

Fig. 2. Ratio of standard fugacity of water and its vapor pressure as a function of pressure and temperature.

Gamson and Watson (6) proposed the following expression for $v_{m,i}$:

$$v_{m,i} = (v\omega)_i (5.7 + 3.0 T_{r,i}) \quad (14)$$

where $(v\omega)_i$ is a constant for each component.

The fugacity $f_{i,L,P}$ relative to the vapor pressure at the temperature T of the system is calculated by the generalized correlation of Gamson and Watson (5, 6) for determining the fugacity coefficient v_i as a function of reduced temperature and reduced pressure:

$$v_i = \frac{f_{i,L,P}}{p_i} \quad (15)$$

Substitution of Equations (14) and (15) into Equation (13) gives the following:

$$\log(f_{i,L,P}^o) = \log p_i + \log v_i + \frac{(v\omega)_i(5.7 + 3.0 \cdot Tr)(P - p_i)}{2.303 RT} \quad (16)$$

The vapor pressure p_i for ammonia and water is calculated with the Antoine equation and is then converted to atmosphere units:

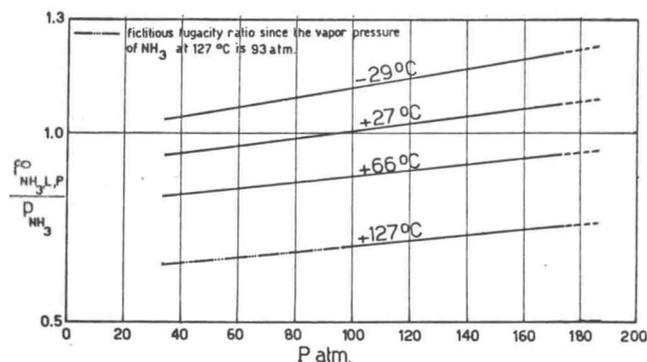


Fig. 3. Ratio of standard fugacity of ammonia and its vapor pressure as a function of pressure and temperature.

$$\log p_i = A - \frac{B}{C + t} \quad (17)$$

The Antoine equation constants have been taken from reference 7:

| | A | B | C |
|---------|---------|----------|---------|
| Water | 8.10765 | 1750.286 | 235.000 |
| Ammonia | 7.55466 | 1002.711 | 247.885 |

The other constants in Equation (16) are:

| | | |
|--------------------|----------|----------------------------|
| $(v\omega)_{NH_3}$ | = 3.10 | cc./g.-mole |
| $(v\omega)_{H_2O}$ | = 2.28 | cc./g.-mole |
| R | = 82.057 | (atm.)(cc.)/(g.-mole)(°K.) |

Equation (16) has been applied in the pressure range from 20 to 200 atm. and at temperatures from -29° to $+127^\circ$ C. In this range $f_{i,L,P}^o$ was seen to be substantially a linear function of pressure at constant temperature for ammonia and water. The values calculated at different temperature are presented in Figures 2 and 3.

$f_{i,v}/Py_i$: Ratio Between Fugacities in Vapor Phase at Nonideal and Ideal Conditions

For a component in the mixture of the vapor phase, Equation (12) becomes

$$\left(\frac{\delta \ln f_{i,v}}{\delta P} \right)_T = \frac{\bar{v}_i}{RT} \quad (18)$$

and by integration at constant temperature

$$\ln \frac{f_{i,v}}{Py_i} = -\frac{1}{RT} \int_0^P \left(\frac{RT}{P} - \bar{v}_i \right) dP \quad (19)$$

TABLE 1. COMPARISON OF EXPERIMENTAL POINTS WITH VALUES CALCULATED WITH EQUATIONS (8) AND (9)
Ratio of hydrogen-nitrogen is 2.1/1.

| No. | $t, ^\circ\text{C.}$ | $P, \text{atm.}$ | x_{NH_3} | $y_{NH_3}^s$ | $y_{NH_3}^c$ | $y_{NH_3}^i$ | $y_{H_2O}^s$ | $y_{H_2O}^c$ | $y_{H_2O}^i$ |
|-----|----------------------|------------------|------------|--------------|--------------|--------------|--------------|--------------|--------------|
| 1 | 50 | 50.5 | 0.663 | — | 0.2640 | 0.2539 | 0.002464 | 0.00260 | 0.00076 |
| 2 | | 58.2 | — | 0.2180 | 0.2308 | 0.2177 | — | 0.00230 | 0.00065 |
| 3 | | 78.6 | — | 0.1850 | 0.1803 | 0.1611 | 0.002490 | 0.00188 | 0.00048 |
| 4 | | 98.0 | — | — | 0.1520 | 0.1282 | 0.002365 | 0.00162 | 0.000384 |
| 5 | | 117.5 | — | 0.1380 | 0.1342 | 0.1078 | 0.002000 | 0.00146 | 0.000321 |
| 6 | | 146.6 | — | 0.1060 | 0.1150 | 0.0864 | 0.001500 | 0.00131 | 0.000257 |
| 7 | | 170.0 | — | — | 0.1060 | 0.07355 | 0.000871 | 0.00122 | 0.00022 |
| 8 | | 185.4 | — | 0.0900 | 0.0991 | 0.06832 | 0.001490 | 0.00117 | 0.000203 |
| 9 | 80 | 58.2 | 0.663 | 0.4807 | 0.4500 | 0.4400 | 0.007960 | 0.0085 | 0.00252 |
| 10 | | 78.5 | — | 0.3600 | 0.3525 | 0.3257 | 0.006600 | 0.00699 | 0.00186 |
| 11 | | 98.0 | — | 0.2768 | 0.2908 | 0.2643 | 0.004600 | 0.00605 | 0.00149 |
| 12 | | 117.5 | — | 0.2600 | 0.2537 | 0.2179 | 0.005600 | 0.00544 | 0.00125 |
| 13 | | 146.6 | — | 0.2120 | 0.2175 | 0.1746 | 0.004480 | 0.00486 | 0.00100 |
| 14 | | 170.0 | — | 0.1885 | 0.1940 | 0.1515 | 0.004500 | 0.00453 | 0.000857 |
| 15 | | 185.4 | — | 0.1850 | 0.1803 | 0.1381 | 0.00398 | 0.00424 | 0.00079 |