $370 \leq T \leq 480°$ K. (1)

o-Terphenyl $\log \eta = -2.4604 + 1153.6/T$ for $370 \leq T \leq 560°$ K. (2)

m-Terphenyl $\log \eta = -2.0444 + 977.0/T$ for $370 \leq T \leq 590°$ K. (3)

p-Terphenyl $\log \eta = -1.6965 + 791.0/T$ for $490 \leq T \leq 620°$ K. (4)

The kinematic viscosity values can be converted to dynamic viscosities in centipoises by multiplying by the following liquid densities, ρ_L (*5, 11*):

Biphenyl $\rho_L = 1.0145 - 0.0328 \times 10^{-2}t - 0.0138 \times 10^{-4}t^2$ for $100 \leq t \leq 450°$ C. (5)

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