

P-V-T PROPERTIES OF AMMONIA WITH SMALL AMOUNTS OF WATER

Tabular data and examples of using same can be helpful to the engineer

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A high degree of metering accuracy is required in the pipeline industry for the custody transfer of pipelined fluids. A meter accuracy or meter factor to the nearest ten-thousandth part (0.01% or 0.0001) is desired for all meter proofs of liquid petroleum hydrocarbons. This meter accuracy has been retained in the pipelining of liquid anhydrous ammonia.

The Interstate Commerce Commission requires that all anhydrous ammonia transported interstate by pipeline must contain a minimum of 0.2% by weight water as a corrosion inhibitor. Water concentrations as high as 0.5% by weight would still meet agricultural grade ammonia specification provided a minimum purity of 99.5% by weight is met.

P-V-T data for liquid ammonia with water concentrations ranging from 0- to 0.5% by weight was not available in the literature. The P-V-T data which is most often referred to is that of Cragoe and Harper, U. S. Bureau of Standards No. 420 (1) and, Table 4, Properties of Liquid Ammonia, Circular of the Bureau of Standards, No. 142 (2). This P-V-T work undertaken by the Bureau of Standards for pure liquid anhydrous ammonia was done during the early 1920's. Based upon the desired meter accuracy, the need for P-V-T data for liquid ammonia with small amounts of water, and the confirmation of the P-V-T data for pure ammonia was evident.

Gulf Central Pipeline Co. requested a project for obtaining new P-V-T data through Gulf Interstate Engineering Co., the agent for the pipeline project. P-V-T, Inc., of Houston, Tex., was authorized to perform the laboratory work for the density measurements.

Laboratory work

The objective of the laboratory work was to generate data which could be used to modify the Cragoe and Harper density equation for pure liquid ammonia as a function of temperature by adding correction terms for pressure and water concentration. Both pressure and water concentration have to be linear with respect to density for this situation to work. A second approach was to curve-fit the data by computer.

The density data for temperature, pressure, and water

concentrations were selected to bracket pipeline operating conditions. Additional data was also obtained inside the brackets for confirmation.

Three grades of ammonia were selected: pure ammonia (99.95% minimum purity), ammonia with 0.2% water by weight, and ammonia with 0.5% water by weight. Five temperatures in conjunction with the three grades of ammonia selected were: 0°F, 35°F, 60°F, 80°F, and 100°F. The three grades of ammonia and five temperatures would give 15 isotherms. Densities at six pressures, saturation, 250-, 500-, 800-, 1,200- and 1,440 lb./sq. in. gauge were requested for each of the 15 isotherms. It was thought that the resulting 90 laboratory density measurements would be more than ample for a computer-fitted curve, if required.

The densities were measured in a standard P-V-T cell with special precautions taken to achieve the high accuracy required for these specific measurements.

The densities for pure liquid ammonia are summarized in Table 1. The temperatures and pressures were measured to the nearest tenth of a degree Fahrenheit and tenth of a pound per square inch gauge, respectively. The desired target pressures were achieved; however, some difficulty was experienced in achieving target temperatures, especially in the upper range. An additional set of data was obtained for all three grades of ammonia. The density measurement was tested by one additional data point taken at 32°F and 1985 lb./sq. in. gauge. The pressures as noted by the asterisk are the laboratory bubble point pressure corresponding to the particular temperature. The density values were calculated by use of the developed equation except those values noted by the double asterisk. These density values for saturated ammonia were taken from the Bureau of Standards Data. The difference of the measured density values and those calculated by use of the developed equation or Bureau of Standards Data are shown in the last column. Positive and negative differences are measured values above and below those calculated, respectively. Table 1 has a total of 38 measured density values for pure ammonia.

Table 2 summarizes 38 measured density values for liquid ammonia containing 0.2% water by weight. The laboratory-measured bubble point pressures are noted by the asterisk for their corresponding temperatures.

Density values for liquid ammonia containing 0.5% water by weight are summarized in Table 3. As with the other two liquid ammonia purities, 38 density values were obtained for a total of 118.

Development of the density equation

The equation for determining the density of liquid ammonia for temperatures ranging from 0- to 100°F, pressures ranging from 15- to 1,985 lb./sq. in. gauge and water concentrations ranging from 0- to 0.5% by weight was developed using the Cragoe and Harper density equation for pure saturated ammonia as a function of temperature. The newly developed density equation has three parts. The first part is the Cragoe and Harper equation. The second part is a correction for effect on the density of liquid pressures above the saturation pressure as a function of temperature, and the third part is a correction for the weight percent water contained in the liquid ammonia also as a function of a temperature.

The pressure and percent water correction factors were developed mathematically by use of the Taylor's Series Expansion:

$$(1) \quad f(x+h) = f(h) + xf'(h) + \frac{x^2 f''(h)}{2!} + \frac{x^3 f'''(h)}{3!} + (1)$$

The coefficients for the terms contained in both correction terms were obtained by processing the laboratory data. Only the first three terms of the Taylor's Series were significant for the pressure correction and the first two terms for the water correction. The density correction terms were therefore given to be linear in pressure and linear in composition with a term quadratic in temperature for the pressure coefficient. Ammonia vapor pressures were calculated by use of the Cragoe, Meyers, and Taylor equation (3). The overall representation of the data is within $\pm 0.04\%$ root mean square error. This is also the order of agreement of the ammonia data with the Bureau of Standards Data compared in Table 1. The equation for density of liquid anhydrous ammonia is:

$$(2) \quad \rho = \rho_{sat. NH_3} + \rho_{cor.}$$

$$\rho_{sat. NH_3} =$$

$$\frac{1 + 0.424805 \sqrt{133 - T^\circ C} + 0.015938(133 - T^\circ C)}{4.283 + 0.813055 \sqrt{133 - T^\circ C} - 0.0082861(133 - T^\circ C)}$$

$$\rho_{cor.} =$$

$$[3.97 \times 10^{-6} + 8.5 \times 10^{-9}(T^\circ F) + 2.08 \times 10^{-10}(T^\circ F)^2] (P - P_{sat.}) + [0.00596 + 3.1 \times 10^{-5}(T^\circ F)] (\% \text{ wt. } H_2O)$$

where $T^\circ C$ = temperature, °C
 $T^\circ F$ = temperature, °F
 P = system pressure, psia
 $P_{sat.}$ = ammonia vapor pressure, psia
 $\% \text{ wt. } H_2O$ = wt. % water in ammonia
 ρ = g./cc.

The equation for vapor pressure of ammonia is:

$$(3) \quad \log \frac{P_{sat.}}{14.696} = 27.376004 - 1914.9569/T^\circ K - 8.4598324 \cdot \log(T^\circ K) + 2.39309 \times 10^{-3}(T^\circ K) + 2.955214 \times 10^{-6}(T^\circ K)^2$$

Volume reduction tables

The P-V-T liquid ammonia density and vapor pressure equations were used to develop a set of volume reduction tables with 60°F, 0.30 wt. % water and equilibrium vapor pressure as the reference density. A partial table for the pressure correction is given in Table 4, and a partial table for the correction for water concentration is given in Table 5. These two tables allow one to correct a known volume of liquid anhydrous ammonia at an observed temperature, pressure, and analyzed water concentration to the above mentioned standard conditions selected by Gulf Central Pipeline Co. The tables give ratios of the above standard to observed and analyzed conditions within the following range of conditions: -28- to 115°F, 0- to 1,540 lb./sq. in. gauge and 0.0- to 0.5 wt. % water. Since the reciprocal of volume is density, these same tables also give the specific gravity ratios of observed and analyzed conditions to the Gulf Central Pipeline Co. standard. The tables also contain vapor pressures corresponding to the -28- to 115°F temperature range.

In keeping with the meter accuracy to the nearest ten-thousandth part, the weight percent water increment was set at 0.01% and 10 lb./sq. in. increments were used for pressures. A 1° increment was used for temperatures ranging from -28- to 35°F and 75- to 115°F and 0.5° increments from 35- to 75°F. The increments used for temperatures, however, were not in keeping with the meter accuracy; instead, the accuracy of field temperature measurements was used. An example on how the tables are used is as follows:

Given: The conditions of temperature, pressure and wt. % water in ammonia.

In the base correction section, a page is enclosed for illustration, find the page which applies to the given temperature and pressure. The temperature and pressure ranges for each page are noted in the upper right-hand corner. The observed temperatures, °F, run vertically and the observed pressures, lb./sq. in. gauge, in 10 lb./sq. in. increments run horizontally across each page. The base correction factor is then obtained corresponding to the given temperature and pressure. In the water correction section, a page is also enclosed for illustration; find the page which applies to the same temperature and weight percent water. The temperature and weight percent water ranges for each page are also noted in the upper right-hand corner. The observed temperatures, °F, run vertically and the analyzed weight percent water concentrations run horizontally across each page. Find the water correction factor corresponding to the given conditions; and, note the sign, plus or minus, in front of the factor. Water concentrations below 0.3% will be minus and those above 0.3% will be plus. The water correction factor is either added to or subtracted from the base correction factor. The resulting volume reduction fac-

tor at the given conditions, when multiplied with the volume of liquid anhydrous ammonia in any units, will result in a corrected volume in the same units based upon 60°F, 0.3 weight % water and equilibrium vapor pressure.

U.S. Bur. Stand. No. 420 (1921).

2. Circular of the Bur. Stand., No. 142, Tables of Thermodynamic Properties of Ammonia, 1923.

3. Cragoe, Meyers and Taylor, *J. Am. Chem. Soc.* 42 (1920) 206; Sci. Pap. U.S. Bur. Stand. No. 369 (1920).

Literature cited

1. Cragoe and Harper, *A.S.R.E.J.*, 7, (1920) 113; Sci. Pap

Table 1. Density data on pure ammonia.

Pressure, lb./sq. in. gauge	Temp., °F		Density, g./cc.		Difference	
	Measured	Calculated	Meas.	-Calc.		
0.2	15.9*	0.66220	0.66200*-	0.00020		
0.2	250.0	0.66320	0.66293	0.00027		
0.2	500.0	0.66430	0.66393	0.00037		
0.2	800.0	0.66540	0.66512	0.00028		
0.2	1200.0	0.66700	0.66671**	0.00029		
0.2	1440.0*	0.66790	0.66766**	0.00024		
35.0	51.6*	0.63630	0.63629**	0.00001		
35.0	250.0	0.63720	0.63718	0.00002		
35.0	500.0	0.63820	0.63831	-0.00011		
35.0	800.0	0.63950	0.63967	-0.00017		
35.0	1200.0	0.64130	0.64148**	-0.00018		
35.0	1440.0	0.64230	0.64256-	0.00026		
59.6	92.1*	0.61670	0.61706**	-0.00036		
59.6	250.0	0.61750	0.61788	-0.00038		
59.6	500.0	0.61890	0.61918	-0.00028		
59.6	800.0	0.62030	0.62075	-0.00045		
59.6	1200.0	0.62240	0.62284**	-0.00044		
59.6	1440.0	0.62350	0.62409	-0.00059		
78.9	135.5*	0.60140	0.60123**	0.00017		
78.9	250.0	0.60210	0.60191	0.00019		
78.9	500.0	0.60360	0.60340	0.00020		
78.9	800.0	0.60520	0.60518	0.00002		
78.9	1200.0	0.60760	0.60755**	0.00005		
78.9	1440.0	0.60900	0.60898	0.00002		
82.5	145.0*	0.59810	0.59820**	-0.00010		
82.5	250.0	0.59870	0.59884	-0.00014		
82.5	500.0	0.60020	0.60036	-0.00016		
82.5	800.0-	0.6020	0.60219	-0.00019		
82.5	1200.0	0.60440	0.60462	-0.00022		
82.5	1440.0	0.60580	0.60608	-0.00028		
82.5	1485.0	0.60600	0.60636	-0.00036		
96.6	186.0*	0.58630	0.58604**	0.00026		
96.6	250.0	0.58670	0.58647	0.00023		
96.6	500.0	0.58830	0.58816	0.00014		
96.6	800.0	0.59020	0.59018	0.00002		
96.6	1200.0	0.59280	0.59287	-0.00007		
96.6	1440.0	0.59440	0.59448	-0.00008		
32.0	1985.0	0.64658	0.64720	-0.00062		

*Bubble point pressure
 **These values correspond to the density of ammonia at saturation from the Bureau of Standards Data.

Table 2.

Density data on 99.8% wt. ammonia 0.2% wt. water.

Pressure, lb./sq. in. gauge	Temp., °F		Density, g./cc.		Difference	
	Measured	Calculated	Meas.	-Calc.		
0.2	15.7	0.66330	0.66320	0.00010		
0.2	250.0	0.66420	0.66413	0.00007		
0.2	500.0*	0.66520	0.66512	0.00008		
0.2	800.0	0.66630	0.66631	-0.00001		
0.2	1200.0	0.66800	0.66790	0.00010		
0.2	1440.0	0.66890	0.66885	0.00005		
34.8	50.9*	0.63740	0.63784	-0.00044		
34.8	250.0	0.63840	0.63874	-0.00034		
34.8	500.0	0.63950	0.63987	-0.00037		
34.8	800.0	0.64100	0.64123	-0.00023		
34.8	1200.0	0.64280	0.64304	-0.00024		
34.8	1440.0	0.64390	0.64412	-0.00022		
60.1	92.6*	0.61790	0.61822	-0.00032		
60.1	250.0	0.61880	0.61904	-0.00024		
60.1	500.0	0.62020	0.62035	-0.00015		
60.1	800.0	0.62170	0.62192	-0.00022		
60.1	1200.0	0.62380	0.62401	-0.00021		
60.1	1440.0	0.62500	0.62527	-0.00027		
74.1	122.9*	0.60590	0.60688	-0.00098		
74.1	250.0	0.60680	0.60761	-0.00081		
74.1	500.0	0.60840	0.60905	-0.00065		
74.1	800.0	0.61020	0.61077	-0.00057		
74.1	1200.0	0.61290	0.61307	-0.00017		
74.1	1440.0	0.61420	0.61445	-0.00025		
74.1	1485.0	0.61450	0.61470	-0.00020		
83.2	146.6*	0.59920	0.59931	-0.00011		
83.2	250.0	0.59980	0.59995	-0.00015		
83.2	500.0	0.6014	0.60147	-0.00007		
83.2	800.0	0.60330	0.60331	-0.00001		
83.2	1200.0	0.60580	0.60576	0.00004		
83.2	1440.0	0.60730	0.60722	0.00008		
100.2	196.6*	0.58460	0.58467	-0.00007		
100.2	250.0	0.58510	0.58504	0.00006		
100.2	500.0	0.58680	0.58677	0.00003		
100.2	800.0	0.58890	0.58884	0.00006		
100.2	1200.0	0.59170	0.59160	0.00010		
100.2	1440.0	0.59330	0.59326	0.00004		
32.0	1985.0	0.64821	0.64859	-0.00038		

*Bubble point pressure.

Table 3.

Density data on 99.5% wt. ammonia 0.5% wt. water.

Pressure, lb./sq. in. gauge	Temp., °F		Density, g./cc.		Difference	
			Measured	Calculated	Meas.	-Calc.
0.1	15.3*	0.66510	0.66505	0.00005		
0.1	250.0	0.66600	0.66599	0.00001		
0.1	500.0	0.66700	0.66698	0.00002		
0.1	800.0	0.66820	0.66817	0.00003		
0.1	1200.0	0.66970	0.66976	-0.00006		
0.1	1440.0	0.67060	0.67071	-0.00011		
35.0	50.9*	0.63990	0.63981	0.00009		
35.0	250.0	0.64080	0.64071	0.00009		
35.0	500.0	0.64190	0.64184	0.00006		
35.0	800.0	0.64320	0.64319	0.00001		
35.0	1200.0	0.64500	0.64500	-0.00000		
35.0	1440.0	0.64600	0.64609	-0.00009		
60.0	91.3*	0.62080	0.62064	0.00016		
60.0	250.0	0.62170	0.62147	-0.00023		
60.0	500.0	0.62300	0.62278	0.00022		
60.0	800.0	0.62460	0.62434	0.00026		
60.0	1200.0	0.62670	0.62644	0.00026		
60.0	1440.0	0.62790	0.62769	0.00021		
80.1	137.0	0.60410	0.60444	-0.00034		
80.1	250.0	0.60480	0.60511	-0.00031		
80.1	500.0	0.60640	0.60661	-0.00021		
80.1	800.0	0.60820	0.60841	-0.00021		
80.1	1200.0	0.61060	0.61080	-0.00020		
80.1	1440.0	0.61200	0.61224	-0.00024		
88.7	160.3*	0.59740	0.59725	0.00015		
88.7	250.0	0.59800	0.59782	0.00018		
88.7	500.0	0.59960	0.59941	0.00019		
88.7	800.0	0.60140	0.60132	0.00008		
88.7	1200.0	0.60390	0.60387	0.00003		
88.7	1440.0	0.60530	0.60539	-0.00009		
88.7	1485.0	0.60560	0.60568	-0.00008		
97.2	185.3*	0.58990	0.58998	-0.00008		
97.2	250.0	0.59050	0.59042	0.00008		
97.2	500.0	0.59220	0.59211	0.00009		
97.2	800.0	0.59420	0.59414	0.00006		
97.2	1200.0	0.59680	0.59684	-0.00004		
97.2	1440.0	0.59840	0.59847	-0.00007		
32.0	1985.0	0.65051	0.65067	-0.00016		

*Bubble point pressure

