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Adiabatic Compressibility of Liquid Ammonia

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Values of the adiabatic compressibility of pure liquid ammonia, derived from sound speed measurements between the freezing point and the normal boiling point are reported. The sound speed was a linear, decreasing function of the temperature. A comparison with other values is given.

VALUES for the adiabatic compressibility of pure liquid ammonia at its vapor pressure between the normal freezing and boiling points are reported. These data were obtained as a part of a detailed study of the physical properties of metal-ammonia solutions and are presented here because of the scant information available on the pure solvent in this temperature and pressure range.

The adiabatic compressibility, defined by (*4*)

$$\beta_s = -(\partial v/\partial p)_s/v \tag{1}$$

was determined by measuring the velocity of sound, C_s, using the published values of the density (*5*), ρ, and the relation (*6*)

$$\beta_s = 1/C_s^2\rho \tag{2}$$

The liquid ammonia was contained in a cylindrical quartz cell 2.0 cm. long and 1.6 cm. in diameter. The velocity of sound was determined by a standard time-of-flight technique using pulsed 10 MHz. compressional waves generated by crystal transducers cemented to the outside of the cell (*6*). This system was calibrated by measuring the velocity in liquids with a well known velocity. The quartz sound cell was placed in a system in which the temperature was regulated to within ±0.1° K. between 200° and 240° K. The temperature was measured by copper-constantan thermocouples, calibrated in liquid N_2(~77° K.) and liquid NH_3(~240°) with interpolations from NBS tables (*3*), placed next to the sample cell. Ammonia, 99.95% pure NH_3 (Matheson Co.), was further purified by preparing a sodium-ammonia solution and allowing the solution to stand for at least 12 hours. The ammonia was then distilled from this solution into the previously evacuated (less than 10^{-3} torr) cell.

With the time-of-flight technique, it is possible to determine the sound velocity to within one part in 10^3 (*9*); however with the present system this was not possible owing to the temperature fluctuations; thus, for these experiments, the velocity as a function of the temperature was determined to about one part in 10^2. The determination of the velocity requires two inputs: the length of the cell; and the time between pulse and echo. As the cell was a modified optical absorption cell, its length could be determined in terms of known absorbances of standard solutions. The authors also made measurements of the sound speed in well known systems such as water, acetone, and methanol and obtained agreement to 3+ significant figures at room temperature. The length was 1.986 ± 0.009 cm. with a 95% confidence level. Time measurements were made using the delayed sweep of a Tektronix 555 oscilloscope. The manufacturer states the precision of the time base to be one part in 10^4 (on the scale used) with an accuracy of 0.2%. Thus a precision of better than one part in 10^3 is attainable if the pulse initiation point can be determined with arbitrarily high precision. In the present apparatus, the measurement of the time between the original pulse and the first echo was limited by the width of the oscilloscope trace to a precision of one part in 10^3. Each datum reported is the average of four to 10 independent measurements of the time interval. Thus, the quoted over-all precision in C_s is reached.

The velocity was measured as the temperature of the system was changed between 194° and 240° K. All data were taken within 4 cm. of Hg of the vapor pressure. The experimental values of C_s are given in Table I and are plotted in Figure 1. Values of C_s obtained by Maybury and Coulter (*7, 8*) are also shown in Figure 1. There is considerable scatter in the data of Maybury and Coulter when compared with the present data.

The sound velocity data were fitted by a straight line in the form

$$C_s = C_0 - C_1T \tag{3}$$

where, by a least squares analysis (*1*), the values of C_0 and C_1 were determined to be

$$C_0 = 3209 \pm 3.6 \text{ meters per second}$$

$$C_1 = 6.19 \pm 0.05 \text{ meters per second degree}$$

The density data of Cragoe and Harper (*5*) are shown in Figure 2. They have determined the density of one part in 10^4. The present authors have chosen to fit this

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Table I. Sound Velocity in Liquid Ammonia

T, °K.	C_s, Meters/Second
240.0	1715
233.0	1775
228.0	1795
219.4	1850
218.7	1860
215.3	1876
213.8	1886
212.5	1897
210.9	1906
210.6	1904
210.5	1909
208.8	1920
208.5	1920
208.3	1923
206.8	1930
206.3	1934
206.1	1937
204.4	1946
204.2	1949
203.6	1948
202.3	1959
201.6	1962
201.2	1963
200.8	1968
199.6	1975
199.1	1979
198.5	1982
196.0	1998

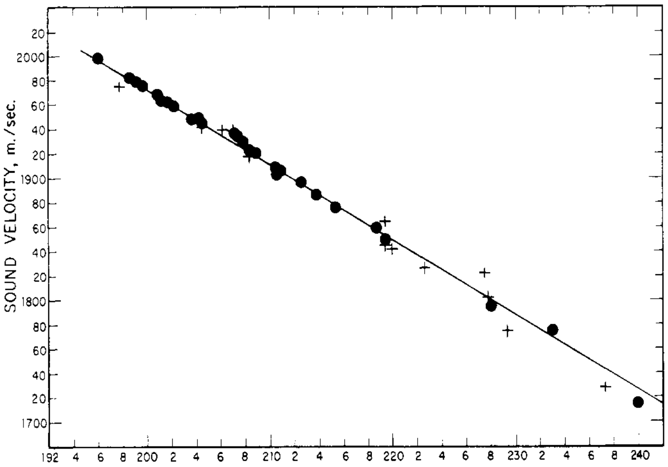

Figure 1. Velocity of sound in liquid ammonia along the vapor pressure curve

● Present data

\+ Data of Maybury and Coulter (*7, 8*)

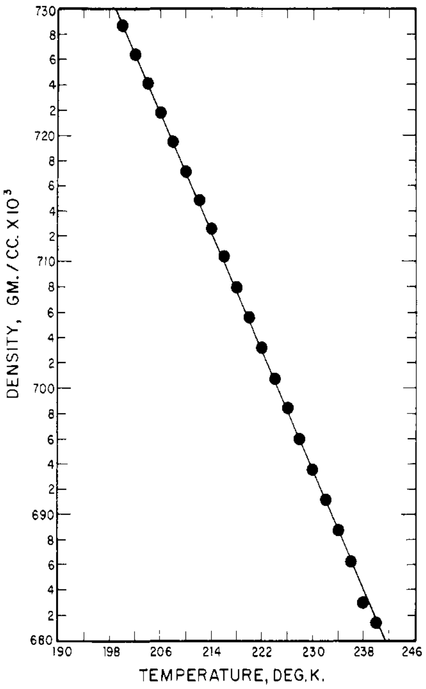

Figure 2. Density of liquid ammonia according to Cragoe and Harper (*5*)

Note the linear form of the curve

Table II. Compressibility of Liquid Ammonia

T, °K.	C_s, Meters /Second	ρ, Grams/Cc.	β_s, Sq. Cm./Dyne
240.2	1724	0.6814	49.38×10^{-12}
238.2	1736	0.6830	48.52×10^{-12}
236.2	1749	0.6863	47.63×10^{-12}
234.2	1761	0.6888	46.82×10^{-12}
232.2	1773	0.6912	46.04×10^{-12}
230.2	1786	0.6936	45.20×10^{-12}
228.2	1798	0.6960	44.44×10^{-12}
226.2	1810	0.6984	43.71×10^{-12}
224.2	1823	0.7008	42.94×10^{-12}
222.2	1835	0.7032	42.23×10^{-12}
220.2	1848	0.7056	41.50×10^{-12}
218.2	1860	0.7079	40.83×10^{-12}
216.2	1872	0.7103	40.17×10^{-12}
214.2	1885	0.7126	39.49×10^{-12}
212.2	1897	0.7149	38.87×10^{-12}
210.2	1900	0.7172	38.26×10^{-12}
208.2	1922	0.7195	37.62×10^{-12}
206.2	1934	0.7218	37.04×10^{-12}
204.2	1947	0.7241	36.43×10^{-12}
202.2	1959	0.7264	35.87×10^{-12}
200.2	1971	0.7287	35.32×10^{-12}
198.2	1984	0.7309	34.76×10^{-12}
196.2	1996	0.7332	34.23×10^{-12}
194.2	2008	0.7354	33.72×10^{-12}

data with a straight line in the temperature range 200° to 240° K. and have obtained

$$\rho = D_0 - D_1 T \qquad (4)$$

where

$$D_0 = 0.9646 \pm 0.0010 \text{ gram per cc.}$$

$$D_1 = (1.1776 \pm 0.0048) \times 10^{-3} \text{ gram per cc. degree}$$

The uncertainties in the numerical coefficients in Equations 3 and 4 were fixed by standard least squares procedures (*1*) and represent one standard deviation.

The compressibility, calculated from Equation 2, is given in Table II and is shown in Figure 3. An analytical expression for the compressibility, obtained by combining Equations 2, 3, and 4, is:

$$\beta_s = (A_0 + A_1 T + A_2 T^2 + A_3 T^3)^{-1} \qquad (5)$$

where

$$A_0 = D_0 C_0^2 = 0.9935 \times 10^{11} \text{ dyne/sq. cm.}$$

$$A_1 = -(2D_0 C_1 C_0 + D_1 C_0^2) = -0.5045 \times 10^{9} \text{ dyne/sq. cm. degree}$$

$$A_2 = (D_0 C_1^2 + 2D_1 C_1 C_0) = 0.8374 \times 10^{6} \text{ dyne/sq. cm. degree}^2$$

$$A_3 = -D_1 C_1^2 = -0.4512 \times 10^{3} \text{ dyne/sq. cm. degree}^3$$

This equation provides a representation of β_s for liquid ammonia at its vapor pressure over the temperature range

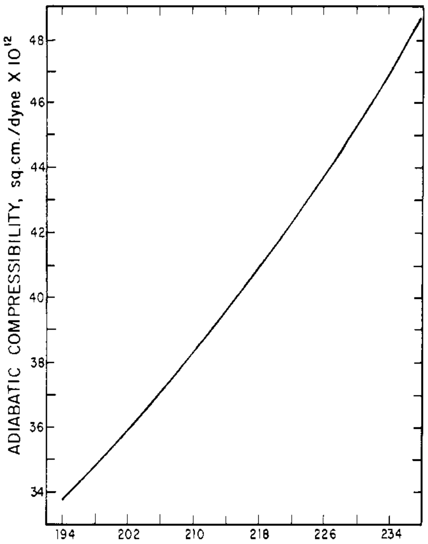

Figure 3. Adiabatic compressibility of liquid ammonia as calculated from the density and sound speed

from the freezing point to the normal boiling point.

Thermodynamic data on saturated NH_3 for the temperature range 222° to 238° K. was reported some time ago by the National Bureau of Standards (*2*). It is possible to calculate β_s from this data by using the thermodynamic relations (*4*)

$$\beta_s = \beta_T - Tk^2v/C_p \tag{6}$$

where

$$k = (\partial v/\partial T)_p/v = \frac{1}{T}\left[1 - (\partial h/\partial p)_T/v\right] \tag{7}$$

C_p is the specific heat at constant pressure, β_T is the isothermal compressibility, and h is the specific enthalpy. Since C_p, β_T, and $(\partial h/\partial p)_T$ were reported by the National Bureau of Standards (*2*), β_s can be calculated by combining Equations 6 and 7

$$\beta_s = \beta_T - \frac{v}{C_pT}\left[1 - \frac{2}{v}(\partial h/\partial p)_T + \frac{1}{v^2}(\partial h/\partial p)_T^2\right] \tag{8}$$

β_s as calculated in this manner is shown in Table III and compared with β_s obtained from Equation 5. With the exception of the point at 233.2° K., these data are higher than the present data by an average of 0.9%. The authors suggest that $(\partial h/\partial p)_T$ as reported by NBS is in error at 233.2° K.

Table III. Comparison of Present and Previous Work

T, ° K.	β_T, NBS	β_s, NBS	β_s, This Paper	γ
222.1	63.8	42.1	42.2	1.51
224.9	65.3	43.5	43.0	1.52
227.6	66.7	44.9	44.5	1.50
230.4	68.2	46.4	45.3	1.51
233.2	69.6	45.0	46.2	1.51
236.0	72.5	47.9	47.5	1.53
238.0	74.0	49.3	48.5	1.53

β_s is in units of (sq. cm./dyne) × 10^{-12}. β_T is in units of (sq. cm./dyne) × 10^{-12}.

By combining β_s and β_T, it is possible to obtain

$$\gamma = \beta_T/\beta_s = C_p/C_v$$

This has been done for the temperature range for which values of β_T have been reported. The results are shown in Table III with

$$\gamma_{av} = 1.52$$

NOMENCLATURE

β_s = adiabatic compressibility
β_T = isothermal compressibility
γ = heat capacity ratio
ρ = density
C_p = specific heat at constant pressure
C_s = speed of sound
C_v = specific heat at constant volume
h = specific enthalpy
k = volume expansivity
p = pressure
T = absolute temperature
v = specific volume

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