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Some Thermodynamic Properties of Liquid Ammonia: *PVT* Data, Vapor Pressure, and Critical Temperature

Manfred Zander* and Wilhelm Thomas
Physikalisch-Technische Bundesanstalt, 3300 Braunschweig, Federal Republic of Germany

As a contribution to the project on thermophysical properties of ammonia, four liquid-phase isochores were measured from −50 to +65 °C with pressures ranging from saturation pressure to 370 bar. The vapor pressure was measured from 20 to 120 °C and the critical temperature was determined with the result t_c = 132.23 °C by the visual observation of the disappearance of the meniscus.

Growing interest in the thermodynamic and transport properties of ammonia requires that accurate tables covering a wide range of pressures and temperatures are produced and that computer programs for the machine calculation of these properties are provided. A project on thermophysical properties of ammonia was instituted by Professor Baehr in the Thermodynamic Department at the Hochschule der Bundeswehr, Hamburg, Federal Republic of Germany, which aims at producing a self-consistent formulation for these properties. After having critically evaluated the data available in literature, the project group came to the result that accurate new measurements were indispensable. Even though numerous investigations cover a considerable part of the *PVT* surface, the low-temperature, high-density fluid remained uninvestigated.

In cooperation with this project, 22 *PVT* data on four isochores in the liquid region, the vapor pressure, and the critical temperature of ammonia were measured in this laboratory.

The research grade ammonia (NH_3) used in the experimental work was supplied by the Linde AG, Munich, with the specification of 99.999% by volume minimum purity. Noncondensibles were removed from the sample by freezing in liquid nitrogen and pumping under vacuum. No further purification of this ammonia was deemed necessary.

Pressure–Volume–Temperature Behavior

For the measurements to investigate the relationship between the pressure p, volume V, and temperature T of a definite quantity m of the test gas, a constant-volume apparatus was employed. Basically this method involves charging a known mass of the fluid into a vessel of known volume and measuring the equilibrium pressure of the material at various temperatures.

The apparatus employed consisted essentially of a calibrated pressure vessel, a differential pressure null indicator, a thermostat, and devices for temperature and pressure measurement. The heavy-walled pressure vessel was made of A 286 stainless steel having a capacity of about 166 cm^3.

The volume of the pressure vessel and associated tubing was calibrated for the temperature and pressure range of interest by the use of the *PVT* data for liquid carbon dioxide of Michels (*1*). Several trials produced the mean value V_0 = 166.28 cm^3 at 0 °C and 1 bar. Additionally the volume was obtained by filling the system with distilled and degassed water and weighing the contents. The results of several water fillings confirmed the volume value obtained with carbon dioxide.

Table I. Experimental *PVT* Data for Liquid Ammonia

density, g cm^{-3}	temp (IPTS-68), °C	pressure, bar
0.5796	44.75	84.294
0.5794	50.58	163.233
0.5794	50.61	163.512
0.5792	55.30	226.709
0.5790	60.02	289.569
0.5788	64.63	352.278
0.6197	15.29	45.250
0.6195	20.48	131.448
0.6192	25.39	212.840
0.6190	30.14	291.268
0.6190	30.47	296.947
0.6190	30.48	296.719
0.6188	35.12	372.908
0.6611	−12.57	105.063
0.6609	−9.23	173.800
0.6606	−4.18	275.924
0.6604	−0.29	353.480
0.7032	−49.40	49.672
0.7030	−47.79	89.711
0.7028	−44.25	179.494
0.7026	−40.74	266.417
0.7024	−37.80	339.028

The effect of temperature and pressure on the volume can be represented as

$$V = V_0[1 + \alpha(T - T_0) + \beta(p - p_0)]$$

where α = 49.5 × 10^{-6} K^{-1} is the cubic thermal expansion coefficient for the vessel material and β = 1.6 × 10^{-6} bar^{-1} is the pressure expansion coefficient calculated according to the usual theory of elasticity. The subscripts "0" refer to standard conditions. The accuracy in the actual volume thus obtained is 0.05%.

A Ruska high-temperature differential pressure null indicator (DPI) was used to separate the test gas in the vessel from the nitrogen in the pressure transmission system. The vessel and DPI were completely immersed in a stirred oil bath. A platinum resistance thermometer, calibrated on the 1968 IPTS scale, was used for the measurement of temperature. The accuracy of the measured temperatures is 0.01 K.

The pressure was measured with a Ruska Type 5000.10 dead-weight gauge by balancing the test gas with nitrogen by means of the DPI (Figure 1). The accuracy of the measured pressures is 0.005%.

Samples were transferred from a weighing bottle to the vessel by condensation at liquid-nitrogen temperature. The mass of the charge was determined by differential weighing with an accuracy of 0.002%. Four different masses of ammonia were charged so that the low-temperature, high-density region was covered. The experimental results are shown in Table I.

Vapor Pressure

Values of the vapor pressure obtained from static measurements by using the constant volume apparatus described above are given in Table II. For these measurements the pressure vessel was filled up to the critical density (0.235 g cm^{-3}) and the weight of the ammonia gas column from the liquid level up to the DPI was taken into consideration.

The measurements reported here have been compared with earlier work. The existing vapor pressure data have been examined critically by Baehr (*2*) and he has reported a most

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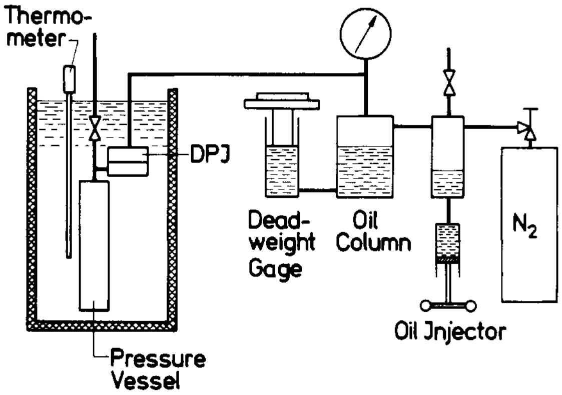

Figure 1. Schematic diagram of constant volume apparatus.

Table II. Vapor Pressure of Ammonia

temp (IPTS-68), °C	pressure, bar	temp (IPTS-68), °C	pressure, bar
20.413	8.6860	70.009	33.1159
20.413	8.6865	79.946	41.3367
20.411	8.6866	79.947	41.3355
30.176	11.7318	79.943	41.3342
30.176	11.7312	89.831	50.9625
30.176	11.7315	89.836	50.9648
40.221	15.6432	89.833	50.9634
40.225	15.6449	99.727	62.1559
40.225	15.6440	99.724	62.1540
50.173	20.4263	99.733	62.1571
50.175	20.4272	109.584	75.0963
50.177	20.4292	109.581	75.1018
60.092	26.1968	109.591	75.1130
60.091	26.1957	119.494	90.1583
60.099	26.2020	119.485	90.1426
70.007	33.1125	119.489	90.1521
70.012	33.1171		

reliable rational vapor pressure equation. The deviations between our experimental vapor pressures (Table II) and those calculated according to the equation of Baehr (*2*) are shown in Figure 2. The agreement is found to be within experimental precision.

Critical Temperature

The critical temperature was determined visually as the temperature at which the liquid meniscus disappeared in the middle of permanently sealed glass tubes. Such tubes were made in our glass shop from Duran 50 glass with a 10 mm outside diameter, having a wall thickness of 4.2 mm and a length of 150 mm. First the tubes were made of quartz, but these did not resist the internal pressure of about 113 bar at the critial temperature. Several tubes were filled to known densities close to the critical density (0.235 g cm^{-3}) taken from literature (*3*). The tube where the meniscus disappeared in the middle was taken for the observations. The temperature was then alternately lowered and raised until the meniscus appeared and disappeared. In Figure 3 it is shown that the critical point was passed very slowly during the experiments producing the very small rate of temperature change of about 0.03 K/h. The true critical temperature of ammonia was taken as the average of the temperatures at which the meniscus would just appear and disappear with the numerical result t_c = 132.23 ± 0.01 °C. In 1918 Berthoud (*4*) determined the value t_c = 132.3 °C for the critical temperature whereas in 1920 Postma found the experimental value t_c = 132.35 °C which is reported by the National Bureau of Standards (*5*).

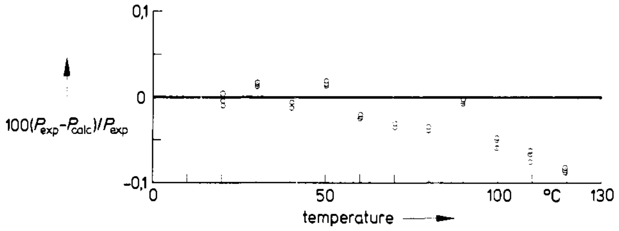

Figure 2. Comparison of experimental vapor pressures with equation of Baehr (*2*).

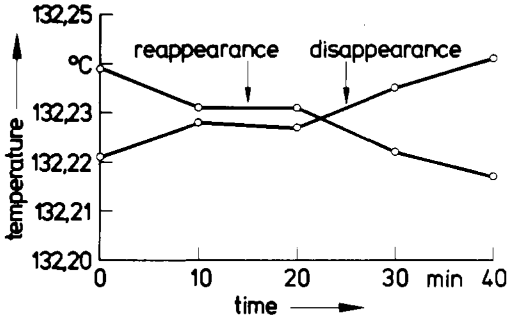

Figure 3. Noted temperatures while observing the disappearance and reappearance of the meniscus.

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