Fig. 1. Ammonia activity coefficients in ammonia-water system as function of ammonia concentration in liquid phase at temperatures of −40°, + 90° and 120°C. Solid lines = calculated with Gompertz equation; $\bigcirc$ = calculated from experimental determination.

in a different way. Substituting K'_i and $\phi_{i,v}$ as determined, respectively, from Equations (3) and (4) and multiplying the numerator and denominator by total pressure P, we obtain the following:

$$\frac{y_i}{x_i} = f^{\circ}_{i,L} \frac{y_i P}{f_{i,v}} \frac{\gamma_{i,L}}{P} K_i \qquad (9)$$

The assumption made on developing Equation (8) is that pressure does not exert any effect on deviation from ideality. It takes account only of deviation from ideality in liquid phase due to differences in molecular type between water and ammonia.

The limiting effect is that the calculated equilibrium is independent of the relative amounts of nitrogen and hydrogen and is valid only for low pressure. In developing Equation (9), these limitations are removed and, as can be seen, the vapor pressure p_i has been replaced by $f^{\circ}_{i,L}(y_i P/f_{i,v})$; that is, the product of the fugacity of the liquid in the standard state and a correction term which is the ratio of the fugacity in the vapor phase with ideal and nonideal behavior assumed.

EVALUATION OF TERMS IN EQUATIONS (8) AND (9)

Liquid Phase Activity Coefficient $\gamma_{i,L}$

This activity coefficient appears in both Equations (8) and (9) because it takes account of deviations from ideal behavior resulting from differences in molecular type between water and ammonia. Wucherer (1, 2) has studied the system ammonia-water at pressure from 760 to 7,600 mm. Hg and ammonia concentration from 2.1 to 81.0%. Clifford and Hunter (3, 4) also studied this system with pressure from 152 to 7,600 mm. Hg and ammonia concentration from 0 to 100%. Bosnjakovic (10) has examined the same system for pressures up to 15,200 mm. Hg. The experimental results of these authors have been

applied to calculate the activity coefficients γ_{NH_3} and γ_{H_2O} by application of Equation (8).

The values of γ so calculated have been arranged to determine an empirical expression for evaluation of γ as a function of ammonia concentration at constant temperature. The following equations have been tried:
Sigmoid equation:

$$\frac{x_{NH_3} - c}{a + bx_{NH_3}} = \log \frac{20 \, \gamma_{NH_3}}{\log (100 - \gamma_{NH_3})}$$

Gompertz equation:

$$\gamma_{NH_3} = l_1 + l_2 \cdot l_3^{l_4 \exp\left(\frac{x_{NH_3}}{0.05} - 1\right)}$$

$$\gamma_{NH_3} = a + b \cdot \sin x_{NH_3} + c \cdot x_{NH_3}^5 + d \cdot x_{NH_3}^{-1}$$

$$\gamma_{NH_3} = a + b \cdot \sin x_{NH_3} + c \cdot x_{NH_3}^5 + d \cdot x_{NH_3}^{1/3}$$

$$\gamma_{NH_3} = a + b \cdot \sin x_{NH_3} + c \cdot x_{NH_3}^5 + d \cdot x_{NH_3}^{-5} \qquad (10)$$

The Gompertz equation (11) has been found to be the best to fit the experimental values of γ_{NH_3} up to $x_{NH_3} = 0.7$.

The values of the constants for each temperature are given in the following table:

t, °C.	l_1	l_2	l_3	l_4
−40	0.04	1.3670	0.005243	0.8342
0	0.07	2.0045	0.00457	0.8630
+30	0.11	1.4800	0.01960	0.8565
50	0.145	1.6860	0.01882	0.8704
70	0.170	1.4250	0.01710	0.8500
90	0.207	1.0160	0.0227	0.8220
120	0.262	0.886	0.0279	0.8080

The experimental values of the water activity coefficients are better fitted by Equation (11):

$$\gamma_{H_2O} = l_5 (x_{NH_3})^{l_6} + 1 \qquad (11)$$

The values of the constants are presented in the following table as function of temperature.

t, °C.	l_5	l_6
−40	−0.310	1.918646
+21	−0.245	2.351825
120	−0.127	2.081918

In Figure 1 a graph shows the agreement between the activity coefficients calculated with Equation (10) and the experimental values for the three temperatures of −40°, 90°, and +120°C. It is seen that the Gompertz $\int$ shape curves are well suited for determining the γ_{NH_3}.

Liquid Phase Fugacity in the Standard State

Integrating (5) the basic thermodynamic equation

$$\left(\frac{\delta \ln f_{i,L}}{\delta P} \right)_T = \frac{v}{RT} \qquad (12)$$

we obtain the following, with constant (average) volume assumed:

$$\ln \frac{f^{\circ}_{i,L,P}}{f_{i,L,p_i}} = \frac{v_{m,i}(P - p_i)}{RT} \qquad (13)$$

Equation (13) is useful only for values of reduced temperature less than 0.8. For a few cases in the present work the reduced temperature of ammonia is higher than 0.8 and less approximate results are to be expected. Fortunately these cases are of less importance in industrial application.