

THE COMPRESSIBILITIES AND THERMAL PRESSURE COEFFICIENTS OF CERTAIN LIQUIDS

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ABSTRACT

Values for the compressibilities of heptane, acetone, carbon tetrachloride, benzene, carbon disulfide, ethylene chloride, ethylene bromide and bromoform, obtained by Westwater, Frantz and Hildebrand from their direct measurements of the thermal pressure coefficient, $(\partial p/\partial T)_v$, were subject to a small error which is here corrected. The corrected values are compared with some recalculated from the adiabatic compressibilities directly measured in 1913 by Tyrer, and obtained recently by Freyer, Hubbard and Andrews by the aid of a sonic interferometer. The data from the three sources and methods show excellent agreement. Values are given for the constant $v^2 T(\partial p/\partial T)_v$, from which can be calculated the coefficients of thermal pressure or of compressibility at various temperatures by the aid of existing data for the densities and coefficients of expansion. In the following list the first number for each substance represents the coefficient of thermal pressure at 20°, the second the compressibility at $20^\circ \times 10^7$ and the third the value of the above mentioned constant: Heptane, 8.66, 1430, 5420; acetone, 11.32, 1260, 5305; carbon tetrachloride 11.47, 1060, 1325; benzene, 12.58, 966, 4800; carbon disulfide, 12.67, 938, 2340; ethylene bromide, 15.20, 633, 936; ethylene chloride, 14.17, 818, 2640; bromoform, 15.32, 594, 537. The unit of pressure is the atmosphere, v is the specific volume.

NOT long ago, the writer, with the collaboration of W. Westwater and H. W. Frantz¹ published values for $(\partial p/\partial T)_v$ (which we will call the thermal pressure coefficient, $T(\partial p/\partial T)_v$ being the thermal pressure), for eight liquids and a number of their mixtures. These values were directly determined by making use of what was in principle a constant volume thermometer. From them the authors calculated the corresponding compressibilities by the aid of the coefficients of expansion. The compressibilities so obtained were somewhat higher than many of those recorded by other observers. Part of the disagreement is due to an error in our calculation. We used the equation $(\partial p/\partial T)_v = \alpha/\beta$, where α and β are, respectively, the coefficients of expansion and compressibility. This is true at 0°C, but since the coefficient of expansion is ordinarily defined as $\alpha = (1/v_0) (\partial v/\partial T)_p$, and the coefficient of compressibility as $\beta = (-1/v) (\partial v/\partial p)$, where v is the specific volume at 1 atmosphere and $t^\circ\text{C}$, v_0 the same at 0°C, our values for β should be multiplied by v_0/v . In giving corrected values, we have availed ourselves of the data given in the International Critical Tables, except that the coefficient of expansion and density of bromoform are from the recent measurement in this laboratory.² The resulting values are still larger than most of those found in the literature,

¹Westwater, Frantz and Hildebrand, Phys. Rev. **31**, 135 (1928).

²A. Sherman and J. Sherman, J. Am. Chem. Soc. **50**, 1119 (1928).

but are strikingly confirmed by two sets of values, one by Tyrer³ calculated from the observed adiabatic compressibility, and another recently published by Freyer, Hubbard and Andrews,⁴ who determined the velocity of sound by a sonic interferometer, which gives the adiabatic compressibility from which, in turn, the isothermal compressibility was calculated. This calculation requires data for the density, the thermal expansion and the specific heat. The last named experimenters used the same data for these quantities as were used by Tyrer, but since newer data are available, we have recalculated their results for the liquids we measured by the aid of data taken from the International Critical Tables.

Table I gives in columns 2 and 3 the adiabatic coefficients of compressibility at 20°C, obtained for these liquids by Tyrer and by Freyer, Hubbard

TABLE I.* Thermal pressure coefficients and compressibilities at 20°C. The unit of pressure is the atmosphere.

Liquid	Adiabatic compressibility		Specific heat	Density, $\rho \times 10^3$	$\partial v/\partial T$	Thermal pressure coef. $\frac{\partial p}{\partial T}$		Isothermal compressibility, $\beta, \times 10^5$		$v^2 T \partial \beta / \partial T$
	Tyrer F., H. & A.	Freyer, H. & A.				Tyrer, F., H. & A. W., F. & H.	Tyrer, F., H. & A. W., F. & H.			
Heptane	111.4			0.6836	1813	8.61	8.66	143.9	143.0	5420
Acetone	90.6		2.182	0.7901	1805	11.35	11.32	125.6	126.0	5305
Carbon tetrachloride	72.45	72.8	0.836	1.5941	763	11.54	11.49	105.3	105.8	1325
Benzene	66.25	65.8	1.69	0.8787	1382	12.68	12.73	95.8	95.4	4800
Carbon disulfide	59.95	59.8	1.005	1.2624	942	12.78	12.82	93.0	92.7	2340
Ethylene bromide				2.1805	441		15.20		63.3	936
Ethylene chloride				1.2537	926		14.17		81.8	2640
Bromoform	41.2			2.8912	315		15.32		59.4	537

* The author is indebted to Mr. A. Wachter for help in the calculations.

and Andrews, respectively. The original observations extend through a range of 50 to 80 degrees but we reproduce here only the values for 20°, since the variation with temperature is adequately taken care of by a relation given below. The specific heats, in column 4, are probably subject to greater error than any of the other factors involved, but fortunately the formula whereby the isothermal compressibilities are calculated reduces the error to about one-third. In the sixth column we give $(\partial v/\partial T)_p$ instead of the ordinary coefficient of expansion, to avoid the confusion mentioned in the opening paragraph. In the seventh and eighth columns are given the values of $(\partial p/\partial T)_v$, a very important thermodynamic quantity, calculated from the adiabatic compressibilities, β_H , from the two sources, by aid of the formula

$$\left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{\beta_H}{\rho \partial v/\partial T} + \frac{0.1013T}{C_p} \cdot \frac{\partial v}{\partial T}\right)^{-1}$$

In the ninth column are the values of the same coefficient directly determined by the author and his collaborators.

The next three columns give values of the isothermal compressibility,

$$\frac{1}{v} \left(\frac{\partial v}{\partial p}\right)_T \text{ or } \rho \left(\frac{\partial v}{\partial p}\right)_T,$$

³ Tyrer, J. Am. Soc. **103**, 1675 (1913).

⁴ Freyer, Hubbard and Andrews, J. Am. Chem. Soc. **51**, 759 (1929).

where ρ is the density corresponding to each value of the coefficient of thermal pressure, calculated from the latter by the aid of the density and expansion coefficient, by the aid of the relation

$$\left(\frac{\partial \rho}{\partial T}\right)_v \left(\frac{\partial v}{\partial \rho}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_\rho.$$

The agreement between the values of the coefficients of thermal pressure and of compressibility from the three sources is very striking, especially when it is remembered that they are derived from as many independent methods, and it goes far towards establishing the fact that the lower values for the compressibility obtained for these substances by many other investigators are of inferior accuracy.

The variation of β with temperature can be calculated with considerable accuracy by the relation used by Westwater, Frantz and Hildebrand, i.e. that $v^2 T (\partial \rho / \partial T)_v$ is constant. Evidence for this was given in their paper and it is further confirmed by the data of the other workers cited in this paper. We will give here only the values of the constant for benzene.

Temperature:	10	20	30	40	50	60	70
Tyrer:	4800	4815	4830	4830	4810	4820	4810
F., H. and A.:	4813	4820	4815	4820	4805		

We therefore give in the last column of Table I, values of this constant, representing weighted means, from which, by the aid of values of the density and of $(\partial v / \partial T)_\rho$, readily obtainable from the International Critical Tables, one may readily calculate either coefficient, that of thermal pressure or of compressibility at 1 atmosphere and any ordinary temperature.