Pressure-Volume-Temperature Relationship of Liquid Ammonia[1]

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A piezometer was designed to measure the specific volumes of liquids at high pressures, especially with a view to studying substances with high vapor pressures at room temperature. The specific volumes of liquid ammonia were measured using the piezometer in the temperature range between –20–40°C under pressures up to 1800 atm with an accuracy better than 0.13%. The constants of the Tait equation were determined using the present data. The standard error of the experimental values from those calculated by the Tait equation is less than 0.07%.

The compressibilities of liquid ammonia at high pressures have been reported by Keyes (8), Tsiklis (9), and Date and Iwasaki (4). However, the experimental data covering a wide range of temperatures and pressures have not been available. Since the accurate measurements of compressibilities of liquid should provide some valuable information on its other physical properties, a more detailed study is desired for the measurements of the compressibility of liquid ammonia.

A new piezometer has been designed for the measurements of specific volumes of liquids at high pressures, the applicability of which was verified by use of benzene as a reference substance. The apparatus and the measurements for liquid ammonia at temperatures of −20°, 0°, 25°, and 40° C will be reported in this paper.

EXPERIMENTAL

Materials. Benzene was obtained in reagent grade and was used after being fractionated once. The boiling range was $80.0° \sim 80.2°$ C and the refractive index (n_D^{25}) was 1.4979.

Liquid ammonia was dried by use of metallic sodium and redistilled three times.

Apparatus and Method. Two piezometers, Types I and II, were designed for the measurement of compressibilities of liquids (Figure 1). Type I is used for the measurement in the temperature range from 0–40° C and Type II from −20–0° C.

The main part of the piezometer is made of borosilicate glass. Inner and outer diameters of a bulb at the upper part are 14 mm and 18 mm, respectively. Approximate volume of the bulb is 4 cm³. A capillary glass tube (10 cm in length, 3 mm in inner and 8 mm in outer diameter) is equipped at the bottom with a platinum spring indicator, a steel float, a steel joint, a rubber O-ring, and a steel screw. The small bulb in the lower part of Type II in Figure 1 serves as an expansion reservoir for liquid when the piezometer charged with liquid was brought up to room temperature.

The piezometer was carefully annealed, before using, by heating at 550° C for 15 min, followed by lowering the temperature at the rate of 1° C/min for 20 min. It was allowed to stand in the furnace overnight after the current was shut off. This procedure was required for obtaining reproducible results, as suggested by Adams (1).

Calibrations of the bulb and the tube in the piezometer were carried out by using mercury as filling liquid. The volumes were corrected for temperature and pressure according to the coefficients, $\alpha = 1.08 \times 10^{-5}/°$C and k
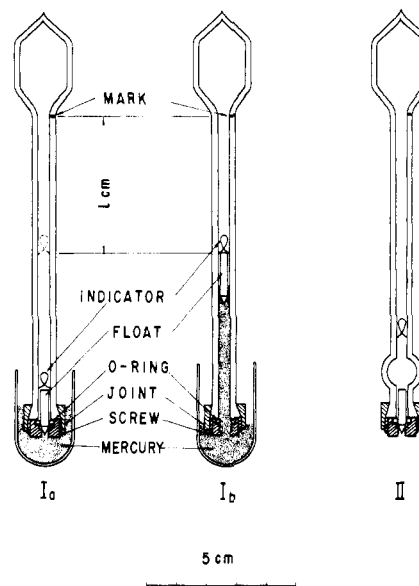
Figure 1. Two piezometers

Ia shows the state under the atmospheric pressure and Ib under the elevated pressure
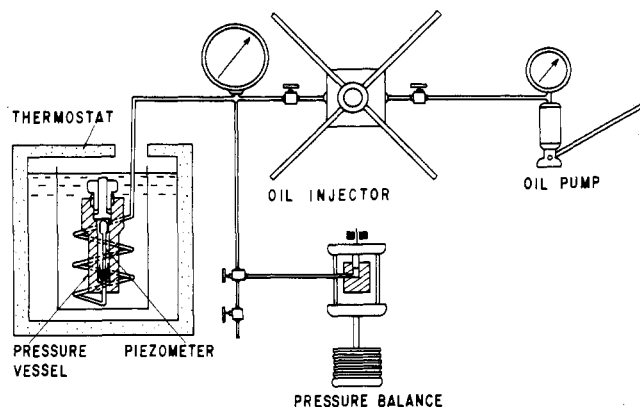

Figure 2. Schematic diagram of compressibility apparatus

$= 3.00 \times 10^{-6}$/atm, reported by Adams and Gibson (2). The volume of liquid, which occupied the space between the tube wall and the float, was calculated as a function of the length from the head of mercury meniscus to the upper end of the float.

The schematic diagram of a compressibility apparatus is shown in Figure 2. A steel high-pressure vessel was
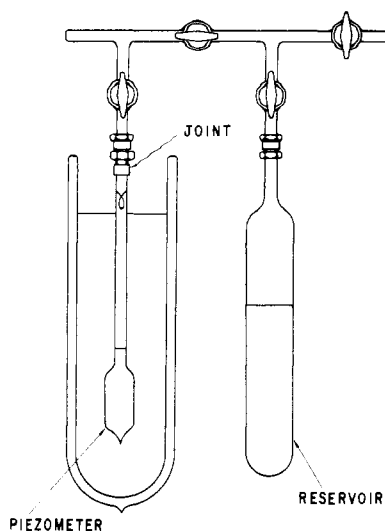
Figure 3. Apparatus for filling piezometer with liquid

Figure 4. Specific volume of liquid ammonia

immersed in a thermostat controlled to ±0.01° C. The temperatures were measured by use of mercury thermometers calibrated by the National Research Laboratory of Metrology (Japan) with an uncertainty of ±0.02° C. A hand oil pump was used for the generation of pressure, and the final adjustment was made with an oil injector. The pressure was applied to the vessel at 20 atm/min, and then maintained at a desired value for 20 min. A free-piston pressure balance, reported earlier (10), was used for the measurement of the pressure. The constant of the pressure balance was calibrated at room temperature against the vapor pressure of liquid carbon dioxide at 0° C with the accuracy of 2 parts in 10,000 at the pressure. Pressure-transmitting fluid is a mixture of vacuum oil with spindle oil.

The apparatus for filling the piezometer with liquid ammonia is shown in Figure 3. The piezometer was connected to a vacuum line by the joint, pumped down under heating at about 150° C for about 30 min to remove traces of adsorbed gases on its inner wall, and then stood at room temperature. The piezometer was cooled to about −60° C, and kept at the temperature until the desired amount of the liquid was condensed into it by opening the stopcock of the reservior. The piezometer was removed
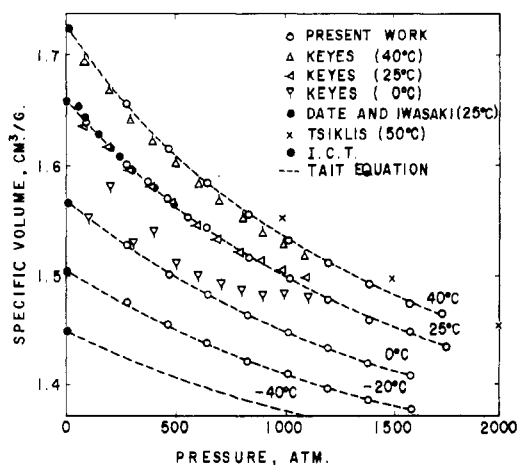
from the line while being cooled and was sealed with the float, the O-ring, and the screw to prevent the leakage of the liquid as shown in Figure 1, Ia or II. This operation was quickly performed in dry air. The air, which might be introduced into the piezometer during the removal of it from the line, was blown off by opening the screw at room temperature. The weighed piezometer was dipped into mercury and immersed in the pressure vessel filled with oil. A small bubble of air, which might have been trapped between the lower end of the float and the screw, was eliminated through the hole penetrating the wall of screw.

As the pressure in the vessel was raised, the compression of the liquid in the bulb and the capillary tube caused the mercury, the float, and the indicator to rise in the capillary tube as shown in Figure 1, Ib. When the pressure was subsequently released, the indicator remained at the position as it was under the elevated pressure. The length from the fiducical mark to the lower end of the indicator was measured to be accurate to within ±0.01 mm with a cathetometer. The specific volume of liquid is then given by an equation:

$$V_p = [(1 + \alpha t)(1 - kp)(v_0 + al) - v_1 + v_2]/m \qquad (1)$$

Table I. Experimental Specific Volumes (V_{exptl}) of Liquid Ammonia and Those Calculated by Tait Equation (V_{calcd})

	Sp vol, cm³/gram							
	−20° C		0° C		25° C		40° C	
Press., atm	V_{exptl}	V_{calcd}	V_{exptl}	V_{calcd}	V_{exptl}	V_{calcd}	V_{exptl}	V_{calcd}
. . .	1.5037[a]	. . .	1.5660[a]	. . .	1.6588[a]	. . .	1.7257[a]	. . .
95.3	. . .	. . .	. . .	. . .	1.6389	1.6384	. . .	. . .
283.1	1.4754	1.4721	1.5268	1.5250	1.6004	1.6003	1.6562	1.6538
376.5	. . .	. . .	. . .	. . .	1.5850	1.5840	. . .	. . .
469.5	1.4538	1.4541	1.5009	1.5023	1.5692	1.5691	1.6152	1.6161
563.0	. . .	. . .	. . .	. . .	1.5531	1.5552	. . .	. . .
654.9	1.4371	1.4379	1.4812	1.4823	1.5424	1.5425	1.5821	1.5849
841.4	1.4207	1.4231	1.4636	1.4642	1.5164	1.5191	1.5548	1.5579
1027.9	1.4093	1.4099	1.4478	1.4479	1.4977	1.4985	1.5299	1.5342
1214.1	1.3949	1.3973	1.4331	1.4330	1.4777	1.4799	1.5101	1.5132
1400.5	1.3839	1.3853	1.4189	1.4193	1.4593	1.4630	1.4911	1.4943
1587.2	1.3757	1.3743	1.4064	1.4065	1.4471	1.4477	1.4735	1.4771
1742.1	. . .	. . .	. . .	. . .	. . .	. . .	1.4644	1.4639
1773.6	. . .	. . .	. . .	. . .	1.4335	1.4334	. . .	. . .
Std error, %[b]	0.05		0.02		0.03		0.07	

[a] Specific volume at the saturated pressure, ref. 7. [b] Standard error = $\{ \Sigma[(V_{calcd} - V_{exptl}) V_{exptl}]^2/[n(n - 1)]\}^{1/2} \times 100$.

Table II. Constants of Tait Equation for Liquid Ammonia

Temp, °C	B, atm	C
−20	1336.8	0.1101
0	1036.4	
25	714.4	
40	567.1	

To ascertain the applicability of the new piezometer, the compression of benzene was measured at 25° C, since it had been accurately determined by Gibson and Kincaid (5) and by Bett et al. (3). The values of compression obtained by the present work are 0.03256 at 405.7 bar and 0.05658 at 811.4 bar, which are satisfactorily close to the values 0.03237 (3), 0.03262 (5) at 405.7 bar, and 0.05634 (3), 0.05678 (5) at 811.4 bar, respectively.

RESULTS

The experimental specific volumes of liquid ammonia at −20°, 0°, 25°, and 40° C up to 1800 atm are shown in Table I and in Figure 4. All points lie on a smooth curve with deviations less than 0.13% over the whole range of measurements. The values of specific volumes at the saturated pressures obtained by extrapolation agree with those presented in the International Critical Tables (7). The values obtained by Keyes (8), Tsiklis (9), and Date and Iwasaki (4) are included in Figure 4 for comparison with the present results. The present results at 25° C below 900 atm agree with those obtained by Date and Iwasaki and by Keyes within experimental accuracy, but the values above 900 atm differ from those by Keyes. The present data are consistently higher at 40° C and lower at 0° C than those of Keyes.

The Tait equation (6),

$$V_p = V_0 \{1 - C \ln [(B + p)/(B + p_0)]\} \qquad (2)$$

has been found to describe most of the isothermal data. The constants of this equation were calculated by means of the method of least squares with the present data. Table II gives the values of B and C for liquid ammonia at four temperatures. The specific volume at the saturated pressure (7) was chosen as V_0.

The standard errors of the experimental values from those calculated by the Tait equation are 0.05, 0.02, 0.03, and 0.07% at −20°, 0°, 25°, and 40° C, respectively.

NOMENCLATURE

a	=	cross-sectional area of capillary tube, cm²
B, C	=	constants of Tait equation (2)
k	=	compression of borosilicate glass, 1/atm
l	=	length from mark to lower end of indicator, cm
m	=	mass of liquid, gram
n	=	number of data
p_0, p	=	pressures, atm
t	=	temperature, °C
v_0	=	volume of glass bulb above mark, cm³
v_1	=	volume of indicator, cm³
v_2	=	volume of liquid occupying space between capillary tube wall and float, cm³
V_{calcd}, V_{exptl}	=	specific volumes calculated by Tait equation and experimental one, respectively, cm³/gram
V_0, V_p	=	specific volumes at pressures p_0 and p atm, respectively, cm³/gram
α	=	cubic expansion coefficient of borosilicate glass, 1/°C

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Phase Equilibrium of Carbon Dioxide and Light Paraffins in Presence of Solid Carbon Dioxide

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Cryogenic processes for separation of hydrocarbons from natural gas can be designed to operate as close to the freezing point of the feed stream as desired, providing the solubility limit of carbon dioxide in hydrocarbons is not exceeded. Carbon dioxide in excess of its solubility limit would precipitate out as a solid due to its relatively high triple point compared to hydrocarbons.

At the limit of saturated condition, the vapor-liquid equilibrium relationship, commonly represented by molal equilibrium ratios, should approach that of the solid-liquid-vapor equilibrium where the solid phase is pure carbon dioxide.

During experimental studies of the solubility of carbon dioxide in multicomponent hydrocarbon systems (3), equilibrium vapor and liquid compositions were determined to evaluate molal equilibrium ratios of hydrocarbons and carbon dioxide along the solid-liquid-vapor loci in the following systems:

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