High-Pressure Vapor-Liquid Equilibria in Ammonia-Water-Nitrogen-Hydrogen System

GIANFRANCO GUERRERI

SNAM Progetti, Milan, Italy

The results of ideal and nonideal vapor-liquid equilibria of ammonia-water-nitrogen-hydrogen, a system of industrial importance, have been examined. Redlich-Kwong equation of state and the Gompertz equation have been used to determine the fugacities and activity coefficients in the vapor and liquid phases, respectively. The standard fugacity in the liquid phase is found by integrating the fundamental thermodynamic equation by using the Gamson-Watson expression.

A trial and error procedure for the determination of a nonideal equilibrium system has been suggested. A comparison has been made between the available experimental values and the calculated ones. The importance of the use of fugacities which include deviations from ideality in calculating thermodynamic equilibria has been pointed out.

In ammonia production process, ammonia is separated from the effluent gas of the reactor by high-pressure liquid absorption in dilute ammonia solution. The components of this gas are mainly nitrogen and hydrogen. For the proper design of the absorber and of any other apparatus in which the four compounds—ammonia, water, nitrogen, and hydrogen—are simultaneously present in the liquid and vapor phases, it is necessary to know the relationships of their thermodynamic equilibrium.

The physical equilibrium between a vapor and a liquid is represented by constant K which is the ratio between the mole fraction y of a component in the vapor phase and the mole fraction x of the same component in the liquid phase.

In the present case we have four values of K, respectively, for the four components but, in order to simplify the solution of the problem, only K values of ammonia and water will be determined, with the assumption that nitrogen and hydrogen are present only in the vapor phase. This assumption seems to be reasonable for the particular circumstances of the case and for the limits in which the problem has to be solved. That is, large quantities of incondensable gases are present in the vapor phase and the mole fraction of ammonia and water in vapor will not be substantially different if small quantities will be absorbed in the liquid phase. On the other hand, small quantities of gas absorbed in the liquid phase will not change the mole fraction of water and ammonia or their molecular attraction.

THERMODYNAMIC BASIS

The general criterion of thermodynamic equilibrium in any heterogeneous system is that the chemical potential of any component be the same in every phase. For the treatment of the problem it is convenient to define a thermodynamic property directly related to fugacity and then also to chemical potential. This is activity a, defined as the ratio of the fugacity of a component in a given state to its fugacity in its standard state at the same temperature.

$$a_i = \left(\frac{f_i}{f_i^\circ} \right)_t \qquad (1)$$

For the system at constant temperature, the fugacity of each component has to be equal in every phase:

$$f_{i,v}^\circ \cdot a_{i,v} = f_{i,L}^\circ \cdot a_{i,L} \qquad (2)$$

$$\frac{a_{i,v}}{a_{i,L}} = \frac{f_{i,L}^\circ}{f_{i,v}^\circ} = K'_i \quad \text{(vaporization constant)} \qquad (3)$$

It is convenient to choose the pure component in the gaseous state at the temperature and pressure of the system as the standard state of the components in the vapor phase and the pure component in the liquid state at the temperature and pressure of the system for the standard state of the components in the liquid phase.

Before using Equation (3) it is necessary to place activity as a function of mole fraction and activity coefficients. This is another term equal to the ratio between activity and mole fraction.

For the vapor phase

$$a_{i,v} = \frac{f_{i,v}}{f_{i,v}^\circ} = \phi_{i,v} \cdot y_i \qquad (4)$$

For the liquid phase

$$a_{i,L} = \frac{f_{i,L}}{f_{i,L}^\circ} = \gamma_{i,L} \cdot x_i \qquad (5)$$

Substituting (4) and (5) into (3), one obtains

$$\frac{a_{i,v}}{a_{i,L}} = \frac{\phi_{i,v} \cdot y_i}{\gamma_{i,L} \cdot x_i} = K'_i \qquad (6)$$

and then

$$\frac{y_i}{x_i} = K'_i \frac{\gamma_{i,L}}{\phi_{i,v}} = K_i \quad \text{(equilibrium constant)} \qquad (7)$$

This is the final thermodynamic expression which has been used in the present work.

Equation (7), which relates to phase equilibria of component i, can be applied in two different ways if one considers an ideal solution of the components or a nonideal solution. The idea of an ideal solution was first introduced by G. M. Lewis, who defined it as a solution in which the fugacity of every component is proportional to its mole fraction for all the values of temperature and pressure.

Assuming ideal solution with the choosen standard states, we have $f_{i,v}^\circ = P$ and $f_{i,L}^\circ = p_i$. Applying the Lewis rule to the vapor phase $f_{i,v} = y_i \cdot P$, from Equation (4) $f_{i,v}/f_{i,v}^\circ = y_i P/P = \phi_{i,v} y_i$, then the activity coefficient $\phi_{i,v}$ equals to unity. For the liquid phase of our system, it is not possible to assume an ideal solution for which $\gamma_{i,L}$ would become equal to one because of the differences in molecular structure between water and ammonia.

Then from Equation (5) $f_{i,L} = p_i \cdot \gamma_{i,L} \cdot x_i$. Applying then Equation (7) to the ideal solution, we obtain Equation (8):

$$\frac{y_i}{x_i} = \frac{f_{i,L}^\circ \gamma_{i,L}}{f_{i,v}^\circ \phi_{i,v}} = \frac{p_i \gamma_{i,L}}{P} = K_i \qquad (8)$$

If one considers a nonideal solution, by choosing the same standard states, Equation (7) has to be transformed
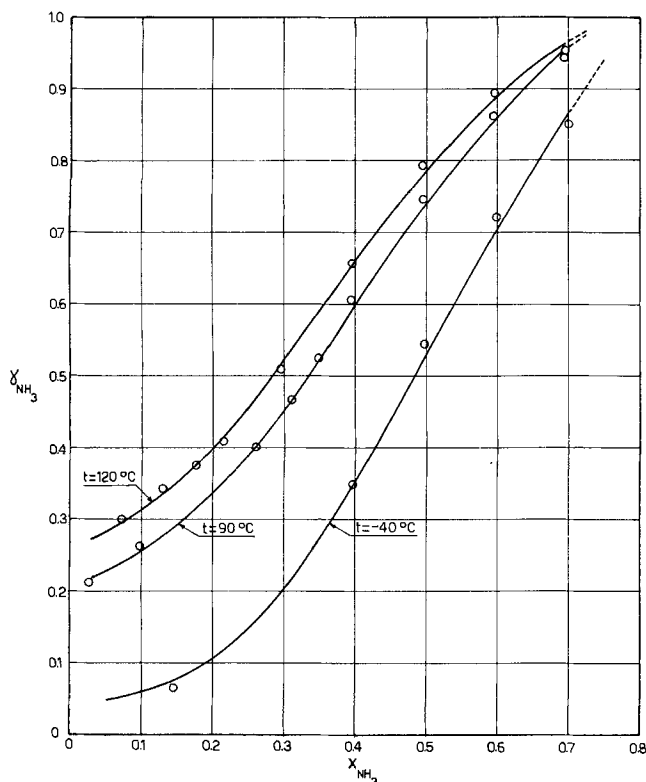
Fig. 1. Ammonia activity coefficients in ammonia-water system as function of ammonia concentration in liquid phase at temperatures of $-40°$, $+90°$ and $120°C$. Solid lines $=$ calculated with Gompertz equation; $O =$ calculated from experimental determination.

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:

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

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 $f°_{i,L}(y_i P/f_{i,v})$; 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_{NH3} and γ_{H2O} 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:

$$\frac{x_{NH3} - c}{a + bx_{NH3}} = \log \frac{20 \gamma_{NH3}}{\log (100 - \gamma_{NH3})}$$

Gompertz equation:

$$\gamma_{NH3} = l_1 + l_2 \cdot l_3^{\ l_4 \exp\left(\frac{x_{NH3}}{0.05} - 1\right)}$$

$$\gamma_{NH3} = a + b \cdot \sin x_{NH3} + c \cdot x_{NH3}^5 + d \cdot x_{NH3}^{-1}$$

$$\gamma_{NH3} = a + b \cdot \sin x_{NH3} + c \cdot x_{NH3}^5 + d \cdot x_{NH3}^{1/3}$$

$$\gamma_{NH3} = a + b \cdot \sin x_{NH3} + c \cdot x_{NH3}^5 + d \cdot x_{NH3}^{-5} \qquad (10)$$

The Gompertz equation (11) has been found to be the best to fit the experimental values of γ_{NH3} up to $x_{NH3} = 0.7$.

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):

$$\gamma_{H2O} = l_5(x_{NH3})^{l_6} + 1 \qquad (11)$$

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_{NH3}.

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:

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

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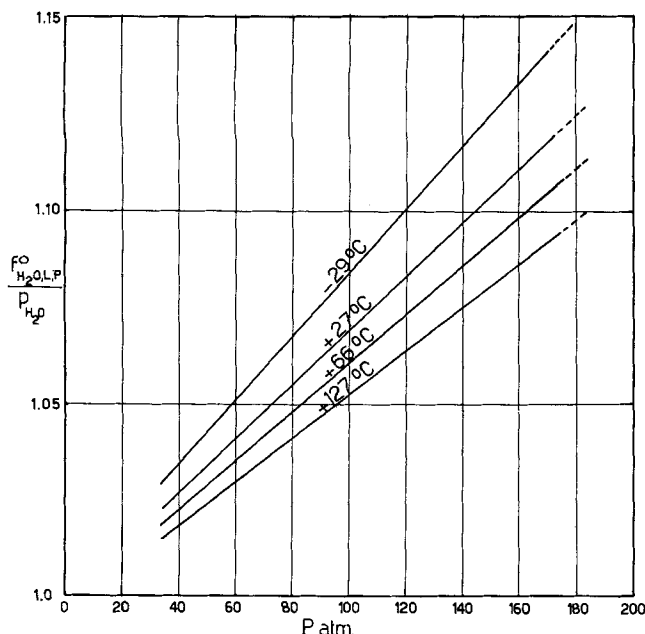
Fig. 2. Ratio of standard fugacity of water and its vapor pressure as a function of pressure and temperature.

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

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

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

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

The fugacity f_{i,L,p_i} 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:

$$v_i = \frac{f_{i,L,p_i}}{p_i} \tag{15}$$

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

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

The vapor pressure p_i for ammonia and water is calculated with the Antoine equation and is then converted to atmosphere units:
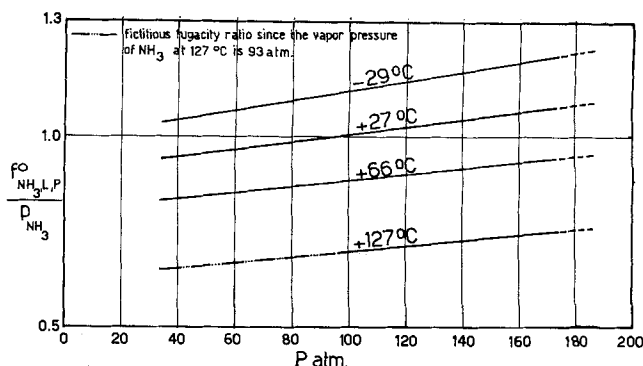
$$\log p_i = A - \frac{B}{C + t} \tag{17}$$

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:

$(v\omega)_{NH3} = 3.10$ cc./g.-mole
$(v\omega)_{H2O} = 2.28$ 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°C. In this range $f^{\circ}_{i,L,P}$ 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

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

and by integration at constant temperature

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

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

No.	t, °C.	P, atm.	x_{NH_3}	$y^s_{NH_3}$	$y^c_{NH_3}$	$y^i_{NH_3}$	$y^s_{H_2O}$	$y^c_{H_2O}$	$y^i_{H_2O}$
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

The Redlich-Kwong two-constant equation of state has been used for integration of the right-hand side of Equation (19):

$$P = \frac{RT}{V - b_i} - \frac{a_i}{T^{0.5} V(V - b_i)}$$

$$a_i = \frac{0.4278 \, R^2 T_c^{2.5}}{P_c}$$

$$b_i = \frac{0.0867 \, RT_c}{P_c} \qquad (20)$$

After integration of Equation (19) with the Redlich-Kwong equation of state, the following expression is obtained:

$$\ln \frac{f_{i,v}}{P \cdot y_i} = (z - 1) \frac{B_i}{B} - \ln (z - BP)$$

$$- \frac{A^2}{B} \left(\frac{2A_i}{A} - \frac{B_i}{B} \right) \ln \left(1 + \frac{BP}{z} \right)$$

$$z = \frac{PV}{RT}; \quad A_i = \frac{0.6541}{T_r^{1.25} P_c^{0.5}}; \quad B_i = \frac{0.0867}{T_r P_c} \qquad (21)$$

The terms with i index refer to the single component and those without i index refer to the mixture.

$$A = \Sigma A_i y_i ; \qquad B = \Sigma B_i y_i ;$$

The value of z can be calculated by solution of the following equation, which represents a form of the Redlich-Kwong equation:

$$z = \frac{1}{(1 - h)} - \frac{A^2}{B} \left(\frac{h}{1 + h} \right)$$

where

$$h = BP/z$$

TRIAL AND ERROR EQUILIBRIUM CALCULATION FOR NONIDEAL SYSTEM

The method of calculating the terms of Equation (9) for equilibrium of a nonideal system has been presented. As can be seen it depends upon the phase compositions, which, in turn, are the unknowns to be calculated. A trial and error solution is suggested which makes use of the system of the following nine equations.

$$y_{NH_3} = \overset{\circ}{f}_{NH_3,L} \left(\frac{y_{NH_3} P}{f_{NH_3,v}} \right) \frac{\gamma_{NH_3,L}}{P} \cdot x_{NH_3} \qquad [\text{Eq. (9)}] \quad (a)$$

$$y_{H_2O} = \overset{\circ}{f}_{H_2O,L} \left(\frac{y_{H_2O} P}{f_{H_2O,v}} \right) \frac{\gamma_{H_2O,L}}{P} \cdot (1 - x_{NH_3})$$
$$[\text{Eq. (9)}] \quad (b)$$

$$y_{N_2} = N_{N_2}/G \qquad (c)$$

$$y_{H_2} = N_{H_2}/G \qquad (d)$$

$$y_{NH_3} + y_{H_2O} + y_{N_2} + y_{H_2} = 1 \qquad (e)$$

$$\overset{\circ}{f}_{NH_3,L,P} = \phi_1 (P, T) \qquad [\text{Eq. (16)}] \quad (f)$$

$$\overset{\circ}{f}_{H_2O,L,P} = \phi_2 (P, T) \qquad [\text{Eq. (16)}] \quad (g)$$

$$\gamma_{NH_3} = \phi_3 (T, x_{NH_3}) \qquad [\text{Eq. (10)}] \quad (h)$$

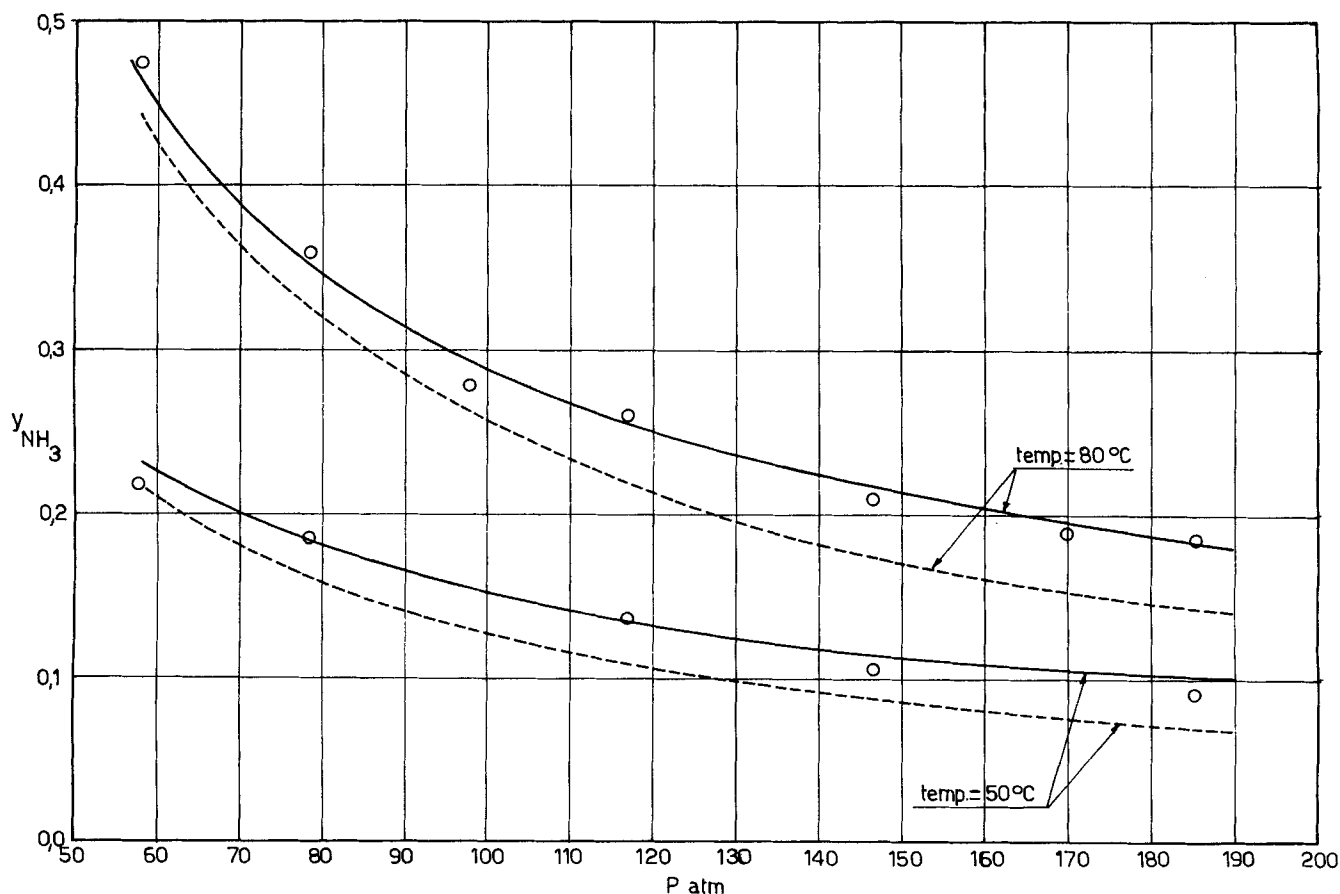$$\gamma_{H_2O} = \phi_4 (T, x_{NH_3}) \qquad [\text{Eq. (11)}] \quad (i)$$

Fig. 4. Mole fraction of ammonia in vapor phase as a function of pressure. Temperatures of 50° and 80°C. Ratio hydrogen-nitrogen = 2.1 to 1.-65% by wt. of ammonia in liquid phase. O = experimental points; solid lines = calculated with Equation (9); dotted lines = calculated with Equation (8).

Fig. 5. Mole fraction of water in vapor phase as a function of pressure. Temperatures of 50° and 80°C. Ratio hydrogen-nitrogen 2.1 to 1.-65% by wt. of ammonia in liquid phase. O = experimental points; solid lines = calculated with Equation (9); dotted lines = calculated with Equation (8).
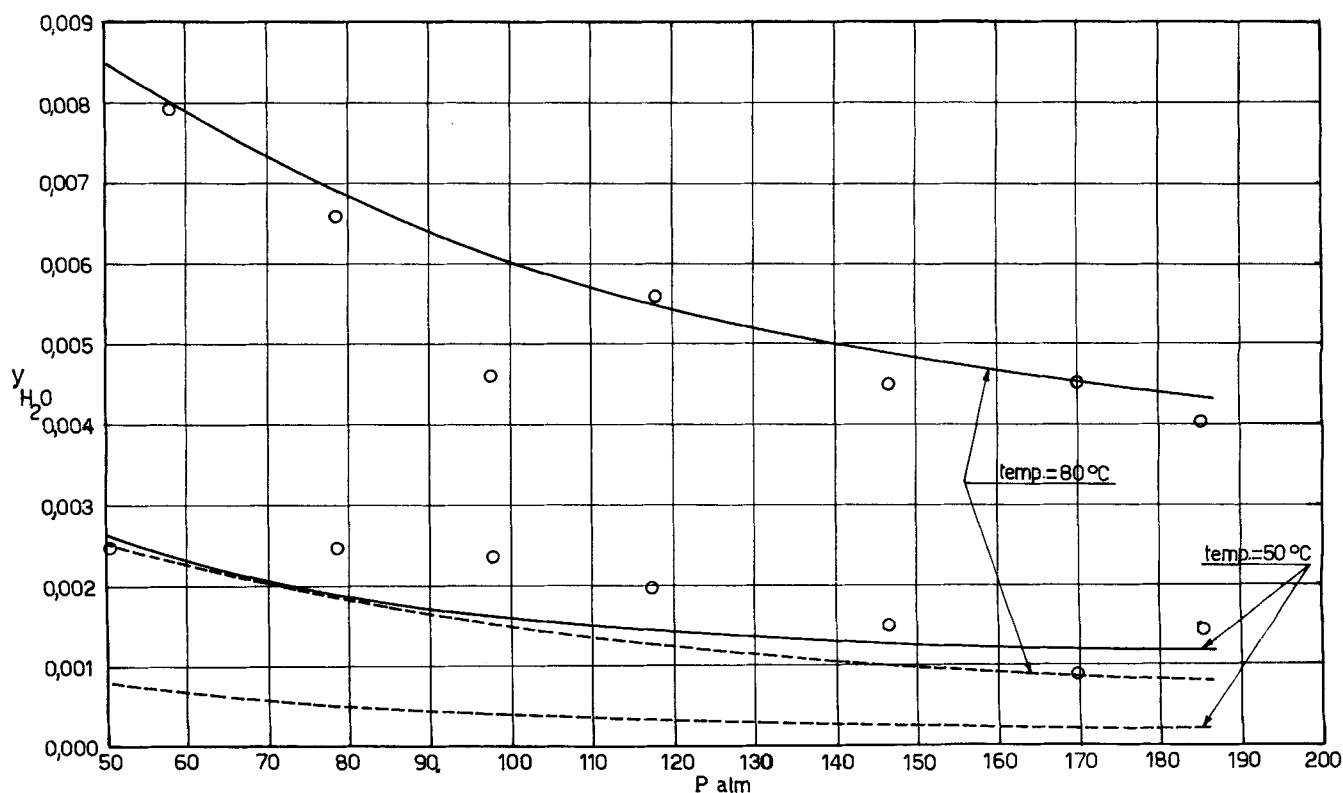
These equations can be applied to solve a boiling point or a dew point.

Data for boiling point solution: T, P, N_{N_2}, N_{H_2}, x_{NH_3}
Data for dew point solution: T, P, N_{N_2}, N_{H_2}, y_{NH_3}, y_{H_2O}

The first part of the solution is the same for both problems:

1. Choose a value of G.
2. Calculate y_{N_2} and y_{H_2} with Equations (c) and (d).

3. By use of T and P calculate $\overset{\circ}{f}_{NH_3,L,P}$ and $\overset{\circ}{f}_{H_2O,L,P}$ with Equation (16) or by use of the graphs of Figure 2 and 3 [Equations (f) and (g)].

The following refers to bubble point solution:

4. Calculate γ_{NH_3} and γ_{H_2O} with Equations (10) and (11) [Equations (h) and (i)].
5. Choose a value of y_{NH_3} and calculate y_{H_2O} with Equation (e).
6. Calculate $(f_{HNH_3,v}/P \cdot y_{NH_3})$ with Equation (21).
7. Calculate y_{HN_3} with Equation (a) and check it with the value assumed at point 5 of this procedure. Return to point 5 if the two values are not sufficiently approximated.
8. Calculate $(f_{H_2O,v}/P \cdot y_{H_2O})$ with Equation (21).
9. Calculate y_{H_2O} with Equation (b) and check it with the value calculated at point 5 with Equation (e). Return to point 1 if the two values are not sufficiently approximated.

The following refers to dew point solution:

4. Calculate y_{NH_3} or y_{H_2O} with Equation (e).
5. Calculate $(f_{NH_3,v}/P \cdot y_{NH_3})$ and $(f_{H_2O,v}/P \cdot y_{H_2O})$ with Equation (21).
6. Choose a value of x_{NH_3} and calculate γ_{NH_3} with Equation (10) [Equation (h)].

7. Calculate y_{NH_3} with Equation (a) and check it with the known value or that calculated at point 4 with Equation (e). If the values are not sufficiently approximated, assume a new value of x_{NH_3} and return to point 6.
8. Calculate γ_{H_2O} with Equation (11) [Equation (i)].
9. Calculate y_{H_2O} with Equation (b) and check it with the known value or that calculated at point 4. If the values are not sufficiently approximated, assume a new value of G and return to point 1.

COMPARISON OF CALCULATED RESULTS WITH EXPERIMENTAL VALUES

To check the reliability of this calculation method for a nonideal solution, the results of a few experimental determinations have been compared with the corresponding calculated values.[*] The comparison is presented in Table 1 for fifteen points. Temperatures of 50° and 80°C. have been examined. The pressure range varies from 50 to 185 atm. For a definite mole fraction in the liquid phase and a constant ratio of nitrogen and hydrogen, mole fractions of ammonia and water in the vapor phase are given as experimental values, calculated from Equations (9) and (8).

In Figures 4 and 5 the same results of Table 1 are given. The solid line curves correspond to values calculated with Equation (9) and the broken line curves to values calculated with Equation (8). The experimental determinations have been repeated many times for each point. By comparing consecutive values of the same point, we see that ammonia experimental points are reproducible, but the laboratory was not in a position to give reproducible experimental points for water. In Figure 4 one notes a better agreement with experimental point of values calculated with Equation (9) than those calculated with

---

[*] The apparatus used for the determination of vapor-liquid equilibria is of the type described by Rigas et al. (20) for natural gas.

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

$a_{i,v}$ = 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

LITERATURE CITED

1. Wucherer, J., Z. Ges. Kälte-Ind., 39, 97, 136 (1932).
2. Chu, Ju Chin, Robert J. Fetty Llewellyn, F. Brennecke, and Rajendra Paul, "Distillation Equilibrium Data," J. W. Edwards, Ann Arbor, Mich. (1950).
3. Clifford, J. C., and E. Hunter, J. Phys. Chem., 37, 101 (1933).
4. Chu, Ju Chin, Shu Lung Wang, Sherman L. Levy, and

Rajendra Paul, "Vapor Liquid Equilibrium Data," J. W. Edwards, Ann Arbor, Mich. (1956).

5. Hougen, O. A., K. M. Watson, and R. A. Ragatz, "Chemical Process Principles," 2 ed., Pt. II, Wiley, New York (1959).

6. Gamson, B. W., and K. M. Watson, Natl. Petrol. News Technol. Sec., 36, R623 (Sept. 6, 1944).

7. Lange, N. A., "Handbook of Chemistry," Handbook Publishers, Sandusky, Ohio (1956).

8. Redlich, O., and J. N. S. Kwong, Chem. Rev., 44, 233 (1949).

9. Edmister, W. C., "Applied Hydrocarbon Thermodynamics," Gulf Publishing, Houston, Tex. (1961).

10. Bosnjakovic, F., "Technische Thermodynamik," T. Steinkopff, Leipzig (1935).

11. Davis, D. S., "Nomography and Empirical Equations," Reinhold, New York (1955).

12. Griswold, J., and S. Y. Wong, Chem. Eng. Progr. Symp. Ser. No. 2, 48, 18 (1952).

13. "International Critical Tables," Vol. 3, p. 59, McGraw-Hill, New York (1928).

14. Watson, K. M., Ind. Eng. Chem., 35, 398 (1943).

15. Comings, E. W., "High Pressure Technology," McGraw-Hill, New York (1956).

16. Vancini, C. A., "La Sintesi dell 'ammoniaca," Hoepli Ulrico, Milan (1961).

17. Larson, A. T., and C. A. Black, J. Am. Chem. Soc., 47, 1015 (1925).

18. Randall, M., and B. Sosnick, ibid., 50, 974 (1928).

19. Cupples, H. L., ibid., 51, 1031 (1929).

20. Rigas, T. J., D. F. Mason, and George Thodos, Ind. Eng. Chem., 50, 1297 (1958).

Diffusion and Chemical Reaction in Isobutylene Hydration Within Cation Exchange Resin

VIJAI P. GUPTA and W. J. M. DOUGLAS

McGill University, Montreal, Canada

The chemical reaction and diffusion rate parameters were determined for the hydration of liquid isobutylene to t-butanol with a cation exchange resin catalyst. High reaction rates were found to result from a high diffusivity of isobutylene within the resin catalyst. Both the high value for diffusivity and its negative temperature coefficient are consistent with the transport mechanism within the resin, being that of surface diffusion of isobutylene in an adsorbed state.

The hydration of isobutylene to t-butanol with cation exchange resin as catalyst is an alternative to the conventional hydration process, the hydrogen form ion exchange resin catalyst replacing the sulfuric acid normally used. The use of a resin catalyst gives rise to a three-phase system: an isobutylene-rich liquid phase, an aqueous liquid phase, and the solid catalyst. Phase equilibrium considerations indicate that one of the reactants, isobutylene, will be present only in very low concentrations in the hydrophilic resin phase. In spite of this the hydration rates are surprisingly high. Therefore the study was oriented toward obtaining an understanding of the mechanism of diffusion within the resin, since it appeared that this must be the key to the anomalously high reaction rates.

THEORETICAL MODEL

The theoretical model used contained the following assumptions.

1. Water is present in such large excess within the resin phase, relative to the isobutylene concentration, that the reaction should be independent of water concentra-

tion. Direct evidence for the validity of this assumption comes from the values of concentrations of isobutylene and water in the resin phase. The concentration of water in the resin was calculated from the data of Gregor et al. (1) and Pepper et al. (2). The concentration of isobutylene, measured as a part of this study (3), was found to be independent of butanol concentration over the existing concentration range. The equilibrium concentrations in fully swollen resin are:

Water	32.3 g.-moles/liter
Isobutylene	0.0172 g.-mole/liter

Furthermore, in the hydration of propylene with cation exchange resin catalyst, Kaiser et al. (4) also found the reaction rate to be independent of the concentration of water.

2. Reaction rate is first order with respect to isobutylene concentration. Lucas and Eberz (5) and Lashmet (6) have shown the reaction rates to be first order with respect to the olefin concentration.

3. Reaction is effectively irreversible for conditions of this study. The equilibrium constant for isobutylene hydration at 100°C. was determined by Smart et al. (7), who found, in terms of mole fractions, $K_x = 38$. For the range of reactant ratios used in this study, this equilibrium

Vijai P. Gupta is with E. I. du Pont de Nemours and Company, Inc., Wilmington, Delaware.