

# Vapor Pressure of (Potassium Hydroxide + Ammonia + Water) Solutions

G. Cacciola,<sup>\*,†</sup> G. Restuccia,<sup>†</sup> and Yu. Aristov<sup>‡</sup>

National Council of Research, Institute of Transformation and Storage of Energy, S. Lucia sopra Contesse, 98126 Messina, Italy, and Boreskov Institute of Catalysis, Prospekt Lavrentieva 5, Novosibirsk 630090, Russia

Experimental results on equilibrium pressure over KOH + NH<sub>3</sub> + H<sub>2</sub>O solutions are reported. The temperature was varied between -6 and +30 °C, while the molalities of NH<sub>3</sub> and KOH were varied in the range 1–12 and 1–10 mol·kg<sup>-1</sup>, respectively. An analytical equation of the equilibrium pressure as a function of temperature and concentrations was obtained. The partial molar enthalpy of solution of ammonia in the KOH + H<sub>2</sub>O mixtures and the Henry coefficients for ammonia were also calculated. For the ternary mixture the Setschenow relation was considered and validated in the range of measured concentrations.

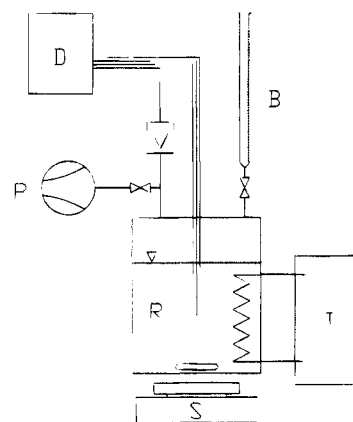
## Introduction

Thermally driven heat pumps or cooling systems were proposed from the beginning of this century, and in particular the ammonia plus water refrigeration system was developed. Afterward, systems based on ternary mixtures were also suggested but not developed because of the subsequent wide use of vapor compression systems. In recent years, research activity on absorption systems has increased and some old proposals have been reviewed. Among these, a demixing–resorption machine utilizing potassium hydroxide + ammonia + water seems to have good characteristics. Aqueous KOH + NH<sub>3</sub> solutions represent an interesting alternative to the traditional vapor–liquid pairs such as ammonia + water and water + lithium bromide that are commonly used in absorption heat pumps and refrigeration systems (1, 2). In fact, with the ternary system which uses KOH + NH<sub>3</sub> + H<sub>2</sub>O the total pressure in the demixing–resorption machine can be lowered with respect to the absorption system in which only water and ammonia are used. The engineering design of these systems requires accurate data on the thermodynamic properties of potassium hydroxide + ammonia + water mixtures over a wide range of conditions. However, published results (3–8) cover a limited range of concentrations, usually at molalities less than 3 mol·kg<sup>-1</sup> of solvent for both KOH and NH<sub>3</sub> and temperature ranges higher than 20 °C. The aim of the present paper is to extend the measurements on the vapor pressure over aqueous KOH + NH<sub>3</sub> solutions to temperatures as low as -6 °C and higher concentrations of both KOH and NH<sub>3</sub>, to  $m = 10$ –12 mol·kg<sup>-1</sup>.

## Experimental Section

The experimental arrangement shown in Figure 1 was used to measure the vapor–liquid equilibrium curves for KOH + NH<sub>3</sub> + H<sub>2</sub>O mixtures.

All experiments were performed in the stainless steel container (R), where the temperature was kept constant in the range -6 to +30 °C by the thermocryostat (T) with an accuracy of ±0.02 °C. Before the start of each series of experiments, the container was evacuated by the pump (P), and then a fixed volume of KOH + H<sub>2</sub>O solution of known



**Figure 1.** Scheme of the experimental setup: R, container; T, thermocryostat; V, vacuum gauge; P, pump; D, recorder; S, mixer; B, burette.

concentration was inserted by means of the burette (B). Once the constant temperature and pressure had been established, they were compared with the equilibrium data presented in ref 9 to verify the validity of the method. Subsequently, a measured volume of NH<sub>4</sub>OH solution of known concentration was added and the total pressure and the temperature were recorded. After equilibrium was reached, the temperature was changed. The measurements were performed in the temperature range  $t = -6$  to +30 °C.

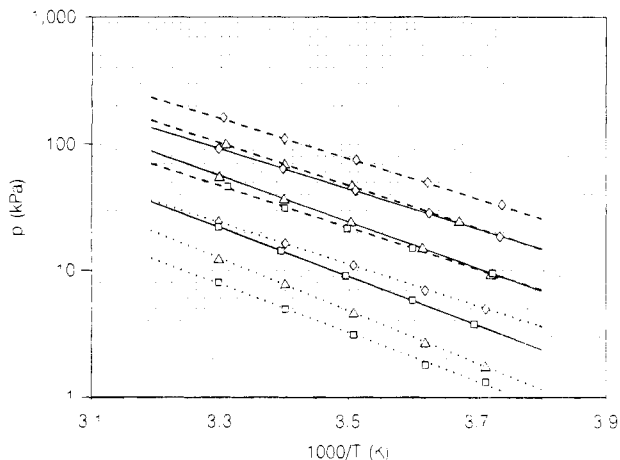
The total pressure over the solution was measured by an absolute pressure vacuum gauge (V) that is composed of a sensor head, where the pressure to be measured acts directly on a fine membrane, and a control unit (Membranovac MV 110S2). The accuracy of the instrument was within 0.05 kPa. The temperature of the mixture was measured by three J-type thermocouples placed at three different levels to verify the homogeneity of the temperature distribution that appeared to be within 0.3 °C.

Commercially available potassium hydroxide (Rudi Point), ammonium hydroxide (Baker grade), and distilled water were used for the mixture preparation. The molalities of NH<sub>3</sub> ( $m_1$ ) and KOH ( $m_2$ ) were varied in the range  $m_1 = 1$ –12 mol·kg<sup>-1</sup> and  $m_2 = 1$ –10 mol·kg<sup>-1</sup>. The accuracy of the ammonia and potassium hydroxide concentration was calculated by taking into consideration all of the measurement errors involved in the solution preparation. From

<sup>†</sup> National Council of Research.  
<sup>‡</sup> Boreskov Institute of Catalysis.

**Table 1. Vapor Pressure  $p$  at Temperature  $t$  for KOH + NH<sub>3</sub> + H<sub>2</sub>O**

|                                     |      |      |      |      |      |      |      |      |      |       |       |      |       |       |       |
|-------------------------------------|------|------|------|------|------|------|------|------|------|-------|-------|------|-------|-------|-------|
| $m_1/\text{mol}\cdot\text{kg}^{-1}$ | 1    | 1    | 1    | 1    | 1    | 1    | 1    | 1    | 1    | 1     | 1     | 1    | 1     | 1     | 1     |
| $m_2/\text{mol}\cdot\text{kg}^{-1}$ | 1    | 1    | 1    | 1    | 1    | 5    | 5    | 5    | 5    | 5     | 10    | 10   | 10    | 10    | 10    |
| $t/^\circ\text{C}$                  | -3.8 | 3.2  | 11.7 | 20.6 | 30.1 | -3.6 | 3.2  | 12   | 21   | 30    | -4.2  | 2.9  | 11.9  | 20.8  | 30.2  |
| $p/\text{kPa}$                      | 1.32 | 1.8  | 3.1  | 4.93 | 8    | 1.76 | 2.71 | 4.64 | 7.91 | 12.42 | 4.96  | 6.93 | 10.96 | 16.35 | 24.24 |
| $m_1/\text{mol}\cdot\text{kg}^{-1}$ | 5    | 5    | 5    | 5    | 5    | 5    | 5    | 5    | 5    | 5     | 5     | 5    | 5     | 5     | 5     |
| $m_2/\text{mol}\cdot\text{kg}^{-1}$ | 1    | 1    | 1    | 1    | 1    | 5    | 5    | 5    | 5    | 5     | 10    | 10   | 10    | 10    | 10    |
| $t/^\circ\text{C}$                  | -2.5 | 4.7  | 12.9 | 21.4 | 30.1 | -4.4 | 3.5  | 12.2 | 21   | 30    | -5.4  | 2.7  | 11.7  | 21.1  | 30.1  |
| $p/\text{kPa}$                      | 3.76 | 5.8  | 9.11 | 14.4 | 22.1 | 9.35 | 15.3 | 24.6 | 37.2 | 55.58 | 18.5  | 28.5 | 43.01 | 64.06 | 91.67 |
| $m_1/\text{mol}\cdot\text{kg}^{-1}$ | 10.7 | 10.7 | 10.7 | 10.7 | 10.7 | 10.7 | 10.7 | 10.7 | 10.7 | 10.7  | 10.7  | 10.7 | 10.7  | 10.7  | 10.7  |
| $m_2/\text{mol}\cdot\text{kg}^{-1}$ | 1    | 1    | 1    | 1    | 1    | 5    | 5    | 5    | 5    | 5     | 10    | 10   | 10    | 10    | 10    |
| $t/^\circ\text{C}$                  | -2.4 | 4.4  | 12.5 | 21.2 | 30   | -3.1 | 3.9  | 12.4 | 21.3 | 30    | -4.7  | 3.1  | 11.9  | 21    | 29.7  |
| $p/\text{kPa}$                      | 8.55 | 13   | 19.9 | 30.9 | 46   | 18.6 | 28   | 42.8 | 64.3 | 94.02 | 29.2  | 46.2 | 69.46 | 103.7 | 151.4 |
| $m_1/\text{mol}\cdot\text{kg}^{-1}$ | 12   | 12   | 12   | 12   | 12   | 12   | 12   | 12   | 12   | 12    | 12    | 12   | 12    | 12    | 12    |
| $m_2/\text{mol}\cdot\text{kg}^{-1}$ | 1    | 1    | 1    | 1    | 1    | 5    | 5    | 5    | 5    | 5     | 10    | 10   | 10    | 10    | 10    |
| $t/^\circ\text{C}$                  | -4.6 | 4.7  | 12.7 | 20.9 | 28.8 | -0.8 | 12.1 | 20.9 | 29.1 |       | -5.6  | 2.9  | 11.6  | 20.7  | 29.4  |
| $p/\text{kPa}$                      | 9.5  | 15   | 21.6 | 31.2 | 46   | 24.7 | 47.5 | 70.4 | 101  |       | 33.11 | 49.9 | 75    | 110.3 | 161.6 |



**Figure 2.** Plot of  $\log(p)$  vs  $1000/T$  at various molalities of ammonia solutions [ $m_1 = 1$  (dotted lines);  $m_1 = 6$  (solid lines);  $m_1 = 12$  (dashed lines)] and various molalities of potassium hydroxide solutions [ $m_2 = 1$  ( $\square$ );  $m_2 = 5$  ( $\Delta$ );  $m_2 = 10$  ( $\diamond$ )]: comparison of the model results (lines) with the experimental data ( $\square$ ,  $\Delta$ ,  $\diamond$ ).

this analysis the calculated error in  $m_1$  and  $m_2$  was less than 4%.

## Results and Discussion

Experimental results of all measured values are reported in Table 1. The equilibrium pressure  $p$  over the KOH + NH<sub>3</sub> + H<sub>2</sub>O mixtures increases as the temperature  $t$  and the concentrations of ammonia and potassium hydroxide increase.

At fixed molalities  $m_1$  and  $m_2$ , the pressure was fit to the relation

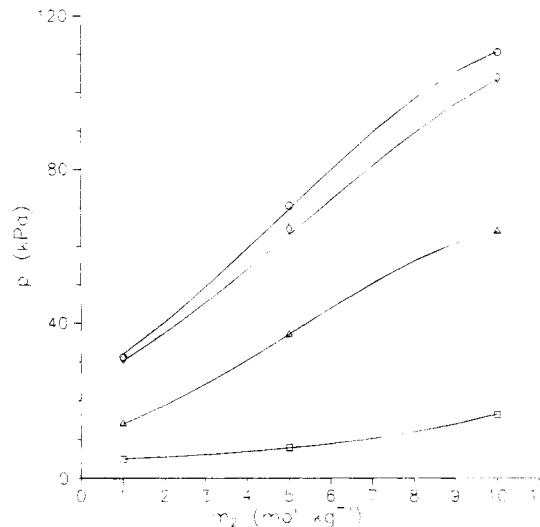
$$\log(p/\text{kPa}) = A + B/(T/\text{K}) \quad (1)$$

where the slope  $B$  and the intersection  $A$  are functions of  $m_1$  and  $m_2$ , the deviation of the original experimental data from eq 1 being rather small. The plots  $\log p$  vs  $1000/T$  for various molalities as parameters are presented in Figure 2 for the range  $t = -6$  to  $+30$  °C. From these plots, the coefficients  $A$  and  $B$  may be determined as functions of  $m_1$  and  $m_2$ .

To find an analytical equation describing the decimal logarithm of the total pressure at different  $T$ ,  $m_1$ , and  $m_2$ , the following expression was used:

$$\log(p/\text{kPa}) = A_0 + A_1m_1 + A_2m_1^2 + A_3m_1^3 + [B_0 + B_1m_1 + B_2m_1^2 + B_3m_1^3]/T \quad (2)$$

The coefficients  $A_i$  and  $B_i$  in turn are the polynomial functions of  $m_2$  (in  $\text{mol}\cdot\text{kg}^{-1}$ ). The best fit of eq 2 to the experimental data at all temperatures and concentrations



**Figure 3.** Total pressure over KOH + NH<sub>3</sub> + H<sub>2</sub>O solutions as a function of potassium hydroxide concentration at  $t = 21$  °C and various molalities of ammonia solutions [ $m_1 = 1$  ( $\square$ );  $m_1 = 5$  ( $\Delta$ );  $m_1 = 10.7$  ( $\diamond$ );  $m_1 = 12$  ( $\circ$ )]: comparison of the model results (—) with the experimental data ( $\square$ ,  $\Delta$ ,  $\diamond$ ,  $\circ$ ).

was reached for

$$A_0(m_2) = 7.23837 + 0.346158m_2 - 0.036028m_2^2 \quad (3a)$$

$$A_1(m_2) = -0.581795 + 0.154016m_2 - 0.0131801m_2^2 \quad (3b)$$

$$A_2(m_2) = 0.169752 - 0.0509724m_2 + 0.00432377m_2^2 \quad (3c)$$

$$A_3(m_2) = -0.0102889 + 0.0030956m_2 - 0.000256778m_2^2 \quad (3d)$$

and

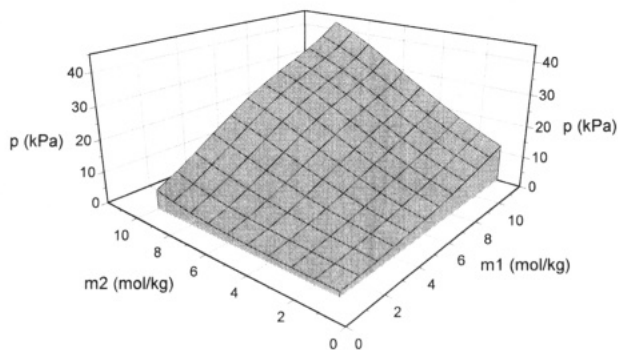
$$B_0(m_2) = -1930.41 - 113.928m_2 + 12.8484m_2^2 \quad (4a)$$

$$B_1(m_2) = 162.25 - 19.3016m_2 + 1.995652m_2^2 \quad (4b)$$

$$B_2(m_2) = -43.7237 + 11.2036m_2 - 0.9996743m_2^2 \quad (4c)$$

$$B_3(m_2) = 2.699365 - 0.74904m_2 + 0.063813m_2^2 \quad (4d)$$

The straight lines in Figure 2 and the curves in Figure 3 were calculated according to eqs 2–4; in the same figures



**Figure 4.** Total pressure over KOH + NH<sub>3</sub> + H<sub>2</sub>O solutions as a function of potassium hydroxide and ammonia concentrations at  $t = 0$  °C.

**Table 2. Total Pressure over KOH + NH<sub>3</sub> + H<sub>2</sub>O Solutions [Experimentally Measured by Sorina (3)  $p_{(\text{exp})}$  and Calculated  $p_{(\text{cal})}$  by the Proposed Model] at Different Molalities of Ammonia ( $m_1$ ) and Potassium Hydroxide ( $m_2$ )**

| $m_1/\text{mol}\cdot\text{kg}^{-1}$ | $m_2/\text{mol}\cdot\text{kg}^{-1}$ | $t/^\circ\text{C}$ | $p_{(\text{exp})}/\text{kPa}$ | $p_{(\text{cal})}/\text{kPa}$ |
|-------------------------------------|-------------------------------------|--------------------|-------------------------------|-------------------------------|
| 0.867                               | 0.946                               | 20.8               | 4.7                           | 4.87                          |
|                                     |                                     | 28.5               | 7.1                           | 6.80                          |
| 1.03                                | 0.946                               | 21.4               | 4.9                           | 5.14                          |
|                                     |                                     | 28.1               | 7.7                           | 7.17                          |
| 1.244                               | 0.946                               | 20.6               | 5.6                           | 5.10                          |
|                                     |                                     | 28.4               | 7.9                           | 7.49                          |
| 1.021                               | 3.15                                | 21.1               | 6.2                           | 6.33                          |
|                                     |                                     | 30.3               | 9.7                           | 10.31                         |
| 1.288                               | 3.15                                | 21.4               | 7.1                           | 7.10                          |
|                                     |                                     | 31.1               | 11.4                          | 11.78                         |

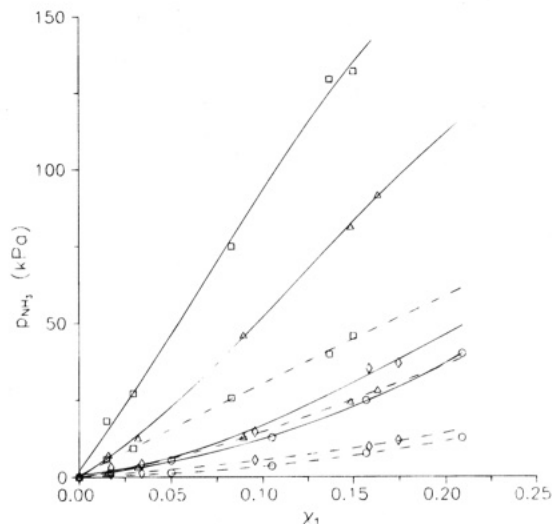
the experimental points are also shown to compare the model and experimental data graphically. The relative difference between experimental  $p_{i(\text{exp})}$  and calculated  $p_{i(\text{cal})}$  data can be expressed by the formula

$$D = \sqrt{\left[ \sum_n \left( \frac{p_{i(\text{exp})} - p_{i(\text{cal})}}{p_{i(\text{exp})}} \right)^2 \right] / n} \quad (5)$$

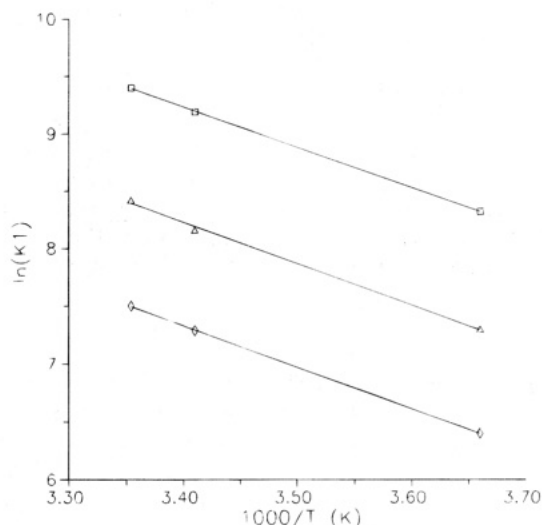
which gives a value of  $D = 0.02$ , indicating a good accuracy of the model. In Figure 4 the behavior of the total pressure as a function of the two concentrations  $m_1$  and  $m_2$ , at  $t = 0$  °C, is shown in a three-dimensional plot.

To our knowledge most of the results presented in the literature for the KOH + NH<sub>3</sub> + H<sub>2</sub>O solution are related to the range of higher temperatures and lower concentrations. The experimental data available for the comparison in the literature are presented in Table 2 together with the pressures calculated with our model under the conditions described in ref 3. The agreement between the two sets of data appears to be rather good despite the experiments in ref 3 being conducted some 30 years ago. Thus, we can conclude that the suggested model describes well all experimental data obtained within the range  $t = -6$  to  $+30$  °C,  $m_1 = 1$ – $12$  mol·kg<sup>-1</sup>, and  $m_2 = 1$ – $10$  mol·kg<sup>-1</sup>.

Another useful parameter for the design of the demixing-resorption machine is the partial molar enthalpy of ammonia solution in the KOH + H<sub>2</sub>O mixtures. In this case the ammonia partial pressure ( $p_{\text{NH}_3}$ ) must be known.  $p_{\text{NH}_3}$  can be easily calculated using the total pressure (measured or calculated according to eqs 2–4) and the partial pressure of the water vapor ( $p_{\text{H}_2\text{O}}$ ). In fact, if the lowering effect on the water vapor pressure due to ammonia is assumed to be negligible compared to the same effect due to potassium hydroxide (6, 9–12),  $p_{\text{H}_2\text{O}}$  can be considered equal to the total pressure over KOH + H<sub>2</sub>O solution and calculated by the following equation (9):



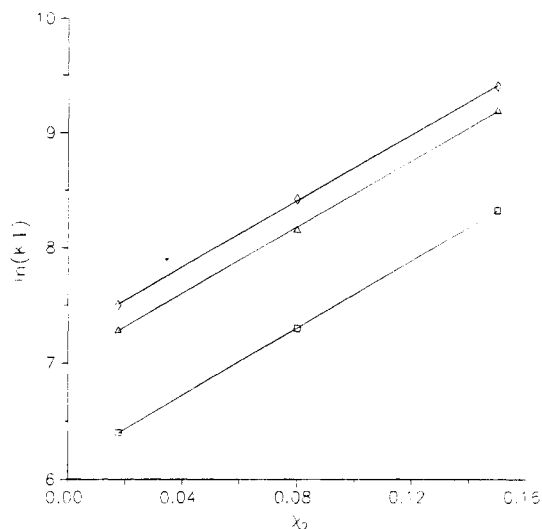
**Figure 5.** Ammonia partial pressure as a function of the ammonia mole fraction  $\chi_1$  in the liquid phase at 0 (dashed lines) and 25 °C (solid lines) for different mole fractions of KOH:  $\chi_2 = 0$  (○);  $\chi_2 = 0.0174$  (◇);  $\chi_2 = 0.08$  (△);  $\chi_2 = 0.15$  (□).



**Figure 6.**  $\ln(K_1)$  vs  $10^3/T$  at different mole fractions of KOH:  $\chi_2 = 0.0174$  (◇);  $\chi_2 = 0.08$  (△);  $\chi_2 = 0.15$  (□).

$$\log(p_{\text{H}_2\text{O}}/\text{kPa}) = 2.0 - 0.01508m_2 - 0.0016788m_2^2 + 2.25887 \times 10^{-5}m_2^3 + (1.0 - 0.0012062m_2 + 5.6024 \times 10^{-4}m_2^2 - 7.8228 \times 10^{-6}m_2^3)(35.4462 - 3343.93/(T/K) - 10.9 \log(T/K) + 0.0041645(T/K)) \quad (6)$$

Figure 5 shows the isotherms of ammonia solution at different concentrations of the potassium hydroxide. The curves at KOH mole fraction  $\chi_2 = 0.0174$  are close to the appropriate curves for two-component NH<sub>3</sub> + H<sub>2</sub>O solutions (12). With higher KOH concentrations, the range within which the ammonia pressure obeys the Henry law becomes larger (Figure 5). This likely indicates that the potassium hydroxide decreases the ability of ammonia to interact with the solvent (water). The Henry coefficients for ammonia  $K_1$  were calculated from the linear part of the isotherms. The plots of  $\ln(K_1)$  vs  $1000/T$  gave straight lines (Figure 6). This allows estimation of the partial molar enthalpy of ammonia solution at infinite dilution in the KOH + H<sub>2</sub>O mixture as  $-29.3$ ,  $-30.1$ , and  $-30.1$  kJ·mol<sup>-1</sup> for  $\chi_2 = 0.0174$ ,  $0.08$ , and  $0.15$ , respectively, with a deviation of about  $\pm 1.3$  kJ·mol<sup>-1</sup>. These values are in reasonably good agreement with those presented in the literature (3).



**Figure 7.**  $\ln(K_1)$  as a function of KOH mole fraction  $\chi_2$  (eq 7) at different temperatures:  $t = 0\text{ }^\circ\text{C}$  ( $\square$ );  $t = 20\text{ }^\circ\text{C}$  ( $\triangle$ );  $t = 25\text{ }^\circ\text{C}$  ( $\diamond$ ).

For ternary mixtures the Setschenow relation is considered to be valid in the range of low concentrations (13). In our case it can be formulated as

$$\ln K_1(p, T, \chi_2) = \ln K_1(p, T, \chi_2=0) + a\chi_2 \quad (7)$$

where  $K_1(p, T, \chi_2)$  is the Henry coefficient of  $\text{NH}_3$  at KOH mole fraction  $\chi_2$ . Figure 7 shows that the  $\text{KOH} + \text{NH}_3 + \text{H}_2\text{O}$  solutions follow the relation 7 in the  $\chi_2$  range 0.017–0.15 with coefficient  $a = 14.4 \pm 0.1$ , close to the value  $13.4 \pm 2.3$  obtained from the elaboration of the literature data (3).

### Conclusions

The total pressure over the  $\text{KOH} + \text{NH}_3 + \text{H}_2\text{O}$  solutions was measured at  $t = -10$  to  $+30\text{ }^\circ\text{C}$  and molalities  $m_1 = 1\text{--}12\text{ mol}\cdot\text{kg}^{-1}$  and  $m_2 = 1\text{--}10\text{ mol}\cdot\text{kg}^{-1}$  for ammonia and

potassium hydroxide, respectively. The analytical equation describing the total pressure over the mixtures at different  $T$ ,  $m_1$ , and  $m_2$  was obtained with a good fit to the experimental data. The Henry coefficients for  $\text{NH}_3$  were calculated in the range  $0\text{--}25\text{ }^\circ\text{C}$ , which allowed estimation of the partial molar enthalpy of solution of ammonia in the  $\text{KOH} + \text{H}_2\text{O}$  mixtures as  $29.7 \pm 1.3\text{ kJ}\cdot\text{mol}^{-1}$ . At the considered conditions the system was shown to obey the Setschnow equation.

### Literature Cited

- (1) Cacciola, G.; Restuccia, G.; Rizzo, G. *Heat Recovery Syst. CHP* **1990**, *10*, 177.
- (2) Cacciola, G.; Restuccia, G.; Sellerio, U. Thermodynamic analysis of an absorption heat pump using a demixing-resorption process; International Symposium on High Efficiency Chemical Heat Pumps, Perpignan, Sept 14–16, 1988. In *Recent progres en genie des procedes—Pompes a chaleur chimiques de hautes performances*; Lavoisier Technique et Documentation: Paris, 1988; Vol. 2, no. 5, pp 106–117.
- (3) Sorina, G. A., et al. Solubility of Ammonia in Aqueous Solutions of Potassium Hydroxide. *Zh. Obshch. Khim.* **1967**, *37*, 2150 (in Russian).
- (4) Katan, T.; Campa, A. B. Vapor Pressure of Ammonia in Aqueous Potassium Hydroxide Solutions. *J. Chem. Eng. Data* **1963**, *8*, 574.
- (5) Abegg, R.; Riesenfeld, H. *Z. Phys. Chem.* **1902**, *40*, 90.
- (6) Conway, E. J.; Byrne, A. *Biochem. J.* **1933**, *27*, 423.
- (7) Konovalow, D. *Ch. Central-Blatt* **1900**, *1*, 938.
- (8) Riesenfeld, H. *Z. Phys. Chem.* **1903**, *45*, 462.
- (9) Balej, J. Water vapour partial pressures and water activities in potassium and sodium hydroxide solutions over wide concentration and temperature ranges *Int. J. Hydrogen Energy* **1985**, *10*, 233.
- (10) *International Critical Tables of Numerical Data, Physics, Chemistry and Technology*; Washburn, E., Ed.; McGraw-Hill: New York, 1928; Vol. 3, p 373.
- (11) Scatchard, G., et al. Thermodynamic Properties-Saturated Liquid and Vapor of Ammonia-Water Mixtures. *Refrig. Eng.* **1947**, *53*, 413–419.
- (12) Perry, R. H.; Chilton, C. H. *Chemical Engineer's Handbook*, 5th ed.; McGraw-Hill, New York, 1982; Table 3-21.
- (13) Setschenow, J. *Z. Phys. Chem.* **1889**, *4*, 117.

Received for review July 6, 1994. Accepted October 8, 1994.\*

JE9401272

\* Abstract published in *Advance ACS Abstracts*, December 1, 1994.