

Figure 4. Plot of $\ln W$ vs. ϵ^n for the adsorption of NH_3 on silica gel.

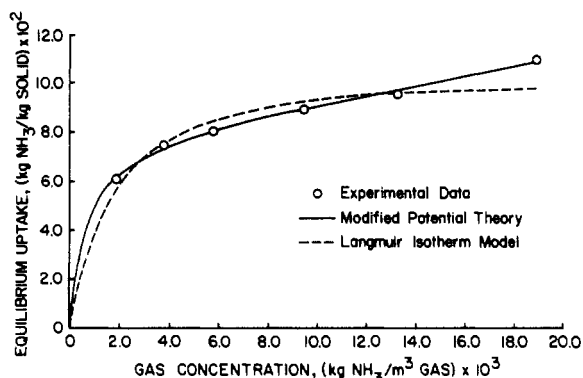


Figure 5. Comparison of experimental and predicted isotherms at 298 K using the Langmuir and potential models.

temperatures. Furthermore, the successful application of the modified potential theory to the experimental data makes it possible to predict equilibrium isotherm data at other temperatures.

Glossary

a_1	first Langmuir constant (m^3 of gas/kg of adsorbent)
a_2	second Langmuir constant (m^3 of gas/kg of adsorbent)
C	gas-phase concentration (kg of adsorbate/ m^3 of gas)
C_0	inlet gas concentration (kg of adsorbate/ m^3 of gas)
E	constant characteristic energy (kcal/(g mol))
H_{iso}	isosteric heat of adsorption (kcal/(g mol))
n	constant in the generalized isotherm equation
P	pressure of the adsorbate (kPa)
P^0	saturation pressure (kPa)
q	equilibrium concentration of adsorbed gas (kg of adsorbate/kg of adsorbent)
R	gas constant
T	absolute temperature (K)
W	volume of the adsorbed phase (cm^3 /g of adsorbent)
W_0	volume adsorbed at saturation (cm^3 /g of adsorbent)
β	affinity factor
ϵ	adsorption potential (kcal/(g mol))

Registry No. NH_3 , 7664-41-7.

Literature Cited

- (1) Clark, A.; Holm, V. C. F.; Blackburn, D. M. *J. Catal.* **1962**, *1*, 244.
- (2) Szczepanska, S.; Malinowski, S. *Rocz. Chem.* **1969**, *43*, 597.
- (3) Tishin, Y. G.; Rummyantsev, O. V. *Khim. Promst. (Moscow)* **1972**, *48*, 754.
- (4) Langmuir, I. *J. Am. Chem. Soc.* **1916**, *28*, 2221.
- (5) Langmuir, I. *J. Am. Chem. Soc.* **1916**, *40*, 1368.
- (6) Polanyi, M. *Verh. Dtsch. Phys. Ges.* **1916**, *18*, 55.
- (7) Polanyi, M. *Z. Phys.* **1920**, *2*, 111.
- (8) Dubinin, M. M. *Chem. Rev.* **1960**, *60*, 235.
- (9) Bering, B. P.; Dubinin, M. M.; Serpinsky, V. V. *J. Colloid Interface Sci.* **1966**, *21*, 378.
- (10) Dubinin, M. M. *J. Colloid Interface Sci.* **1967**, *23*, 487.
- (11) Bering, B. P.; Dubinin, M. M.; Serpinsky, V. V. *J. Colloid Interface Sci.* **1972**, *38*, 186.
- (12) Hersh, C. K. "Molecular Sieves", Reinhold: New York, 1961.
- (13) Huber, U.; Stoeckli, F.; Houriet, J. P. *J. Colloid Interface Sci.* **1978**, *67*, 195.

Received for review August 20, 1984. Accepted January 28, 1985.

Vapor-Liquid Equilibrium Data for the Binary System Water-Ammonia at 403.1, 453.1, and 503.1 K up to 7.0 MPa

Jean-Luc Guillevic, Dominique Richon,* and Henri Renon

Ecole Nationale Supérieure des Mines de Paris, Centre Réacteurs et Processus Equipe de Recherche Associée au C.N.R.S. No. 768, Laboratoire de Thermodynamique, 77305 Fontainebleau, France

A static method described in a previous paper has been used to obtain vapor-liquid equilibrium data for the water-ammonia system at three temperatures, 403.1, 453.1, and 503.1 K, and pressures up to 7 MPa. Comparison with lower pressure literature data is presented.

Introduction

The thermodynamic properties of the water-ammonia system, especially vapor-liquid equilibria, are needed to design absorption heat pumps and refrigeration processes. Some data

on this system are already available in the literature (2-13), but only for pressure and temperature ranges up to 3.5 MPa and 503.1 K, except in the work of Tskils et al. (8). Unfortunately, the data are often smoothed or scattered and therefore difficult to use. The present work extends the range of pressure up to 7 MPa, at three temperatures, two of them above the critical temperature of ammonia (405.6 K).

Experimental Section

Apparatus. The experimental setup described in a published paper (1) is based on a static method. The equilibrium cell is made of nonmagnetic stainless steel 316 LSS (AFNOR:

Table I. Vapor-Liquid Equilibrium Data for the System Ammonia (1)-Water (2) at $T = 403.1$ K^a

P , MPa	W_1^L	x_1	δW_1^L	W_1^V	y_1	δW_1^V
0.775				0.650	0.663	0.006
0.95				0.728	0.739	0.005
1.335	0.211	0.220	0.004			
1.34				0.820	0.828	0.004
2.11				0.900	0.905	0.003
2.68	0.374	0.387	0.006			
3.73				0.941	0.944	0.002
3.74	0.485	0.499	0.006			
5.13	0.611	0.624	0.006	0.970	0.972	0.001
5.46	0.629	0.642	0.006	0.972	0.973	0.001
5.74				0.972	0.974	0.001
5.96	0.684	0.696	0.006			

^a $\delta T = 0.2$ K; $\delta P = 10^{-2}$ MPa.**Table II. Vapor-Liquid Equilibrium Data for the System Ammonia (1)-Water (2) at $T = 453.1$ K^a**

P , MPa	W_1^L	x_1	δW_1^L	W_1^V	y_1	δW_1^V
1.70				0.364	0.377	0.006
1.90	0.098	0.103	0.002			
1.95				0.447	0.461	0.006
2.00	0.105	0.110	0.003			
3.155				0.666	0.642	0.006
3.245	0.225	0.235	0.004			
3.27				0.685	0.697	0.006
4.78				0.819	0.827	0.004
4.81	0.322	0.335	0.006			
5.06	0.350	0.362	0.006	0.844	0.852	0.003
5.29	0.358	0.371	0.006			
6.17	0.423	0.437	0.006			
6.20				0.871	0.878	0.003
6.71				0.878	0.884	0.004

^a $\delta T = 0.2$ K; $\delta P = 10^{-2}$ MPa.

Z2.CND.17.12, Aubert et Duval) to withstand corrosion by the mixture. The equilibrium cell (internal capacity 50 cm³) is kept at a constant temperature in an air thermostat. Pressure measurements are performed inside the cell, within 0.01 MPa, through a membrane pressure transducer (Kaman, KP 1911, 0.0, 7.0 MPa) calibrated at each working temperature against a dead-weight balance (Budenberg, Type 280 H). The temperature of the cell is kept constant within 0.1 K and measured within 0.2 K through calibrated thermocouples. The mixture is efficiently stirred with a magnetic rod. Four solenoids located outside the cell are used to create a rotating magnetic field and to drive the internal magnetic rod placed on a fixed axis. When constant temperature and pressure are observed, samples are withdrawn to perform GLC analyses. The samples, taken out by opening microvalves during a very short time, are small enough to give proper operating conditions of the chromatograph with negligible change of the equilibrium conditions inside the cell.

Chemicals. Water was distilled twice and was free of chlorides. Ammonia was supplied by L'Air Liquide with a specified minimum purity of 99.995 vol % containing less than 10 ppm of water. The two components have been used without any further purification; water was just degassed before mixing.

Results and Discussion

The experimental results are reported in Tables I-III and represented on Figures 1-3. The absolute errors are calculated for each weight fraction W_1 by using the following formula

$$\frac{\delta W_1}{W_1} = \frac{M_2}{M_1} \frac{S_{2/1} \delta K_r + K_r \delta S_{2/1}}{1 + S_{2/1} K_r \frac{M_2}{M_1}}$$

obtained from derivation of the expression of W_1 : $W_1 = 1/(1$

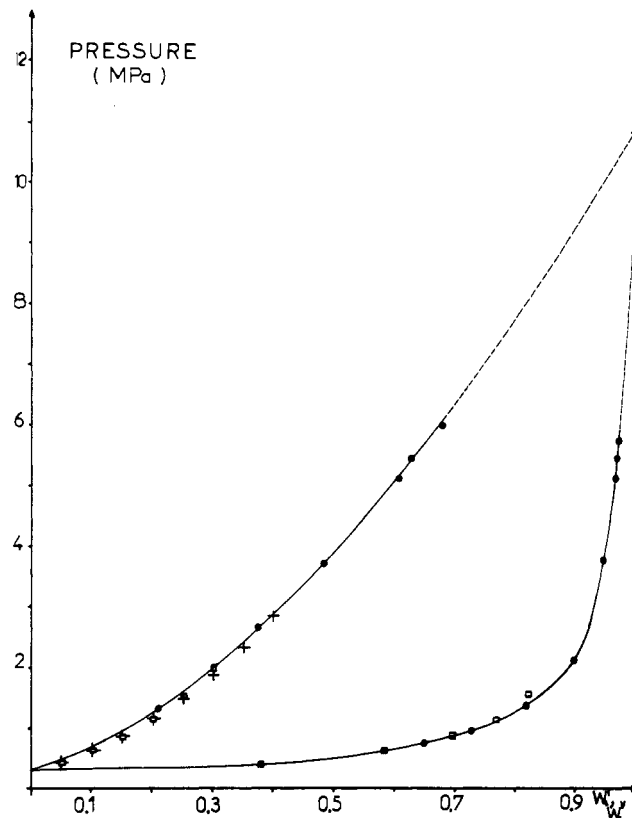


Figure 1. Vapor-liquid equilibrium data for the ammonia (1)-water (2) system at 403.1 K: ●, present work; the dashed line is an extrapolation and the full line a graphical interpolation; □, ref 6; +, ref 13; ○, ref 15.

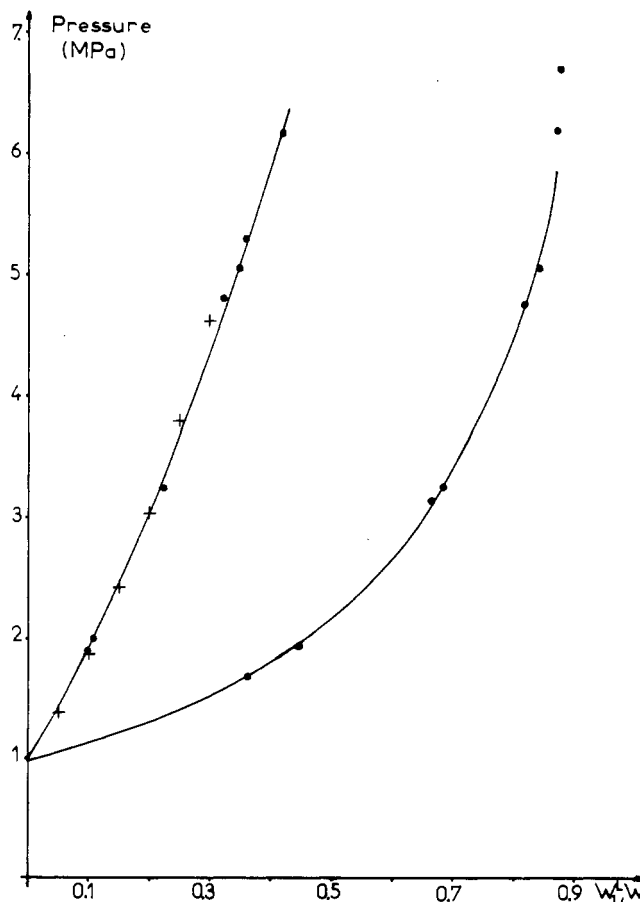
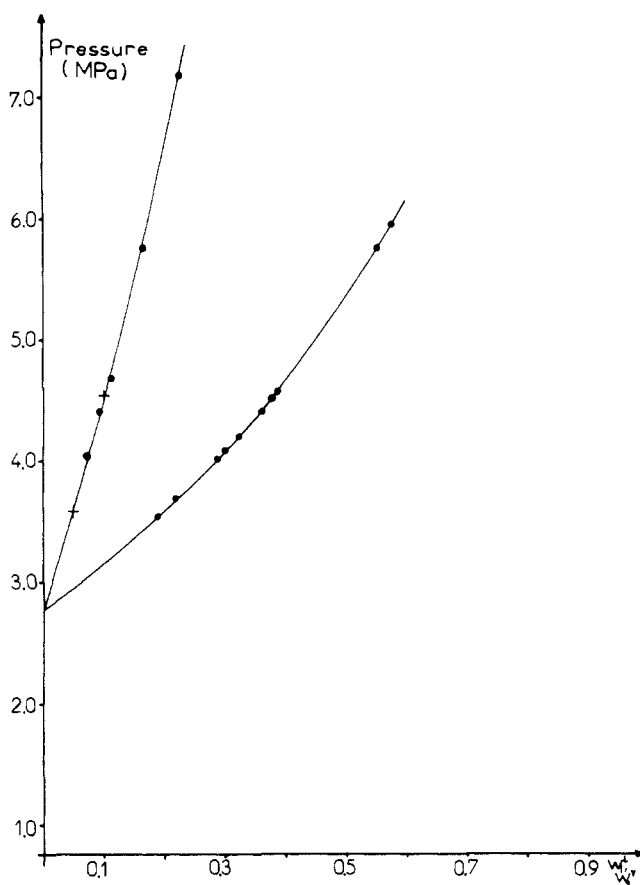


Figure 2. Vapor-liquid equilibrium data for the ammonia (1)-water (2) system at 453.1 K: ●, present work; +, ref 13; —, graphical interpolation.

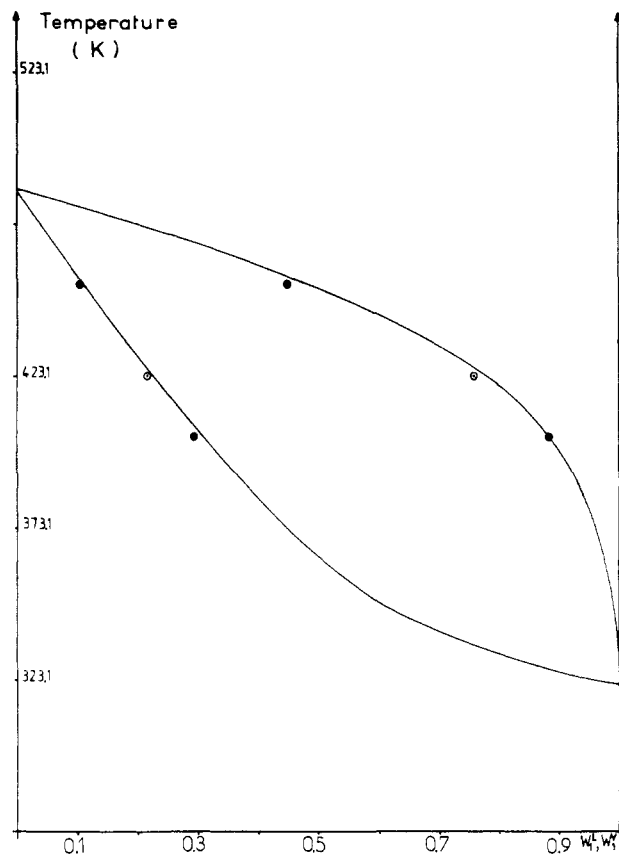
Table III. Vapor-Liquid Equilibrium Data for the System Ammonia (1)-Water (2) at $T = 503.1$ K^a

P , MPa	W_1^L	x_1	δW_1^L	W_1^V	y_1	δW_1^V
3.55				0.186	0.195	0.004
3.70				0.219	0.229	0.004
4.01				0.289	0.301	0.005
4.06	0.072	0.076	0.002			
4.08				0.300	0.312	0.006
4.17				0.321	0.333	0.006
4.40	0.092	0.097	0.002	0.364	0.377	0.006
4.51				0.380	0.394	0.006
4.55				0.387	0.400	0.006
4.67	0.115	0.121	0.003			
5.75	0.168	0.176	0.004	0.551	0.565	0.006
5.95				0.576	0.590	0.007
7.17	0.228	0.238	0.005			

^a $\delta T = 0.2$ K; $\delta P = 10^{-2}$ MPa.**Figure 3.** Vapor-liquid equilibrium data for the ammonia (1)-water (2) system at 503.1 K: ●, present work; +, ref 13; —, graphical interpolation.

+ $S_{2/1}K_r(M_2/M_1)$. They are reported in columns 4 and 7 of Tables I-III. M_1 and M_2 are respectively the molar mass of component 1 and 2. K_r is the ratio of the detector responses for the two components. δK_r is calculated from the uncertainties estimated for the detector responses relative to the two components; $\delta K_r/K_r = 3\%$ with $K_r = 1.05$. $S_{2/1}$ is the ratio of the two chromatographic peak areas. $\delta S_{2/1}$ is estimated from the dispersion observed on several determinations of the same equilibrium point.

Experimental data at 403.1 K are plotted on Figure 1, along with those from Clifford and Hunter (6) and Pierre (13). The agreement between the three bubble curves (present work and ref 6 and 13) is found within experimental error: deviation of 0.005 in ammonia liquid weight fraction at 1.335 MPa. Experimental errors are given in Tables I-III for present work. They are around 0.01 for ref 6 as stated in the paper of Clifford

**Figure 4.** Comparison of vapor-liquid equilibrium data for the ammonia (1)-water (2) system at 1.96 MPa: ●, present work; ○, ref 11; —, ref 5, graphical interpolation.

and Hunter; Pierre did not give any estimation. The agreement between the dew curve data of Clifford and Hunter (6) and ours is also within experimental error except only for the highest pressure point of Clifford with a deviation of 0.02 in ammonia mole fraction ($P = 1.52$ MPa). The data of Clifford and Hunter (6) used in the comparisons are the isothermal results they obtained by a curve fitting interpolation of their isothermal experimental data at 370.1, 380.1, 390.1, 400.1, 410.1, and 420.1 K. The experimental liquid weight fractions determined at 453.1 K can be compared with those of Pierre (13) in Figure 2. The deviations are smaller than 0.01 up to 4 MPa. The same agreement with Pierre's data (13) is also observed at 503.1 K as illustrated in figure 3.

Figure 4 illustrates the comparison between the data of Wucherer (5), Pawlikowsky et al. (11), and this work at $P = 1.96$ MPa. The bubble curves according to the interpolated results from Pawlikowsky et al. (11) and our results can be drawn very close while the bubble curve drawn from data of Wucherer (5) appears to deviate from the other results (with a maximum deviation of 0.01 in weight fraction at $T = 403.1$ K). The dew temperatures of Wucherer (5) are in good agreement at 403.1 K (less than 1 K), but separated by three degrees at 453.1 K. Such a difference is not surprising, taking account of all of the experimental difficulties encountered and related by Wucherer (5). In Figures 4-6, pressures have been chosen to minimize interpolation of author's or present data.

Figures 5 and 6 illustrate comparisons of isobaric diagrams at $P = 0.98$ and 1.013 MPa between the results of Wucherer (5), Clifford and Hunter (6), Pawlikowsky et al. (11), and the present work. Our bubble temperatures are lower than those of Wucherer (5) and Clifford and Hunter (6) (≈ 5.0 K at 403.1 K), and the results of Pawlikowsky et al. (11) are very scattered.

Comparisons between the results of Perman (2), Mollier (3), and Wilson (4) have been already made by Wucherer (5). For

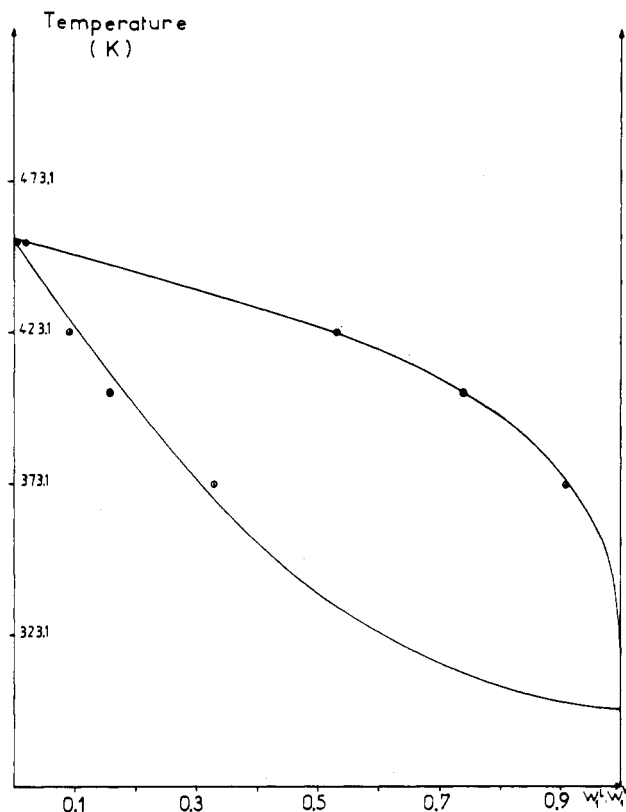


Figure 5. Comparison of vapor-liquid equilibrium data for the ammonia (1)-water (2) system at 1.01 MPa: ●, present work; ○, ref. 11; —, ref. 6, graphical interpolation.

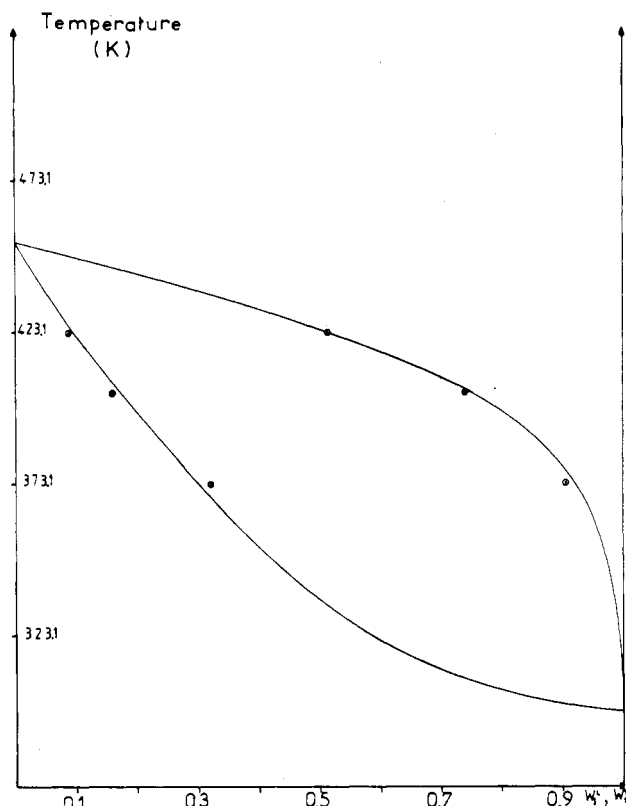


Figure 6. Comparison of vapor-liquid equilibrium data for the ammonia (1)-water (2) system at 0.98 MPa: ●, present work; ○, ref. 11; —, ref. 5, graphical interpolation.

the bubble pressures at low weight fractions in ammonia (between 0.0 and 0.2) the agreement is fair, but for weight fractions greater than 0.2 the data of Wilson (4) are lower (maximal deviation 5 K for $W_1^L = 0.4$ for pressures between 0.1 and 1

MPa). For the dew curves, the agreement between the data of Wucherer (5) and those of Wilson (4) is good (maximal deviation 3 K at 0.98 MPa for an ammonia weight fraction around 0.9). The data of Polak and Lu (10) are too isolated to be used, and the works of Tsiklis et al. (8) and Jennings (9) are difficult to use because these authors did not present numerical results. Results from the compilation of Macriss et al. (7) and data treatment of Scatchard et al. (12) are not used here because they include the experimental raw data already compared in this work.

It appears that present work data are useful below 3 MPa to resolve some of the disagreement between literature data. They extend the range of available data toward the higher pressures up to 7 MPa. More data are still needed in the higher pressure range. They will become soon available through the Gas Processors Association as obtained by Wilson and associates. Regression of present data with those of Scatchard and Pawlikowsky using Mathias equation of state (16) has shown that data of Wilson at 313, 333, and 353 K are in agreement with calculated results.

Acknowledgment

We are grateful to Dr. J. Vidal and Dr. A. Rojey for fruitful discussions about this work.

Glossary

K_i	catharometer detector response for component i
K_r	ratio of the catharometer detector responses for component 1 and 2 ($K_r = K_1/K_2$)
M_i	molecular weight of component i
P	pressure, MPa
$S_{2/1}$	ratio of chromatograph peak areas
T	temperature, K
W_i^L	weight fraction of component i in the liquid phase
W_i^V	weight fraction of component i in the vapor phase
x_i	mole fraction of component i in the liquid phase
y_i	mole fraction of component i in the vapor phase
δK_r	absolute error on K_r
$\delta S_{2/1}$	absolute error on $S_{2/1}$
δW_1	absolute error on W_1

Subscript

1	ammonia
2	water

Superscript

L	liquid
V	vapor

Registry No. NH_3 , 7664-41-7.

Literature Cited

- (1) Guillevic, J. L.; Richon, D.; Renon, H. *Ind. Eng. Chem. Fundam.* **1983**, *22*, 495.
- (2) Perman, E. P. *J. Chem. Soc.* **1901**, *79*, 718.
- (3) Moller, P. *VDI Z.* **1908**, *52*, 1315.
- (4) Wilson, T. A. *Univ. Ill., Eng. Expt. Stn. Bull.* **1925**, 146.
- (5) Wucherer, J. *Z. Gesamte Kaelte.-Ind.* **1932**, *39*, 97-104, 136-140.
- (6) Clifford, I. L.; Hunter, E. J. *J. Phys. Chem.* **1933**, *37*, 101.
- (7) Macriss, R. A.; Eakin, B. E.; Ellington, R. T.; Huebler, J. Research Bulletin No. 34, Institute of Gas Technology, Chicago, 1964.
- (8) Tsiklis, D. S.; Linshits, K. R.; Gorynova, N. D. *Russ. J. Phys. Chem.* **1965**, *39*, 1590.
- (9) Jennings, B. H. *Prog. Refrig. Sci. Technol., Proc. Int. Congr. Refrig.* **12th**, 1967, **1968**, *2*, 329.
- (10) Polak, J.; Lu, B. C. *J. Chem. Eng. Data* **1975**, *20*, 182.
- (11) Pawlikowsky, E. M.; Newman, J.; Prausnitz, J. M. *Ind. Eng. Chem. Process Des. Dev.* **1982**, *21*, 764.
- (12) Scatchard, G.; Epstein, L. F.; Warburton, J.; Cody, P. *J. Refrig. Eng.* **1947**, *53*, 413.
- (13) Pierre, B. *Kyitek. Tidskr.* **1959**, Sheet 14.
- (14) Haar, K.; Gallagher, J. "The Equation of State for Ammonia"; NBS Internal Report 75770, Washington, 1975.
- (15) "ASME Steam Tables"; United Engineering Center: New York, 1967.
- (16) Mathias, P. M. *Ind. Eng. Chem. Process Des. Dev.* **1983**, *22*, 385.

Received for review November 22, 1983. Revised manuscript received July 30, 1984. Accepted January 9, 1985. We are grateful to the Institut Français du Pétrole for financial support.