Equation (8). Even if the water experimental points are more scattered, in Figure 5 one can see that the curves calculated with Equation (9) are closer to the experimental points than the curves calculated with Equation (8).

The same observations can be made by examining Table 1. All points present negative deviation when calculated with Equation (8), while an approximately even distribution of negative and positive deviations is obtained when calculated with Equation (9). The absolute value of the mean percentage difference decreases when calculated with Equation (9) with respect to the corresponding results of Equation (8).

The fact that real values of concentrations of ammonia and water in vapor phase at high pressure are higher than those calculated with ideal behavior assumed [Equation (8)] has already been recognized by others (15 to 19).

COMPARISON OF CORRESPONDING RESULTS OF EQUATIONS (8) AND (9)

Equilibrium calculations have been worked out by applying Equations (8) and (9) for the following conditions:†

Pressure, atm.: 3, 20, 40, 60, 80, 100, 120, 160, 190
Temperature, °C.: −28, −15, 0, +30, 60, 90, 120
x_{NH_3}: 0.20, 0.40
% nitrogen in the
nitrogen-hydrogen mixture: 0, 25, 50, 75, 100

The values obtained from Equation (8), with complete ideality of the vapor phase assumed, may be very different with respect to those obtained from Equation (9). This difference is pointed out by the ratios $(y(9)/y(8))_{HN_3}$ and $(y(9)/y(8))_{H_2O}$.

For water the difference increases continuously by increasing the pressure and the values of Equation (9) are always higher than those of Equation (8). For ammonia the difference is not so pronounced and there is a pressure at which they become equal. Only beyond this pressure do the values of Equation (9) become higher than those of Equation (8). This pressure is not the same for every temperature. It increases by increasing the temperature. For the low temperature examined here, the value of this pressure is so low that it falls outside the limit of pressure considered and the concentrations from Equation (9) are all higher than those of Equation (8). For the high temperature examined here the value of this pressure is so high that it falls outside the other limit of pressure considered and the concentrations of Equation (9) are all smaller than those of Equation (8).

By taking into account the effects of pressure, temperature, nitrogen-hydrogen ratio, and x_{NH_3}, it can be revealed that the curves representing the variations of y_{NH_3} and y_{H_2O} as a function of pressure, all the other terms remaining constant, tend to a constant value. The pressure corresponding to this constant value is a function of temperature, x_{NH_3} and of nitrogen content in the incondensable gases. It is lower for higher nitrogen content, for higher values of x_{NH_3}, and for lower values of temperature. This is supposed to be due to approximations resulting from the use of a two-constant equation of state.

NOTATION

a_i = activity of component i
$a_{i,L}$ = activity of component i in liquid phase

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† Tables of calculated values of Equations (8) and (9) have been deposited as document 9349 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $2.50 for photoprints or $1.75 for 35-mm. microfilm.

$a_{i,v}$ = activity of component i in vapor phase
f_i = fugacity of component i, atm.
f_i° = fugacity of component i at standard condition, atm.
$f_{i,v}^\circ$ = fugacity of component i at standard condition in vapor phase, atm.
$f_{i,L}^\circ$ = fugacity of component i at standard condition in liquid phase, atm.
$f_{i,L,P}^\circ$ = fugacity of component i in liquid phase at standard condition (total pressure P), atm.
$f_{i,v}$ = fugacity of component i in vapor phase, atm.
$f_{i,L}$ = fugacity of component i in liquid phase, atm.
f_{i,L,p_i} = fugacity of component i in liquid phase at temperature of system and corresponding vapor pressure, atm.
G = total moles in vapor phase
K_i' = vaporization constant of component i
K_i = equilibrium constant of component i
N = moles of hydrogen or nitrogen in vapor phase
P = pressure of the system, atm.
P_c = critical pressure, atm.
p_i = vapor pressure of component i at temperature of system, atm.
R = gas constant 82.057 atm., cc./(g.-mole)(°K.)
t = temperature of the system, °C.
T = temperature of the system, °K.
T_c = critical temperature, °K.
T_r = reduced temperature, T/T_c
V = molal volume in vapor phase, cc./g.-mole
v = molal volume in liquid phase, cc./g.-mole
$\bar{v}_i$ = partial molal volume in vapor phase, cc./g-mole
$v_{m,i}$ = mean molal volume of liquid phase, cc./g.-mole
x_i = mole fraction of component i in liquid phase
y_i = mole fraction of component i in vapor phase
y_i^i = mole fraction of component i in vapor phase as calculated by Equation (8)
y_i^c = mole fraction of component i in vapor phase as calculated by Equation (9)
y_i^s = mole fraction of component i in vapor phase by experimental determination
z = gas compressibility factor

Greek Letters

$\phi_{i,v}$ = activity coefficient of component i in vapor phase
$\gamma_{i,L}$ = activity coefficient of component i in liquid phase
ω_i = expansion factor of component i
ν_i = fugacity coefficient

Subscripts

v = vapor phase
L = liquid phase
P = total pressure of the system, atm.
p_i = vapor pressure of component i at temperature T of the system

Superscripts

s = experimental value
c = calculated values with nonideal solution assumed
i = calculated values with ideal solutions assumed
$\circ$ = standard state

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