Vapor–Liquid Equilibria in the Ammonia–Water System

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Isothermal vapor–liquid equilibrium data were obtained for the ammonia–water system at temperatures from 306 to 618 K and at pressures up to 22 MPa. The equilibrium temperatures, pressures, and the compositions of both liquid and vapor phases were measured simultaneously. The data were extended into the critical regions of the seven-phase envelopes at temperatures between the critical points of ammonia and water.

Introduction

Mixtures of ammonia and water occur in a variety of industries. Coal, shale oil, and other low-grade hydrocarbon feed stocks include significant amounts of nitrogen. The nitrogen is often produced in the form of aqueous ammonia solutions during the processing of such feed stocks. Since the economic production capacities of refineries and other fuel processing installations based on these feed stocks are always large, even a small percentage of nitrogen in the feed stock would produce huge aqueous streams containing ammonia and other water-soluble polar gases. The design of industrial equipment for the processing of these streams requires vapor–liquid equilibrium data on the ammonia–water system covering wide ranges of temperature and pressure.

Further, accurate extensive vapor–liquid equilibrium data for the ammonia–water system could be useful for thermodynamic model testing. Equation of state models that correlate other systems very well often fail to correlate polar and water-containing systems.

The earliest work on the ammonia–water system in the 19th century was done in connection with absorption of polar gases in water within the application range of Henry's law. Carius (1), Roscoe and Dittmar (2), Sims (3), Watts (4), Raoult (5), and Mallet (6) were the pioneers who worked on the ammonia–water system.

The eutectic region and the three-phase line in the ammonia–water system were studied by Pickering (7), Rupert (8, 9), Smits and Postma (10), Postma (11), Elliott (12), and Mironov (13). The existence of two solid hydrates of ammonia, $NH_3 \cdot H_2O$ and $2NH_3 \cdot H_2O$, was experimentally observed, questioned, and then confirmed. It was Mendeleev who first identified the existence of the compound NH_4OH through his analysis of the behavior of aqueous ammonia solutions (Mironov, ref 13). Mendeleev anticipated that NH_4OH could be obtained in the solid form, possibly with intense cooling.

Later, the main thrust of experimental investigation on the system was to obtain data which were suitable for the design of refrigeration equipment. The researchers who investigated the ammonia–water system in the first half of the 20th century are Perman (14, 15), Mollier (16), Wilson (17), Wucherer (18), and Clifford and Hunter (19). Kracek (20) correlated the experimental data on total vapor pressure of ammonia–water solutions available prior to 1930, using the Ramsay–Young rule. Wucherer (18) reported his measurements in three tables up to 1.961 MPa. Entries in the tables are bubble-point temperatures, dew-point temperatures, and vapor-phase compositions

vs. equilibrium pressure under constant composition. Wucherer prepared these tables by smoothing his experimental data graphically. The actual experimental measurements were never reported. However, his data are considered the most reliable obtained in the first half of the 20th century.

Kracek (20) and Wucherer (18) both criticized Wilson's data (17), stating that his data did not compare well with the data of other researchers. The ammonia–water tables in Perry's Handbook (21) were obtained by smoothing and extrapolating Wilson's measurements, reportedly (22) with the introduction of significant errors.

Scatchard et al. (23) claimed that the smoothed Wucherer PTy data on the ammonia–water system were not precise enough to apply the second law of thermodynamics and to caculate the entropies and free energies for refrigeration purposes. Therefore, they smoothed Wucherer's bubble-point data and applied the Gibbs–Duhem equation to calculate the vapor-phase composition.

Pierre (24) measured P–T data at constant composition from 1.2 MPa to 4.0 MPa, with up to 40 wt % ammonia in the liquid. These data compare well with Wucherer's data.

In order to check the Wucherer (18) experimental data and the Scatchard et al. (23) calculated PTy data, Macriss et al. (25) conducted a dew point study. They measured a few dew point pressures and temperatures from 1.531 to 3.591 MPa and from 338.87 to 389.59 K, at 0.47%, 0.93%, 1.76%, and 3.59% water in ammonia by weight. Their measured vapor-phase concentrations of water were less than in the data of Wucherer (18) and higher than the calculated concentrations of Scatchard et al. (23). Macriss et al. (25) reported that the lack of precision in early ammonia–water data led to serious errors in the design of commercial refrigeration units.

There have been several significant sets of ammonia–water data published since the Macriss et al. (25) compilation. Tsiklis et al. (26) published a phase diagram for the ammonia–water system from 370.15 to 623.15 K. The figure is very difficult to read. Two types of points are shown on the isotherms, experimental and correlated, but apparently most of the points are correlated.

Polak and Lu (27) measured vapor–liquid equilibria in dilute solutions of ammonia in water. Pawlikowsky, Newman, and Prausnitz (28) have also reported isothermal measurements at 373.15 and 423.15 K, covering a pressure range from 0.4 to 2.44 MPa.

Recently, Gillespie et al. (22) have measured vapor–liquid equilibria in the ammonia–water system from 313 to 589 K. The data cover a pressure range up to 20 MPa. While most of the data are of the PTx type, some PTxy measurements are also reported.

Guillevic et al. (29) have measured vapor–liquid equilibria in the ammonia–water system at 403.1, 453.1, and 503.1 K up to 7.0 MPa.

The literature on the ammonia–water system shows that the greatest difficulty was encountered in measuring the vapor-phase composition, when these measurements were attempted at all. The uncertainty in the amount of water present in the vapor phase became an issue and some of the data were judged to be inconsistent by Edwards et al. (30).

Most of the vapor-phase equilibrium compositions that have been reported were measured by passing the ammonia and

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water vapors thorugh a preweighed acid which was contained in an absorption apparatus. The mass of ammonia was determined by titrating the excess acid and that of the water was calculated by difference. In this type of analysis, the total mass of vapor absorbed in the acid is small compared to the mass of the absorption apparatus. The mass of water vapors determined by difference could fall into the range of uncertainty in the mass balance. There is also a very high cooling effect whenever mixed ammonia and water vapors are passed through the small opening of a valve. With the temperature decrease, condensation can occur in the valve body, affecting the analysis of the vapor phase.

The most likely consequence of these and similar experimental difficulties is that vapor analyses would tend to show less water than is present in the equilibrium vapors.

Errors in the liquid-phase composition might be due to insufficient mixing. Also, partial vaporization of the liquid sample in sampling lines and valves could lead to the measurement of high concentrations of the least volatile component in the liquid phase. This difficulty could occur even if the liquid sample was drawn from the system at the equilibrium temperature. It is therefore advantageous to keep the liquid sampling system supercooled.

Present Study

Materials Used. Electronic grade ammonia from Matheson Gas with 99.999% purity was used for all experiments. Deionized water with a resistivity of 18 MΩ was further distilled and was stored in a stainless steel reservoir for use. After the water was charged in the equilibrium cell it was degassed by connecting the equilibrium cell to a vacuum system.

Equilibrium Cells. Two different static cells were employed in the study. At temperatures up to 180 °C a visual cell with a volume of approximately 208 cm³ was used. At temperatures above 180 °C it was necessary to employ a blind cell because of diffficulties encountered in sealing windows. The blind cell has a volume of approximately 174 cm³.

Both cells were machined from 316 stainless steel. Ports were drilled through the cell bodies to permit insertion of temperature probes and to permit withdrawal and injection of fluids in both the liquid and vapor portions of the cells.

The cells were mounted in a rocker assembly inside an electric oven. When the visual cell was used, observations were made with the aid of mirrors because of concern for safety.

Temperature and Pressure Measurement. A platinum resistance probe (6.25 mm o.d. and 25 ohms) was inserted into the liquid phase in the cells. Temperatures up to 325 °C were measured with this probe. Above this temperature, E-type thermocouples were used. A high-precision digital multimeter (Fluke Model 8502A) indicated resistance or emf as needed. The resistance probe was calibrated against a standard probe to an accuracy of ±0.01 K. At the higher temperatures, several E-type thermocouples mounted in and on the equilibrium cell were used together to determine temperatures.

The oven temperature was regulated only through the regulation system provided by the manufacturer (the oven is Blue M, Model POM-256B-1.) It was impossible to set the oven temperature precisely. Also, some long-term temperature variations occurred because of changing ambient conditions. Because of difficulty in replicating the oven setting, each point is reported at its own temperature.

The temperatures reported are the averages of several readings made during the course of a given equilibrium determination. Variations in the measured temperatures were variable, but in most instances were less than 0.1 K.

Pressure was measured with a strain gauge transducer Vitran, Model 304). The transducer was mounted in the tubing of the liquid sampling loop, outside the oven. Care was taken to keep the fluid inside the transducer cavity at room temperature by providing cooling. The pressure transducer was calibrated with a dead-weight tester that was accurate to better than 0.18% full scale.

Pressure uncertainties in the data are mainly due to variations observed while establishing a given data point, not to calibration uncertainties. These variations are given for each data point by Rizvi (31).

To check the calibration of temperature and pressure instruments, the vapor pressure of pure water was always measured at each new oven temperature.

Sampling and Composition Determination. Compositions of equilibrium fluids were measured with a Hewlett Packard Model 5840a chromatograph. The compositions of both phases were determined at most of the points reported.

A technique was employed in which the equilibrium phases were withdrawn from the liquid or vapor regions of the equilibrium cell, circulated through a sampling valve of the chromatograph, then returned to the cell. A bellows pump was developed for this purpose. The pump was driven by high-pressure nitrogen and was operated simply by opening and closing valves on either side of the pump and varying the nitrogen pressure to compress or expand the bellows.

The hold-up in exterior tubing was kept very small. The detailed design of the pump and sample circulating system is discussed by Rizvi (31).

The bellows pumps could be used to circulate liquid to the top of the cell and vapor to the bottom, thus providing a mechanism for enhancing mixing and reducing equilibration times.

Vapor lines and the vapor sampling valve in the chromatograph were all held at temperatures above the equilibrium cell temperature. The liquid lines, in contrast, were cooled below the cell temperature. These steps prevented unwanted condensation or vaporization and assisted in ensuring accurate analyses.

At higher temperatures it became impossible to circulate through the chromatograph vapor sampling valves because those valves failed at the temperatures necessary to prevent condensation. Two alternative sampling procedures were developed. Both involved expanding a small volume of vapor into a larger volume so that the pressure was sharply decreased and condensation could be avoided. More detail is given by Rizvi (31).

The packing material used in the chromatograph column was Poropak T. This material permitted essentially complete separation of ammonia and water in a reasonable time, and without excessive tailing of the water peak.

The ratio of chromatograph areas was used as the indicator of composition. This ratio was calibrated against the ratio of moles over the whole composition range. The "response factor" was found to vary with the ammonia/water molar ratio in both dilute regions.

Some of the chromatographic composition results were verified by titrating samples withdrawn from the cell.

The uncertainties in mole fractions reported in Tables I–XVI are based on the expected accuracy in the calibration and on variation in composition in replicate samples. In most cases, the mole fraction variations were less than ±0.005.

The accuracy of measurements was established by the following procedures.

1. Measurement of each datum was repeated 3–5 times.

2. Whole phase envelopes were replicated. This was achieved by taking measurements between points previously measured. Phase envelope determinations at 376, 382, 412, 483, and 526 K were all repeated, with a time interval as long as a few months between sets of measurements.

Table I. Ammonia–Water Equilibrium Data, Average Temperature 305.6 K

no.	T, K	P, MPa	x_{NH_3}	y_{NH_3}	K_{NH_3}	K_{H_2O}
1	305.64	0.005	0.0000	0.0000		
2	304.08	0.023	0.0342			
3	303.24	0.036	0.1122	0.7660	6.827	0.2636
4	304.32	0.038	0.1157	0.8039	6.948	0.2218
5	303.69	0.066	0.1263	0.8632	6.835	0.1566
6	304.32	0.052	0.1883	0.8862	4.706	0.1402
7	304.87	0.176	0.2648	0.9633	3.638	0.0499
8	305.40	0.239	0.3740	0.9832	2.629	0.0268
9	305.94	0.331	0.4017	0.9891	2.462	0.0182
10	306.90	0.520	0.5046	0.9935	1.969	0.0131
11	306.93	0.507	0.5645	0.9930	1.759	0.0161
12	306.10	0.567	0.6051	0.9953	1.645	0.0119
13	306.89	0.725	0.6710	0.9960	1.484	0.0122
14	307.19	0.942	0.7670	0.9976	1.301	0.0103
15	309.03	1.232	0.9085	0.9989	1.100	0.0120
16	305.64	1.254	1.0000	1.0000		

Table II. Ammonia–Water Equilibrium Data, Average Temperature 341.8 K

no.	T, K	P, MPa	x_{NH_3}	y_{NH_3}	K_{NH_3}	K_{H_2O}
1	341.81	0.029	0.0000	0.0000		
2	343.51	0.089	0.0621	0.3825	6.159	0.6584
3	339.66	0.086	0.0666			
4	340.87	0.132	0.0985	0.6254	6.349	0.4155
5	340.87	0.136	0.1029	0.6336	6.157	0.4084
6	340.96	0.118	0.1030	0.6184	6.004	0.4254
7	340.97	0.130	0.1143	0.6597	5.772	0.3842
8	341.18	0.154	0.1491	0.7371	4.944	0.3090
9	341.03	0.169	0.1497	0.7357	4.914	0.3108
10	343.95	0.202	0.1688	0.8633	5.114	0.1645
11	344.84	0.267	0.2214	0.8930	4.033	0.1374
12	340.96	0.273	0.2416	0.8691	3.597	0.1726
13	341.23	0.405	0.3102	0.9235	2.977	0.1109
14	344.84	0.534	0.3322	0.9550	2.875	0.0674
15	341.49	0.561	0.3603	0.9542	2.648	0.0716
16	343.78	0.719	0.3900	0.9744	2.498	0.0420
17	341.26	0.722	0.4188	0.9693	2.314	0.0528
18	340.79	0.900	0.4702	0.9778	2.080	0.0419
19	344.95	0.915		0.9770		
20	344.81	1.125		0.9832		
21	340.60	1.142	0.5160	0.9879	1.915	0.0250
22	340.80	1.436	0.5815	0.9895	1.702	0.0251
23	340.69	1.467	0.5909	0.9906	1.676	0.0230
24	340.81	1.749	0.6369	0.9937	1.560	0.0174
25	340.89	2.175	0.7414	0.9960	1.343	0.0155
26	339.51	2.884	0.9560	0.9970	1.043	0.0682
27	341.81	3.212	1.0000	1.0000		

Table III. Ammonia–Water Equilibrium Data, Average Temperature 359.7 K

no.	T, K	P, MPa	x_{NH_3}	y_{NH_3}	K_{NH_3}	K_{H_2O}
1	359.66	0.061	0.0000	0.0000		
2	359.49	0.116	0.0368	0.2025	5.503	0.8280
3	359.68	0.121	0.0428	0.2352	5.495	0.7990
4	359.70	0.153	0.0777	0.4114	5.295	0.6382
5	359.56	0.192	0.1064	0.5534	5.201	0.4998
6	359.60	0.253	0.1399	0.6826	4.879	0.3690
7	359.61	0.386	0.2054	0.8150	3.968	0.2328
8	359.64	0.623	0.2837	0.8948	3.154	0.1469
9	359.74	0.644	0.2935	0.9053	3.084	0.1340
10	359.73	0.767	0.3261	0.9154	2.807	0.1255
11	359.75	1.189	0.4173	0.9517	2.281	0.0829
12	359.72	1.510	0.4724	0.9635	2.040	0.0692
13	359.75	1.516	0.4805	0.9655	2.009	0.0664
14	359.76	1.917	0.5442	0.9750	1.792	0.0548
15	359.75	2.415	0.6162	0.9831	1.595	0.0440
16	359.67	3.093	0.7257	0.9890	1.363	0.0401
17	359.66	3.147	0.7337	0.9898	1.349	0.0383
18	359.61	3.523	0.7997	0.9918	1.240	0.0409
19	359.57	4.062	0.8934	0.9957	1.115	0.0403
20	359.64	4.524	0.9711	0.9980	1.028	0.0692
21	359.66	4.743	1.0000	1.0000		

Table IV. Ammonia–Water Equilibrium Data, Average Temperature 376.3 K

no.	T, K	P, MPa	x_{NH_3}	y_{NH_3}	K_{NH_3}	K_{H_2O}
1	376.28	0.113	0.0000	0.000		
2	376.11	0.158	0.0192	0.1752	9.125	0.8409
3	376.09	0.171	0.0275	0.2508	9.120	0.7704
4	376.91	0.177	0.0318			
5	376.06	0.192	0.0424	0.3557	8.389	0.6728
6	377.15	0.191	0.0426			
7	376.03	0.228	0.0629	0.4812	7.650	0.5536
8	376.08	0.294	0.0965	0.6121	6.343	0.4293
9	377.02	0.329	0.1050			
10	377.00	0.327	0.1188			
11	375.85	0.382	0.1350	0.7057	5.227	0.3402
12	375.94	0.401	0.1404	0.7261	5.172	0.3186
13	376.34	0.533	0.1861	0.7960	4.277	0.2506
14	375.94	0.740	0.2442	0.8603	3.523	0.1848
15	376.37	0.885	0.2640	0.8839	3.348	0.1577
16	375.99	1.224	0.3418	0.9203	2.693	0.1211
17	376.17	1.468	0.3759	0.9344	2.486	0.1051
18	376.12	1.936	0.4452	0.9522	2.139	0.0862
19	376.20	2.117	0.4556	0.9566	2.100	0.0797
20	376.18	2.376	0.5008	0.9626	1.922	0.0749
21	376.21	2.781	0.5468	0.9686	1.771	0.0693
22	376.30	3.024	0.5575	0.9685	1.737	0.0712
23	376.27	3.493	0.6402	0.9756	1.524	0.0678
24	376.33	3.909	0.6570	0.9691	1.475	0.0901
25	376.10	3.948	0.6842	0.9777	1.429	0.0706
26	376.36	4.630	0.7388	0.9709	1.314	0.1114
27	376.27	5.239	0.7662	0.9777	1.276	0.0954
28	376.28	6.626	1.0000	1.0000		

3. Temperature, pressure, and composition calibrations were repeated over the period of the experiment.

The data along the three lowest temperature nominal isotherms include some additional uncertainties for several reasons. Temperature variations and pressure fluctuations during operation of the sampling loop were more significant. Also, there were difficulties in operating below atmospheric pressure, which was necessary for at least some compositions at temperatures below the normal boiling point of water.

Experimental Procedures. A schematic diagram of the apparatus is presented in Figure 1. The figure shows the windowed cell with ports for the temperature sensor and liquid and vapor injection and removal.

Receivers for ammonia and water were brought to pressure with the aid of a Ruska pump. Also, nitrogen for operating bellows pumps was compressed with mercury using the same Ruska pump.

The figure shows the main valves for charging materials to the equilibrium cell and connections to the sampling loops.

The cell was evacuated at oven temperature. Then measured amounts of ammonia and water were charged. It was usual to vent some vapor to vacuum in order to remove the last remnants of air from the cell.

After a set of measurements of phase compositions, temperature, and pressure, additional ammonia or water or both were charged to the cell. By controlling the relative amounts added it was possible to cover the full pressure range for an isotherm.

For some isotherms, the equilibrium cell was first charged with enough ammonia and water to establish equilibrium near the critical point. In other cases, the initial charge was nearly pure ammonia. Ammonia-rich vapor was then purged from the cell to decrease cell pressure in small steps, with equilibrium compositions measured at each pressure, until the vapor pressure of water was approached. This method was especially useful in obtaining equilibrium conditions in the dilute regions of the phase envelopes.

Results

The results of the measurements are presented in Tables I–XVI and Figures Figures 2–5. The data in each table are at

Table V. Ammonia-Water Equilibrium Data, Average Temperature 381.9 K

no.	T, K	P, MPa	x_{NH_3}	y_{NH_3}	K_{NH_3}	K_{H_2O}
1	381.93	0.137	0.0000	0.0000		
2	381.72	0.184	0.0165	0.0729	4.418	0.9427
3	382.03	0.188	0.0175	0.0980	5.600	0.9181
4	381.60	0.256	0.0553	0.3390	6.130	0.6997
5	381.66	0.318	0.0829	0.4755	5.736	0.5719
6	381.70	0.381	0.1078	0.5699	5.287	0.4821
7	381.68	0.470	0.1375	0.6593	4.795	0.3950
8	382.12	0.463	0.1415	0.7273	5.140	0.3176
9	382.09	0.535	0.1529	0.7071	4.625	0.3458
10	381.94	0.679	0.1981	0.8203	4.141	0.2241
11	381.52	0.818	0.2358	0.8454	3.585	0.2023
12	382.20	0.919	0.2546	0.8734	3.430	0.1698
13	381.54	1.128	0.2989	0.8940	2.991	0.1512
14	382.10	1.333	0.3244	0.9218	2.842	0.1157
15	381.89	1.525	0.3570	0.9334	2.615	0.1036
16	381.62	1.589	0.3688	0.9339	2.532	0.1047
17	382.05	2.031	0.4267	0.9473	2.220	0.0919
18	382.13	2.598	0.5000	0.9593	1.919	0.0814
19	382.28	3.105	0.5531	0.9663	1.747	0.0754
20	381.78	3.563	0.5964	0.9746	1.634	0.0629
21	382.24	3.615	0.6048	0.9714	1.606	0.0724
22	381.87	4.176	0.6635	0.9785	1.475	0.0639
23	382.07	4.176	0.6762	0.9758	1.443	0.0747
24	382.12	4.516	0.7080	0.9778	1.381	0.0760
25	382.20	4.735	0.7320	0.9785	1.337	0.0802
26	381.76	5.073	0.7621	0.9847	1.292	0.0643
27	381.93	5.908	0.8064	0.9863	1.223	0.0708
28	382.01	5.919	0.8542	0.9893	1.158	0.0734
29	382.03	6.470	0.8853	0.9918	1.120	0.0715
30	382.00	6.603	0.9181	0.9937	1.082	0.0769
31	381.96	6.752	0.9457	0.9943	1.051	0.1050
32	381.93	7.363	1.0000	1.0000		

Table VI. Ammonia-Water Equilibrium Data, Average Temperature 399.1 K

no.	T, K	P, MPa	x_{NH_3}	y_{NH_3}	K_{NH_3}	K_{H_2O}
1	399.14	0.239	0.0000	0.0000		
2	399.46	0.366	0.0460	0.3445	7.489	0.6871
3	399.84	0.618	0.1206	0.6281	5.208	0.4229
4	399.59	0.874	0.1750	0.7415	4.237	0.3133
5	399.32	1.233	0.2419	0.8199	3.389	0.2376
6	399.28	1.653	0.3042	0.8671	2.850	0.1910
7	399.13	1.955	0.3420	0.8884	2.598	0.1696
8	399.38	2.487	0.4006	0.9120	2.277	0.1468
9	399.45	3.637	0.5006	0.9362	1.870	0.1278
10	398.92	4.762		0.9535		
11	399.27	4.863	0.5751	0.9516	1.655	0.1139
12	399.19	5.365	0.6306	0.9540	1.513	0.1245
13	398.99	6.763	0.6997	0.9623	1.375	0.1255
14	399.15	8.321	0.8896	0.9682	1.088	0.2880
15	396.96	9.458		0.9930		
16	399.14	10.125	1.0000	1.0000		

Table VII. Ammonia-Water Equilibrium Data, Average Temperature 405.5 K

no.	T, K	P, MPa	x_{NH_3}	y_{NH_3}	K_{NH_3}	K_{H_2O}
1	405.51	0.290	0.0000	0.0000		
2	405.21	0.358	0.0111	0.1111	10.009	0.8989
3	405.52	0.452	0.0350	0.3077	8.791	0.7174
4	405.55	0.665	0.0942	0.5691	6.041	0.4757
5	405.76	1.158	0.1848	0.7839	4.242	0.2651
6	405.48	2.085	0.3085	0.8780	2.846	0.1764
7	405.54	3.128	0.4113	0.9169	2.229	0.1412
8	405.53	4.226	0.5063	0.9348	1.846	0.1321
9	405.48	5.066	0.5790	0.9557	1.651	0.1052
10	405.31	5.909	0.6375	0.9680	1.518	0.0883
11	405.39	6.259		0.9637		
12	405.67	7.686		0.9743		
13	405.75	8.465	0.7919			
14	405.30	10.066	0.9318	0.9897	1.062	0.1510
15	405.71	11.193	0.9931	0.9932	1.000	0.9855
16	405.51	11.301	1.0000	1.0000		

roughly the same temperature, with the mean temperature indicated at the top of the table.

Table VIII. Ammonia-Water Equilibrium Data, Average Temperature 411.9 K

no.	T, K	P, MPa	x_{NH_3}	y_{NH_3}	K_{NH_3}	K_{H_2O}
1	411.85	0.348	0.0000	0.0000		
2	411.71	0.430	0.0231	0.1485	6.429	0.8716
3	411.43	0.544	0.0495	0.2814	5.685	0.7560
4	411.56	0.552	0.0512	0.2944	5.750	0.7437
5	412.01	0.830	0.1128	0.5131	4.549	0.5488
6	411.78	1.179	0.1500	0.6117	4.078	0.4568
7	411.91	1.496	0.2252	0.7427	3.298	0.3321
8	411.78	1.902	0.2406	0.8167	3.394	0.2414
9	412.24	2.512	0.3487	0.8496	2.436	0.2309
10	411.75	2.996	0.3540	0.8991	2.540	0.1562
11	411.24	3.268	0.4158	0.9182	2.208	0.1400
12	411.74	4.055	0.4463	0.9147	2.050	0.1541
13	412.27	3.447	0.4470	0.8951	2.002	0.1897
14	411.65	4.575	0.5074	0.9317	1.836	0.1387
15	412.24	5.091	0.5581	0.9299	1.666	0.1586
16	411.65	6.049	0.5798	0.9349	1.612	0.1549
17	412.16	6.614	0.6672	0.9470	1.419	0.1593
18	412.02	7.632	0.7320	0.9547	1.304	0.1690
19	412.05	8.690	0.8077	0.9601	1.189	0.2075
20	411.97	9.778	0.8808	0.9690	1.100	0.2601

Table IX. Ammonia-Water Equilibrium Data, Average Temperature 422.5 K

no.	T, K	P, MPa	x_{NH_3}	y_{NH_3}	K_{NH_3}	K_{H_2O}
1	422.53	0.468	0.0000	0.0000		
2	422.41	0.563	0.0192	0.1303	6.786	0.8867
3	422.44	0.625	0.0348	0.2240	6.437	0.8040
4	422.48	0.642	0.0374	0.2429	6.495	0.7865
5	422.46	0.708	0.0512	0.3216	6.281	0.7150
6	422.42	0.881	0.0848	0.4727	5.574	0.5762
7	422.54	1.105	0.1297	0.5913	4.559	0.4696
8	422.70	1.832	0.2220	0.7620	3.432	0.3059
9	422.53	2.669	0.3078	0.8279	2.690	0.2486
10	422.56	3.671	0.3934	0.8701	2.212	0.2141
11	422.73	4.989	0.4876	0.8951	1.836	0.2047
12	422.70	7.010	0.6098	0.9140	1.499	0.2204
13	422.80	8.223	0.6780	0.9169	1.352	0.2581
14	422.78	10.214	0.7852	0.9163	1.167	0.3897
15	421.74	11.396	0.8588	0.9429	1.098	0.4044
16	422.45	11.473	0.8714	0.9140	1.049	0.6687
17	422.77	11.763	0.8740	0.9153	1.047	0.6722

Table X. Ammonia-Water Equilibrium Data, Average Temperature 451.5 K

no.	T, K	P, MPa	x_{NH_3}	y_{NH_3}	K_{NH_3}	K_{H_2O}
1	451.52	0.966	0.0000	0.0000		
2	451.51	1.106	0.0174	0.1302	7.483	0.8852
3	451.38	1.194	0.0352	0.2518	7.153	0.7755
4	451.46	1.416	0.0571	0.3695	6.471	0.6687
5	451.55	1.709	0.0859	0.4659	5.424	0.5843
6	451.84	2.364	0.1720	0.6829	3.970	0.3830
7	451.90	3.353	0.2391	0.7524	3.147	0.3254
8	452.14	5.172	0.3354	0.8326	2.482	0.2519
9	452.03	7.072	0.4668	0.8834	1.892	0.2187
10	451.90	8.851	0.5480	0.9013	1.645	0.2184
11	451.94	10.045	0.5857	0.8995	1.536	0.2426
12	451.87	11.677	0.6817	0.9023	1.324	0.3069
13	452.00	13.057	0.7335	0.8927	1.217	0.4026
14	452.03	13.939	0.7764	0.8879	1.144	0.5013
15	452.01	14.723	0.8167	0.8863	1.085	0.6203
16	451.40	15.164	0.8602	0.8695	1.011	0.9335
17	451.02	15.114	0.8717	0.8854	1.016	0.8932
18	449.07	15.458	0.8779			
19	450.31	15.026	0.8831			

Figures 2 and 3 contain *Pxy* diagrams for the 15 isotherms. Figure 2 shows isotherms up to the critical temperature of ammonia. The higher temperature results are contained in Figure 3. Figures 4 and 5 contain equilibrium ratio

$$K = y/x \qquad (1)$$

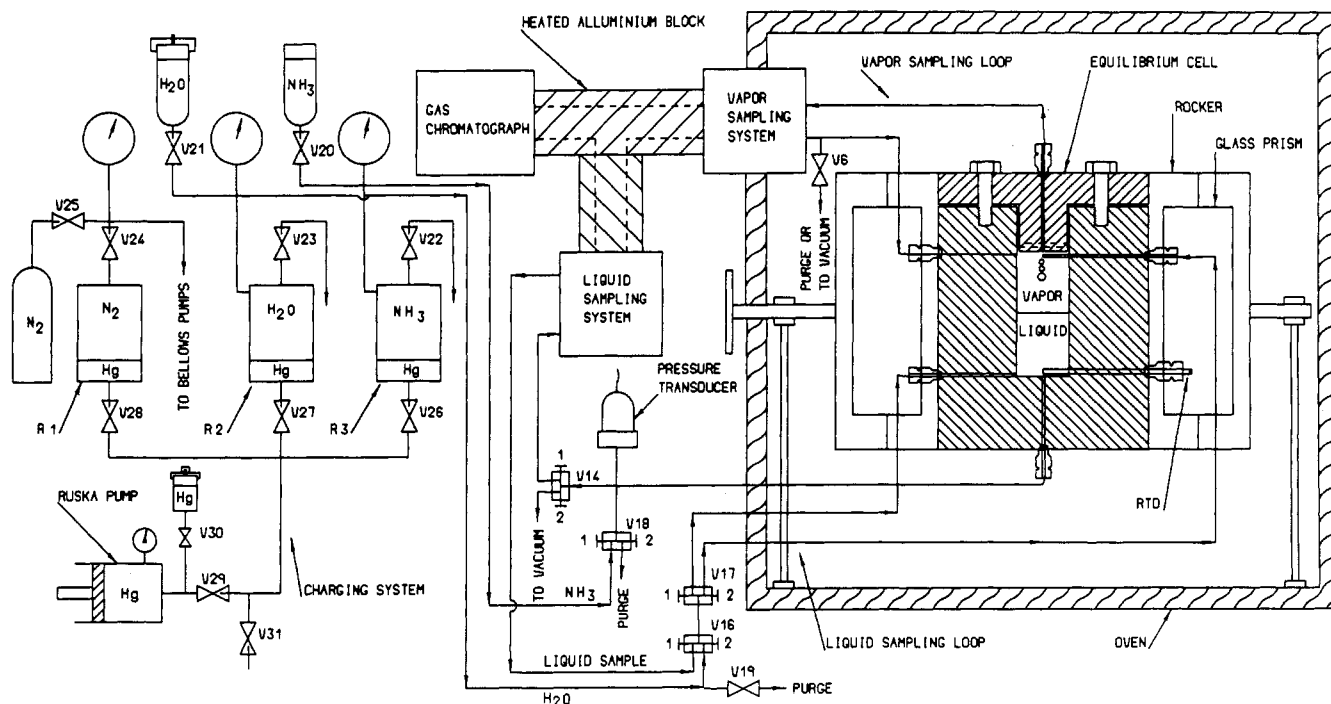corresponding to the *Pxy* isotherms of Figures 2 and 3, respectively.

Figure 1. Experimental apparatus.

Table XI. Ammonia-Water Equilibrium Data, Average Temperature 483.3 K

no.	T, K	P, MPa	x_{NH_3}	y_{NH_3}	K_{NH_3}	K_{H_2O}
1	483.28	1.913	0.0000	0.0000		
2	480.83	2.035	0.0139	0.0724	5.209	0.9407
3	482.75	2.231	0.0205			
4	480.68	2.161	0.0266	0.1300	4.887	0.8938
5	481.25	2.342	0.0371	0.1760	4.744	0.8557
6	483.22	2.440	0.0407	0.1855	4.558	0.8491
7	482.59	2.727	0.0665	0.2334	3.510	0.8212
8	482.98	2.909	0.0746	0.3124	4.188	0.7430
9	483.30	2.867	0.0785			
10	482.64	3.288	0.1049	0.4103	3.911	0.6588
11	484.47	3.919	0.1195			
12	483.65	3.950	0.1273	0.4839	3.801	0.5914
13	483.31	4.063	0.1315			
14	482.71	4.009	0.1510	0.5240	3.470	0.5607
15	483.99	4.907	0.1818			
16	484.01	5.186	0.2036	0.6504	3.194	0.4390
17	482.90	5.149	0.2156	0.6268	2.907	0.4758
18	483.74	5.586	0.2276	0.6229	2.737	0.4882
19	483.25	6.000	0.2471	0.6854	2.774	0.4179
20	482.89	6.764	0.2972	0.7046	2.371	0.4203
21	482.88	6.989	0.2991	0.7056	2.359	0.4200
22	484.21	8.075	0.3448	0.7444	2.159	0.3901
23	484.47	8.890	0.3622	0.7465	2.061	0.3975
24	483.65	9.974	0.3732	0.7810	2.093	0.3494
25	484.31	9.555	0.4063			
26	484.31	9.678	0.4073			
27	483.72	9.931	0.4139	0.7891	1.906	0.3598
28	484.39	11.682	0.4350	0.8068	1.855	0.3419
29	484.69	12.028	0.4724	0.7921	1.677	0.3940
30	483.76	12.712	0.5078	0.8052	1.586	0.3958
31	483.77	13.077	0.5164	0.7838	1.518	0.4471
32	484.23	13.527	0.5409	0.8088	1.495	0.4165
33	479.98	14.527		0.8507		
34	483.77	14.565	0.5743	0.8325	1.450	0.3935
35	484.12	15.084	0.5839	0.8153	1.396	0.4439
36	484.16	15.294	0.5909	0.8195	1.387	0.4412
37	483.71	14.974	0.5952	0.8190	1.376	0.4471
38	483.34	15.192	0.5992	0.8232	1.374	0.4411
39	483.72	15.620	0.6134	0.8205	1.338	0.4643
40	482.64	16.688	0.6317			
41	482.93	17.803	0.6543	0.8012	1.225	0.5751
42	483.34	17.131	0.6564	0.8359	1.273	0.4776
43	482.99	17.974	0.6720			
44	483.34	18.243	0.6787	0.8153	1.201	0.5749
45	482.79	18.566	0.6936	0.7946	1.146	0.6704

Table XII. Ammonia-Water Equilibrium Data, Average Temperature 526.2 K

no.	T, K	P, MPa	x_{NH_3}	y_{NH_3}	K_{NH_3}	K_{H_2O}
1	526.16	4.185	0.0000	0.0000		
2	523.88	4.246	0.0160			
3	526.18	4.675	0.0240	0.0885	3.688	0.9339
4	526.04	4.736	0.0301	0.1064	3.535	0.9213
5	525.58	5.611	0.0733	0.2242	3.059	0.8372
6	525.26	6.321	0.1031	0.3166	3.071	0.7620
7	526.05	6.802	0.1050			
8	525.73	6.830	0.1153			
9	526.07	7.203	0.1371	0.3755	2.739	0.7237
10	526.09	7.193	0.1473	0.4034	2.739	0.6997
11	525.97	8.487	0.1901	0.4859	2.556	0.6348
12	525.54	9.215	0.2142	0.5015	2.341	0.6344
13	525.80	9.231	0.2191	0.4964	2.266	0.6449
14	525.71	9.975	0.2400	0.5410	2.254	0.6039
15	525.78	11.617	0.2944	0.5969	2.028	0.5713
16	525.86	12.423	0.3081	0.6160	1.999	0.5550
17	526.05	12.636	0.3090	0.5960	1.929	0.5847
18	525.81	13.535	0.3681	0.6477	1.760	0.5575
19	526.00	14.857	0.3941	0.6721	1.705	0.5412
20	526.36	15.956	0.4227	0.6591	1.559	0.5905
21	525.89	16.992	0.4647	0.6856	1.475	0.5873
22	525.81	17.033	0.4702	0.6752	1.436	0.6131
23	526.98	18.099	0.4800			
24	526.62	18.042	0.4833	0.6638	1.373	0.6507
25	526.44	17.804	0.4863	0.6753	1.389	0.6321
26	527.19	18.334		0.6630		
27	526.13	19.142	0.4956	0.6784	1.369	0.6376
28	527.10	18.416	0.5132	0.6527	1.272	0.7134
29	526.66	19.647	0.5229	0.6506	1.244	0.7323
30	526.68	19.248	0.5239	0.6669	1.273	0.6996
31	526.94	20.344	0.5352	0.6572	1.228	0.7375
32	526.96	20.683	0.5422	0.6398	1.180	0.7868
33	526.97	20.929	0.5448	0.5946	1.091	0.8906
34	527.13	20.989	0.5449	0.5547	1.018	0.9785

The lines drawn in Figures 2–5 were obtained by curve fitting the data. The equations are not presented here but are given by Rizvi (*31*).

Critical Points. Some of the measurements made were apparently very close to the critical composition at the temperature of the cell. In particular, at 451.5 K critical opalescence was observed in the form of a reddish brown cloud at the interface that became dispersed as a continuous trans-

Table XIII. Ammonia-Water Equilibrium Data, Average Temperature 579.7 K

no.	T, K	P, MPa	x_{NH_3}	y_{NH_3}	K_{NH_3}	K_{H_2O}
1	579.71	9.415	0.0000	0.0000		
2	578.36	9.895	0.0166			
3	577.91	9.826	0.0170	0.0379	2.229	0.9787
4	577.94	9.831	0.0186	0.0414	2.226	0.9768
5	577.86	9.822	0.0204	0.0385	1.887	0.9815
6	577.80	10.947	0.0467	0.1076	2.304	0.9361
7	577.80	10.914	0.0475	0.1025	2.158	0.9423
8	578.32	11.994	0.0768	0.1625	2.116	0.9072
9	578.48	12.040	0.0814	0.1780	2.187	0.8948
10	578.37	13.343	0.1147	0.2194	1.913	0.8817
11	578.54	13.370	0.1199	0.2476	2.065	0.8549
12	578.92	15.005	0.1668	0.3336	2.000	0.7998
13	578.14	15.698	0.1861	0.3213	1.726	0.8339
14	578.71	15.833	0.1920	0.3373	1.757	0.8202
15	578.53	16.017	0.1951			
16	580.14	17.745	0.2339	0.4044	1.729	0.7774
17	580.64	19.480	0.2842	0.4072	1.433	0.8282
18	581.81	19.769	0.2893	0.4311	1.490	0.8005
19	581.55	20.842		0.4301		
20	581.65	21.637	0.3238	0.4096	1.265	0.8731
21	582.58	21.515	0.3337	0.4319	1.294	0.8526
22	582.71	21.636	0.3518	0.4232	1.203	0.8898
23	583.80	22.101	0.3691	0.3947	1.069	0.9594
24	582.85	21.854	0.3698	0.4082	1.104	0.9391

Table XIV. Ammonia-Water Equilibrium Data, Average Temperature 610.2 K

no.	T, K	P, MPa	x_{NH_3}	y_{NH_3}	K_{NH_3}	K_{H_2O}
1	610.23	14.080	0.0000	0.0000		
2	611.94	14.821	0.0076			
3	611.86	14.318	0.0087	0.0158	1.816	0.9928
4	612.06	14.889	0.0157			
5	611.33	15.117	0.0157	0.0279	1.777	0.9876
6	612.26	14.948	0.0234	0.0403	1.722	0.9827
7	607.77	15.060	0.0261	0.0452	1.732	0.9804
8	608.64	15.300		0.0808		
9	608.84	15.566	0.0440	0.0759	1.725	0.9666
10	608.49	15.808	0.0498	0.0841	1.689	0.9639
11	608.37	15.892	0.0513			
12	609.01	16.144	0.0531	0.0939	1.768	0.9569
13	610.37	16.626	0.0599	0.1156	1.930	0.9408
14	610.10	16.827	0.0703	0.1229	1.748	0.9434
15	610.20	17.229	0.0775	0.1375	1.774	0.9350
16	610.40	18.003	0.0930	0.1537	1.653	0.9331
17	612.00	18.537	0.1167			
18	612.30	19.159	0.1311			
19	609.89	20.321	0.1370	0.2034	1.485	0.9231
20	608.91	20.653	0.1546	0.2225	1.439	0.9197
21	609.19	21.422	0.1623	0.2548	1.570	0.8896
22	610.01	21.887	0.1751	0.2485	1.419	0.9110
23	610.10	21.869	0.1803	0.2522	1.399	0.9123
24	611.42	21.917	0.1884			
25	613.22	21.691	0.1904			
26	609.44	22.406	0.2251	0.2529	1.124	0.9641
27	607.90	22.468	0.2282	0.2551	1.118	0.9651

Table XV. Ammonia-Water Equilibrium Data, Average Temperature 618.1 K

| no.	T, K	P, MPa	x_{NH_3}	y_{NH_3}	K_{NH_3}	K_{H_2O}
1	618.09	15.536	0.0000	0.0000		
2	617.68	16.273	0.0160			
3	617.48	16.371	0.0211	0.0345	1.635	0.9863
4	617.94	16.705	0.0260	0.0463	1.781	0.9792
5	617.74	17.654	0.0340	0.0585	1.721	0.9746
6	618.64	17.629	0.0357	0.0495	1.387	0.9857
7	618.77	17.919	0.0486			
8	617.76	18.643	0.0570	0.0714	1.253	0.9847
9	618.66	19.263		0.0796		
10	618.15	20.436	0.0741			

parent reddish phase over the whole visible area of the window. This phase and the two bright phases which resulted when some water was added were analyzed and are reported in Table XVII.

Table XVI. Ammonia-Water Equilibrium Data, Extra Points

no.	T, K	P, MPa	x_{NH_3}	y_{NH_3}	K_{NH_3}	K_{H_2O}
1	373.10	0.118	0.0138			
2	373.63	0.126	0.0195	0.2146	11.005	0.8010
3	373.03	0.146	0.0282	0.2768	9.816	0.7442
4	372.78	0.147	0.0320			
5	372.88	0.172	0.0450	0.2919	6.487	0.7415
6	374.91	0.208	0.0538	0.4410	8.197	0.5908
7	372.21	0.280	0.1116	0.7171	6.426	0.3184
8	374.58	0.332	0.1135	0.6641	5.851	0.3789
9	446.08	1.159	0.0405	0.2602	6.425	0.7710
10	446.18	2.064	0.1268	0.6154	4.853	0.4404

Table XVII. Ammonia-Water Critical Points

mole fracn NH_3	temp, K	press., MPa
0.116	618.1	22.37
0.244	610.2	22.52
0.387	579.7	22.39
0.570	526.2	21.42
0.748	483.3	19.00
0.870	451.5	16.05
0.936	422.5	13.85
0.972	411.9	12.47
1.000	405.5	11.15
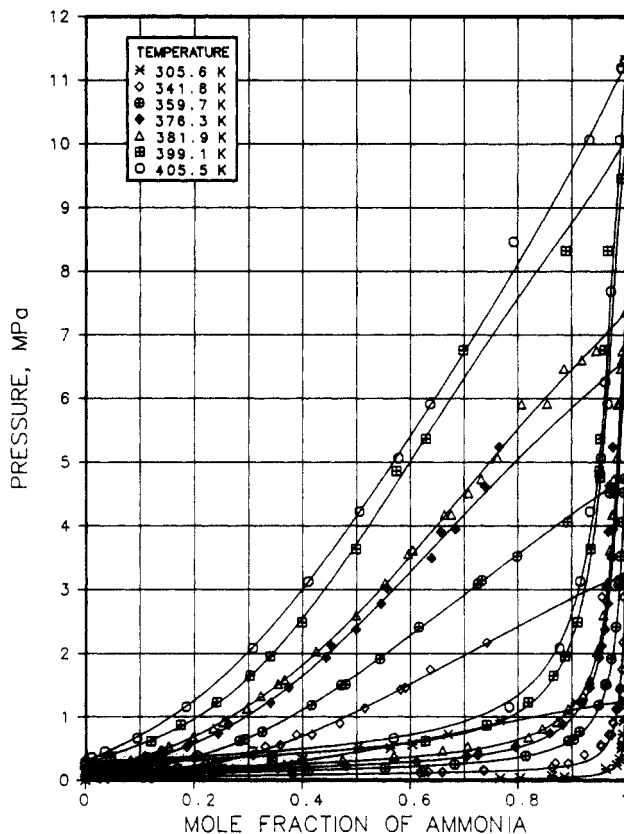
Figure 2. Phase diagram for ammonia-water up to the critical point of ammonia.

Other critical points were estimated by extrapolating. Estimated critical points are presented in the table.

Comparison with Other Work. Figures 6-10 present some of the current results in comparison with selected data of Wucherer, Gillespie et al., and Guillevic et al. The lines in these figures are those fitted to the present data and plotted in Figures 2 and 3.

Data from Wucherer (*18*) are compared with three of our isotherms in Figure 6. It has been necessary to interpolate points from Wucherer's tables of smoothed data in order to
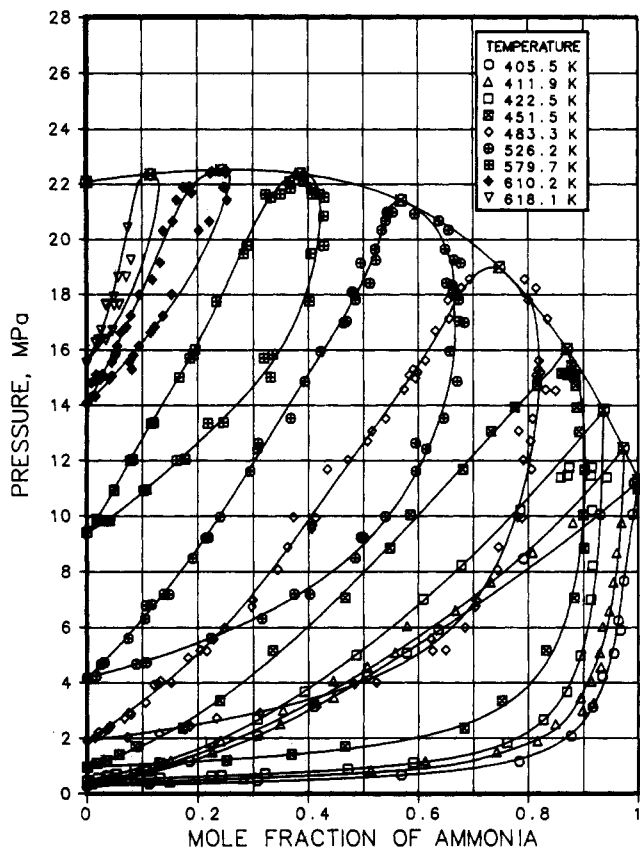
Figure 3. Phase diagram for ammonia–water from the critical point of ammonia to the critical point of water.
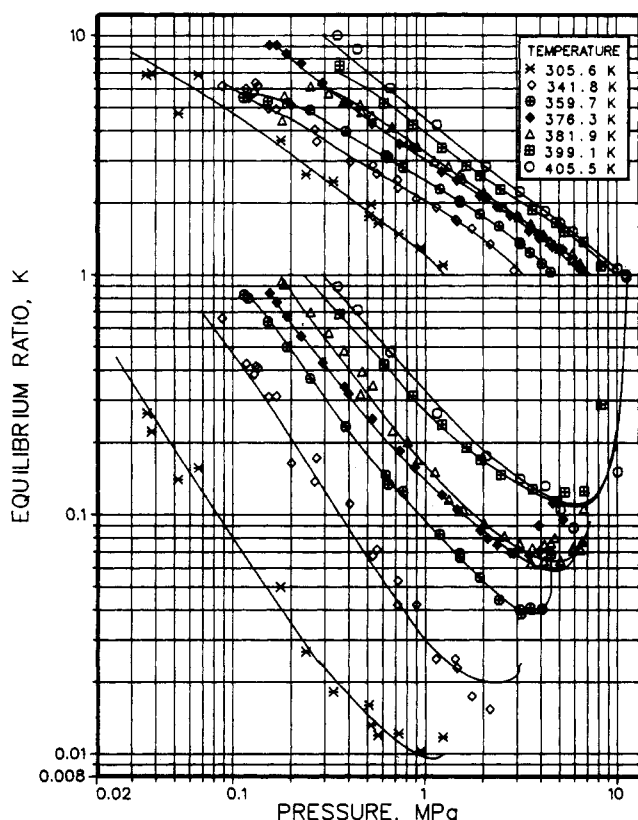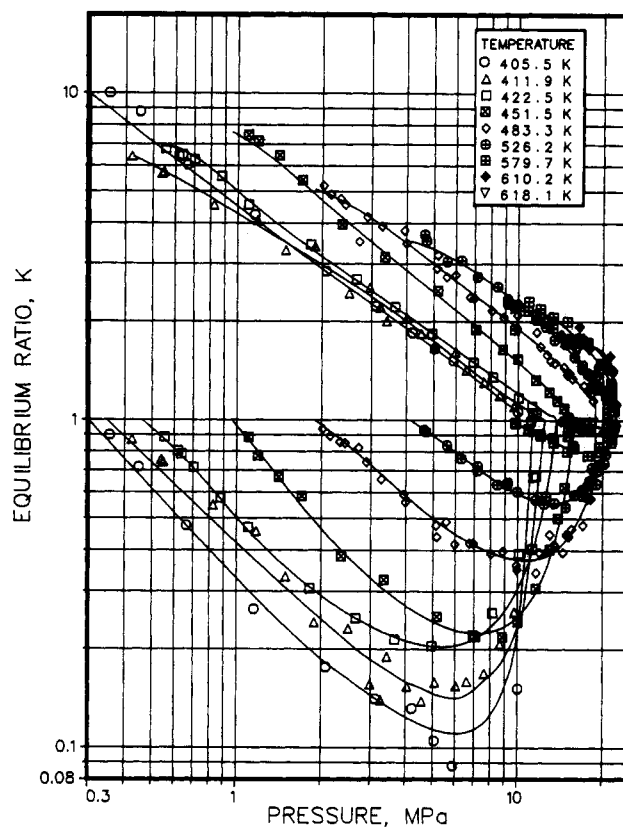

Figure 5. Equilibrium ratios for ammonia–water from the critical point of ammonia to the critical point of water.

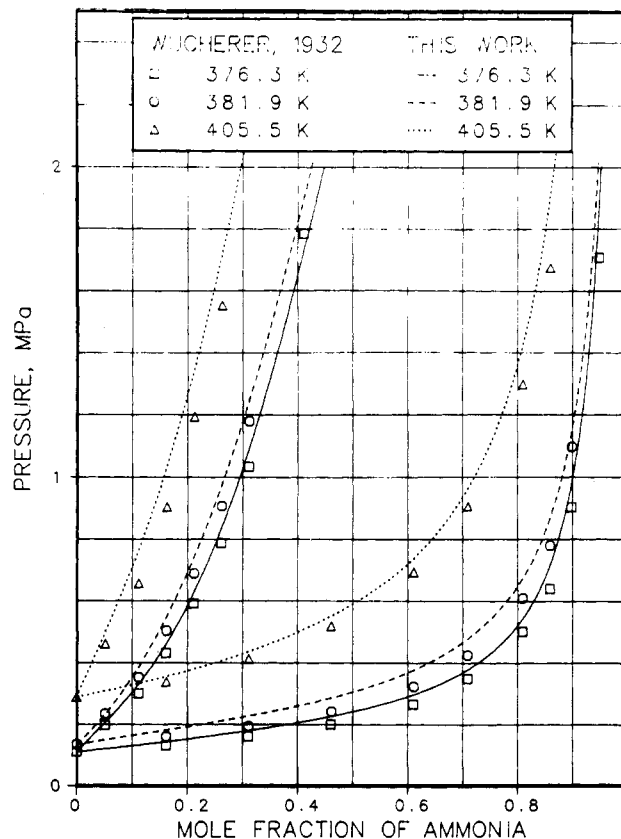**Figure 4.** Equilibrium ratios for ammonia–water up to the critical point of ammonia.

Figure 6. Comparison with data of Wucherer (1932).

prepare this figure. In general, Wucherer's vapor and liquid phases are somewhat richer in ammonia at a given temperature and pressure than is indicated by our measurements. In

general, however, the agreement is reasonable when viewed on *Pxy* axes.

We have chosen to compare the *Pxy* measurements of Gillespie et al. (*22*) for two isotherms close to isotherms we
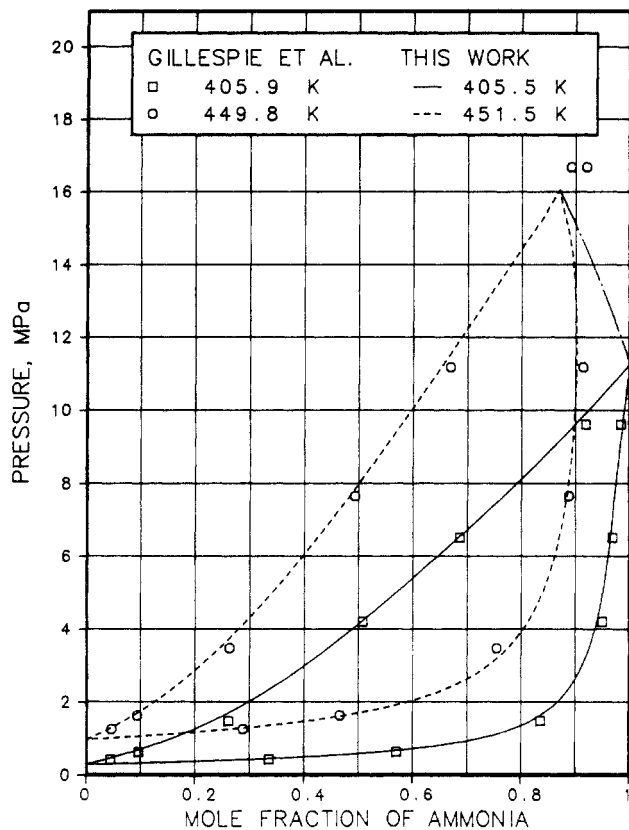
Figure 7. Comparison with *PTxy* data of Gillespie, Wilding, and Wilson.

Figure 9. Comparison with relative volatility data of Gillespie, Wilding, and Wilson.

Figure 8. Comparison with equilibrium ratio data of Gillespie, Wilding, and Wilson.
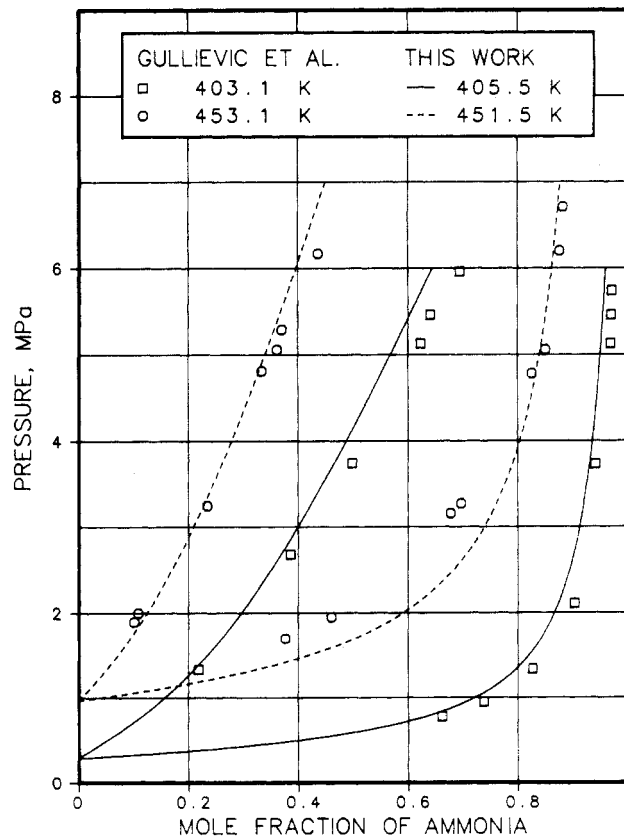
Figure 10. Comparison with data of Guillevic, Richon, and Renon.

measured. The comparisons are made in Figures 7, 8, and 9, (Gillespie et al. (*22*) report many more *PTx* measurements than *PTxy* measurements.)

Gillespie et al. (*22*) had access to our data in an early form when preparing their report. In this early form, the isotherm

at 405.5 K included some points (two points on the *P–x* curve and one point on the *P–y* curve) that we have since decided were faulty, due to unexplained errors. The elimination of these points permits the conclusion that our data and those of Gil-

lespie et al. are in quite reasonable correspondence, as viewed even on relative volatility axes which exaggerate any scatter.

Figure 10 shows data of Guillevic et al. (29) at two temperatures along with isotherms from our data at temperatures near their values. The temperature differences leave room for question, but there seem to be differences between their data and ours, particularly along the dew-point curve at 453.1 K. The difference in relative volatility may be around 25% at some compositions.

Correlation of Data. The data have been fitted with a number of equation-of-state models, as reported elsewhere by Rizvi (*31*) and Heidemann and Rizvi (*32*).

Registry No. NH_3, 7664-41-7.

Literature Cited

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Binary Gaseous Diffusion Coefficients. 5. Cyclooctane and *trans*-1,2-Dimethylcyclohexane with Helium, Argon, Methane, and Sulfur Hexafluoride at 1 atm and 313–343 K

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The binary gaseous diffusion coefficients for cyclooctane and *trans*-1,2-dimethylcyclohexane diffusing into helium, argon, methane, and sulfur hexafluoride were measured at about 313.15, 328.15, and 343.15 K and atmospheric pressure by the capillary tube method of Stefan. The experimental results are compared with diffusion coefficients calculated via the first-order Chapman–Enskog approximation. For the gases, effective Lennard-Jones (6, 12) pair potential parameters were taken from recent literature; for the liquids they were obtained from an extended corresponding-states correlation suggested by Tee, Gotoh, and Stewart.

Introduction

This study continues our earlier investigations (*1–4*) into binary gaseous diffusion coefficients. We now report on eight systems involving spherical molecules of a wide range of sizes (He, Ar, CH_4, SF_6) with two isomeric alicyclic C_8 compounds of different ring size, viz., cyclooctane (C_8H_{16}) and *trans*-1,2-dimethylcyclohexane (*trans*-1,2-$(CH_3)_2C_6H_{10}$). In particular, we wished to determine whether there were any discernible effects associated with differences in ring size of otherwise quite similar alicyclic isomers.

Experimental Section

The experimental procedures were identical with those described in detail in our earlier papers (*1–4*). Thus, only a brief summary will be presented. The Stefan capillary tube method (*5*) was used, running each solvent/gas pair in duplicate at about 313.15, 328.15, and 343.15 K and approximately atmospheric pressure. Temperature was controlled to better than ±0.01 K in a 80-L water bath over the periods of the measurements, which ranged from 2 to 10 days. Temperatures were measured with a calibrated platinum resistance thermometer on IPTS-68. The total pressure of about 1 atm (=101.325 kPa) was controlled with a mercury-filled Cartesian manostat to better than ±0.9 kPa for all runs except for helium

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