6). Only a postulation of behavior can be made for this region of flow. It may be that the rate of increase in holdup exceeds the rate of increase in area and surface renewal resulting in an over-all increase in H_L due to a greater effective depth of penetration required. This hypothesis is based on the observation of columns in this zone of operation where the gas tends to channel and bubble and where large masses of liquid flow in a laminar regime.

The change in the relative contributions of the gas and liquid phases to mass transfer kinetics is highly dependent on the variation of interfacial area with gas flow at constant liquid flow at rates below loading. The increase in H_G with gas flow is moderated by the rate of increase of interfacial area in the preloading zone. This phenomenon is causative of the slope inversion of the plot of H_{oG} vs. G generally encountered in systems where the gas phase provides a major portion of the resistance to mass transfer.

NOTATION

a = area, sq. ft./cu. ft.
a_i = interfacial area
a_w = wetted area
B_F = thickness of liquid film, ft.
D = diffusivity, sq. ft./hr.
G = gas phase flow rate, lb./(hr.) (sq. ft.)
G_m = gas phase flow rate, lb. moles/(hr.) (sq. ft.)
H = height of transfer unit, ft.
k = transfer rate, lb. moles/(hr.) (sq. ft.) (mole fraction driving force)
k_L = liquid phase mass transfer coefficient
L = liquor flow rate, lb./(hr.) (sq. ft.)
L_m = liquor flow rate, lb. moles/(hr.) (sq. ft.)
m = slope of equilibrium curve y^*/x
n = unirrigated packing characterization factor
N_{Sc} = Schmidt number, dimensionless
N_{Re} = Reynolds number, dimensionless
P_{BM} = log means partial pressure of inerts, atm.
z = length of surface, ft.
ρ = density, lb./cu. ft.
Γ = linear rate of liquid flow, lb./(hr.) (ft. of wetted perimeter)

Subscripts

i = interfacial
G = gas phase
L = liquid phase
oG = overall based on gas phase compositions or equivalent
t = total physical dry
w = wetted

LITERATURE CITED

1. Chilton, T. H., and A. P. Colburn, *Ind. Eng. Chem.*, **27**, 255 (1935).
2. *Ibid.*, **26**, 1183 (1934).
3. Danckwerts, P. V., *ibid.*, **43**, 1460 (1951).
4. Elgin, J. C., and B. W. Jesser, *Trans. Am. Inst. Chem. Engrs.*, **39**, 277 (1943).
5. Fellinger, L. L., Thesis, Mass. Inst. Technol., Cambridge, Massachusetts (1941).
6. Gamson, B. W., George Thodos, and O. A. Hougen, *Trans. Am. Inst. Chem. Engrs.*, **39**, (1943).
7. Grimley, S. S., *Trans. Inst. Chem. Engrs. (London)*, **23**, 228 (1945).
8. Hatta, S, and M. Katori, *J. Soc. Chem. Ind. (Japan)*, **37**, 820B (1934).
9. Higbie, Ralph, *Trans. Am. Inst. Chem. Engrs.*, **31**, 365 (1935).
10. Mayo, F., T. G. Hunter, and A. W. Nash, *J. Soc. Chem. Ind. (London)*, **44**, 375T (1935).
11. McAdams, N. H., J. B. Pohlenz, and R. C. St. John, *Chem Eng. Progr.*, **45**, 241 (1949).
12. Nikuradse, J., *Forschungsheft*, No. 356 (1932); No. 361 (1933).
13. Powell, R. W., *Trans. Inst. Chem. Engrs. (London)*, **18**, 36 (1940).
14. ———, and E. Griffiths, *ibid.*, **13**, 175 (1935).
15. Pratt, *ibid.*, **29**, 195 (1951).
16. Sherwood, T. K., *Trans. Am. Inst. Chem. Engrs.*, **36**, 817 (1940).
17. ———, and F. A. L. Holloway, *ibid.*, 21 (1940).
18. Sherwood, T. K., and Robert Pigford, "Absorption and Extraction," McGraw-Hill, New York (1952).
19. Shulman, H. L., and J. J. de Gouff, *Ind. Eng. Chem.*, **44**, 1915 (1952).
20. Shulman, H. L., C. F. Ulrich, and N. Wells, *A.I.Ch.E. Journal*, **1**, 247 (1955).
21. Taeker, R. G., and O. A. Hougen, *Chem. Eng. Progr.*, **45**, 188 (1949).
22. Teller, A. J., *ibid.*, **50**, 65 (1954).
23. Thoenes, D., and H. Kramers, *Chem. Eng. Sci.*, **8**, 271 (1958).
24. von Karman, T., *Trans. Am. Soc. Mech. Engrs.*, **61**, 705 (1939).
25. Weisman, Joel, and C. F. Bonilla, *Ind. Eng. Chem.*, **42**, 1099 (1950).

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Vapor-Liquid Equilibrium in Ammonia Complex Systems

C. H. MUENDEL, H. B. LINFORD, and W. A. SELKE

Columbia University, New York, New York

The vapor-liquid equilibrium in ammonia complex systems has been studied with a view toward design methods for separational and leaching processes. It is felt that the previously reported equilibrium constants for these systems are subject to considerable question with regard to the method used to measure the activity of the free ligand, or coordinating species. It is shown how this difficulty can be surmounted by the use of ammonia vapor pressure measurements and fugacities. A method of correlating complex equilibrium data from measurements of over-all metal concentration and free metal ion concentration is proposed. Vapor liquid equilibrium measurements have been made on the systems copper hydroxide, ammonia, water, nitrogen and nickel hydroxide, ammonia, water, nitrogen at 40° and 60°C. under 1 atm. total pressure with a continuously recirculating batch contactor. The correlation method is illustrated with the data of these measurements.

It has long been known that aqueous complex systems with volatile ligands, or complexing groups such as ammonia, involve equilibrium not only within the liquid phase but also between the solution and the vapor over it. When an excess of an insoluble compound of the complexed metal ion is present, equilibria in three phases are involved. Systems of this type are becoming increasingly important in the metallurgical industry. In order to study the behavior of such systems and develop

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C. H. Muendel is with E. I. du Pont de Nemours & Company, Newport, Delaware; W. A. Selke is with Peter J. Schweitzer Division, Kimberly-Clark Corporation, Lee, Massachusetts.

methods for measuring and correlating their equilibria, measurements were made with copper and nickel ammonium hydroxide. The chemical species present were:

Vapor NH_3, H_2O, N_2

Liquid $M(NH_3)_x(H_2O)^{++}_{N-x}$, NH_3, NH_4OH, NH^+_4, OH^-, H^+, H_2O

Solid $M(OH)_2$

It should be noted that the expression $M(NH_3)_x(H_2O)_{N-x}^{++}$ refers to a complete series of species with the value of x ranging from zero for the simple hydrate to N. The maximum coordination number for copper is five (*1, 2*); that for nickel may be four or six (*1*). It is also apparent that the stability of complexes of this type in aqueous solution involves ligand exchange, that is ammonia for water and vice versa, rather than true compound formation from the constituent groups.

LITERATURE REVIEW

In 1904 Lance (*3*) patented an ammonia leaching process for oxide ores. He found that distillation of the resulting solution caused successive precipitation of the metals present. Several related processes for extracting metals have been developed since that time. Of this work the most important are the Forward process (*4, 5*) for extracting nickel and the Nicaro process (*6, 7*) for extracting nickel and cobalt. In both cases the published data involve combinations of effects so that they cannot be readily generalized.

A large amount of work has been done on the determination of coordination numbers and dissociation constants for complexes such as those under discussion (*8 through 14*). These measurements were generally restricted to 18° to 30°C. and low solution concentrations. The most systematic and complete study of the ammonia complexes was carried out by Bjerrum (*1*). In his early measurements Bjerrum used ammonia pressure over the solution and Henrys Law constants for pure aqueous ammonia to determine the free ammonia concentration in copper ammonium nitrate solutions. From these data plus total analyses for copper and ammonia he was able to calculate the five successive dissociation constants for the complex. In his later work with other metals he utilized the glass electrode to determine the free ammonia concentration.

THEORY

For purposes of data generalization, it is convenient to consider chemical equilibrium in the solution as the key effect. Complex ion equilibrium is normally treated in terms of the law of mass action; that is for individual ligand substitution

$$M(A)_{x-1}(B)_{N-(x-1)} + A \rightleftharpoons M(A)_x(B)_{N-x} + B$$

$$k_x = \frac{a_{M(A)_x\,(B)_{N-x}}\,a_B}{a_{M(A)_{x-1}\,(B)_{N-(x-1)}}\,a_A}$$

and for over-all ligand substitution

$$M(B)_N + xA \rightleftharpoons M(A)_x(B)_{N-x} + xB$$

$$K_x = \frac{a_{M(A)_x\,(B)_{N-x}}\,a_B{}^x}{a_{M(B)_N}a_A{}^x}$$

Obviously $k_1\,k_2\,k_3\,\ldots\,k_x = K_x$. Application of the mass action law requires data and methods by which the activity of each constituent of the reaction may be calculated or approximated.

Determination of the Activity of NH_3 in the Liquid Phase

Most of the ammonia complex equilibrium constants reported to date are not strictly thermodynamic constants for reactions such as $M(H_2O)_N^{++} + NH_3 \rightleftharpoons M(H_2O)_{N-1}\,(NH_3)^{++} + H_2O$, since they are calculated with the analytical concentration of ammonia used as the free ammonia activity. The use of concentrations for activities is justified if the solution is sufficiently dilute; however considerable uncertainty exists about the state of ammonia in aqueous solution. If the ammonia is assumed to consist of two species, ammonia and ammonium hydroxide, some means would have to be found to distinguish between them in order to calculate constants for an equation as written above. Previous measurements (*15*) of the ratio ammonia/ammonium hydroxide are very limited.

Since a direct method of analysis for the ammonia concentration is not available and calculation from other measurements is rendered very difficult by the nonideality of the solution, the use of liquid-phase concentration and activity coefficients is not feasible here. It is thus proposed to evaluate the ammonia activity as

$$a_{NH_3} = \frac{f_{NH_3}}{f^\circ{}_{NH_3}} = f'_{NH_3} = (f/P)_{PT}Py_{NH_3} \tag{1}$$

The standard state for ammonia is taken as a solution having $f_{NH_3} = 1$ atm. This standard state was chosen because it required no additional data and assumptions. The standard free-energy change calculated from

$$\underset{a_1}{M(NH_3)_{x-1}(H_2O)_{N-(x-1)}} + \underset{a_2}{NH_3} \rightleftharpoons \underset{a_3}{M(NH_3)_{x-1}(H_2O)_{N-x}} + \underset{a_4}{H_2O}$$

$$-\Delta G^\circ = RT\ln\frac{a_3a_4}{a_1a_2} = RT\ln\frac{a_3a_4}{a_1f_2} = RT\ln k_x \tag{2}$$

would be numerically different from that calculated from the classical equilibrium constants because of the different standard state. The soundness of the vapor-phase approach is evident when one realizes that the only assumptions involved are the use of the generalized fugacity-coefficient charts and the Lewis and Randall rule which can both be checked for any particular set of conditions by pure gas-phase measurements.

The Determination of the Water Activity in the Liquid Phase

In the past the activity of the water in complex systems has been generally disregarded, either because complex equilibria, such as those under investigation here, were considered to involve formation rather than ligand exchange reactions, or because the activity of water was thought to be constant. Bjerrum (*1*) calculated equilibrium constants taking the activity of water equal to one, and then applied a correction derived from vapor pressure lowering and freezing point depression data to his results.

For reasons similar to those outlined in the previous section it is proposed that water be treated in the same way as ammonia; that is the equilibrium constant would be calculated by means of the fugacity of water found from the partial pressure of water over the solution. The standard state for water is defined as a solution having $f_{H_2O} = 1$ atm.

Calculation of the Individual Equilibrium Constants

In addition to the activity of the free ammonia and water the calculation of mass action equilibrium constants requires two further pieces of information: a measure of the total metal concentration in the solution and a measure of the degree of complex formation. The exact definition of the latter depends on the measurement techniques applicable to the particular chemical system. It, in turn, defines the method used to calculate the equilibrium constants. For example the concentration of bound ligand may be taken as a measure of the degree of complex formation. In circumstances where this is a measurable quantity it would be used, and corresponding calculational techniques would be applied. Alternatively the concentration of free metal ion, that is pure hydrate, could also be used.

Various methods for calculating complex equilibrium constants have been devised (*1*, *16* through *19*), and two comparative studies of these methods have been made (*19* and *20*). The constants found from one set of data have been shown to differ somewhat between methods of calculation because of different weighting of the individual data points.

For the case at hand the following method has been developed. The total concentration of a metal in the solution is given by

$$C = \sum_{x=0}^{N} [M(NH_3)_x(H_2O)_{N-x}]$$

Substituting for the terms within the summation, using the individual equilibrium constants, and collecting terms one finds

$$C = [M(H_2O)_N] + \sum_{x=1}^{N} \frac{K_x\,[M(H_2O)_N]\ \gamma_{M(H_2O)_N}\, f^x{}_{NH_3}}{\gamma_{M(NH_3)_x(H_2O)_{N-x}}\, f^x{}_{H_2O}}$$

When one divides through by the concentration of pure hydrate

$$\frac{C}{[M(H_2O)_N]} = 1 + \sum_{x=1}^{N}\left[K_x\left(\frac{f_{NH_3}}{f_{N_2O}}\right)^x \left(\frac{\gamma_{M(H_2O)_N}}{\gamma_{M(NH_3)_x(H_2O)_{N-x}}}\right)\right] \quad (3)$$

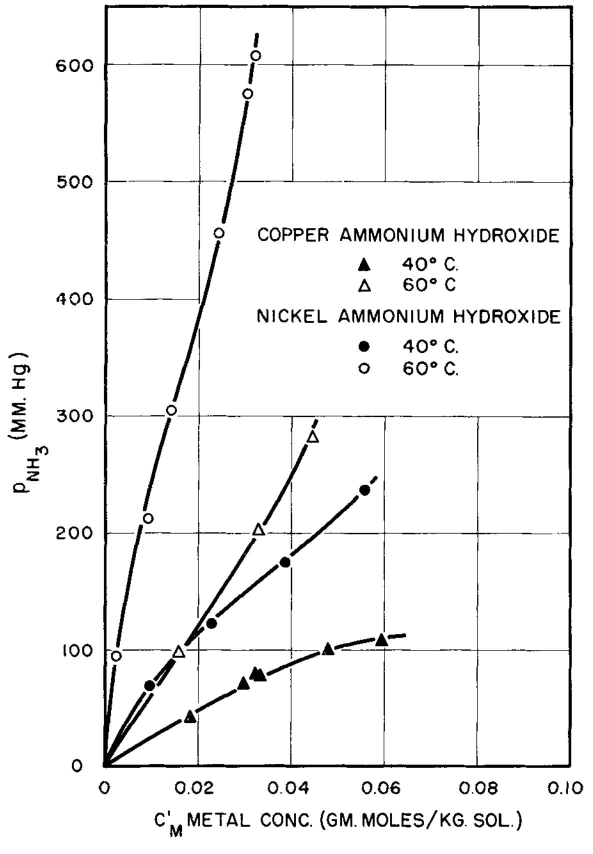

Fig. 1. Vapor-liquid equilibrium for the systems copper hydroxide, ammonia, water, nitrogen and nickel hydroxide, ammonia, water, nitrogen.

This expression assumes only the validity of the mass action law. Knowing the value of total metal concentration and pure hydrate concentration as a function of the ammonia-water fugacity ratio for N points at a given temperature one can proceed to calculate numerical values of K_x by the solution of simultaneous equations.

MEASUREMENTS

Vapor-liquid equilibrium measurements were made with a continuously recirculating batch contactor. By this method a relatively large volume of vapor was cycled through the liquid until the system reached steady state. This method was chosen because it affords large gas samples than can be easily separated from the solution and a reasonable certainty of achieving true equilibrium.

The equipment consisted of a 1-liter equilibrium vessel, two 9-liter gas sample bottles connected in series, a circulating pump that squeezes fluids through flexible tubing, connecting lines, and facilities for controlling the amount of ammonia in the system. The entire unit was maintained at constant temperature in an air bath. Clear solution, saturated with the metal hydroxide under 1 atm. of ammonia pressure, was placed in the equilibrium vessel and nitrogen cycled through it. An absorber was used to remove ammonia from the system until solid hydroxide was precipitated in the vessel and the desired overall ammonia concentration had been reached. The absorber was then removed and the system allowed to cycle at constant temperature and pressure until solution conductivity measurements and experience gained by runs made for various elapsed times indicated no further changes in solution concentration. The gas sample bottles were then closed off and the solution drawn from the vessel at constant pressure. pH readings of the solution were made at this time via an in-line cell fitted with a glass electrode at operating temperature.

The gas samples were analyzed by absorption in standard sulfuric acid and back titration with sodium hydroxide. Total ammonia in the liquid samples was determined by Kjeldahl distillation into standard sulfuric acid and titration. Total copper and nickel were determined by electrodeposition. The solids present in the equilibrium system were shown to be the unamminated hydroxides of the respective metals by direct analysis.

RESULTS

The measured equilibrium values for the systems copper hydroxide, ammonia, water, nitrogen and nickel hydroxide, ammonia, water, nitrogen at 40° and 60°C. and 1 atm. total pressure are shown in Figures 1 and 2.*

The experimental data were correlated by means of Equation (3). It can be shown that the Lewis and Randall rule applies to the vapor phase at the conditions of the experiments (*21*). Since the fugacity coefficient f/P equals unity at these conditions to the accuracy of the experimental data, the ratio f_{NH_3}/f_{H_2O} was simply found from the partial pressures of ammonia and water. Of these the former was directly measured; the latter was calculated from the vapor pressure of water and the mole fraction of water in the solution. Activity-coefficient data for the systems studied is not available; however it has been shown (*21*) that the activity-coefficient ratio γ_M/γ_{MA_x} may reasonably be taken as unity at the conditions of the measurements. The free metal ion concentration could not be measured directly and was therefore approximated via the pH and the solubility products of the solid hydroxides as follows: The hydroxyl ion activity of an equilibrium solution was taken as being equal to that of a potassium hydroxide solution at the same temperature and pH reading. Thus by calibrating the pH meter with potassium hydroxide solutions of known concentrations and using the activity coefficient data of Harned and Cook

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[*] Tables of the measured and derived equilibrium values have been deposited as document 6527 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $1.25 for photoprints or for 35-mm. microfilm.

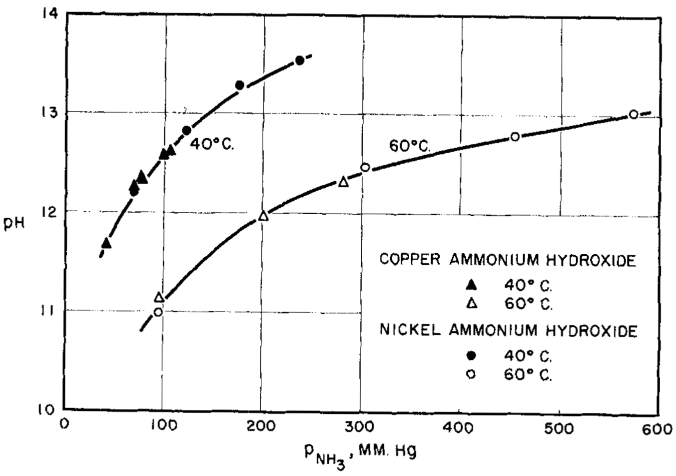

Fig. 2. *pH* of equilibrium solutions for the systems copper hydroxide, ammonia, water, nitrogen and nickel hydroxide, ammonia, water, nitrogen.

(22) for this system one can calculate the hydroxyl ion activity in the equilibrium solutions. The known solubility product constants for copper and nickel hydroxide were then corrected to the equilibrium temperatures and used to calculate the free metal ion activity in the solutions. These values were in turn converted to concentrations by means of activity coefficients calculated from the Debye-Hückel equation.

Substitution of the derived equilibrium values into Equation (3) yielded an equation of the form $a = 1 + bK_1 + b^2K_2 + b^3K_3$ — for each data point. Southwell's relaxation method, as described by Hartree (23), was adapted for fitting values of K_x to the experimental data. By systematic variation of K's it was possible to demonstrate that a certain set of positive values produced a minimum remainder. The criterion of best fit is identical to that used in the method of least squares. It was found that the experimental data could usually be fitted by two constants, one of which is dominant. In other words over the concentration range of the measurements one complex form is present in much larger quantity than the others. Hence, to the experimental precision, the remaining K's may be taken as equal to zero over this range. The values of K_x obtained are as follows:

$Cu(NH_3)_x(H_2O)_{5-x}^{++}$

40°C.

$K_5 = 4.52 \times 10^{12}$

$K_4 = 0.2 \times 10^{12}$

$K_3, K_2, K_1 << K_4$

60°C.

$K_5 = 0.774 \times 10^{12}$

$K_4 = 0.28 \times 10^{12}$

$K_3, K_2, K_1 << K_4$

$Ni(NH_3)_x(H_2O)_{6-x}^{++}$

40°C.

$K_6 << K_5$

$K_5 = 0.279 \times 10^{10}$

$K_4 = 0.56 \times 10^{10}$

$K_3, K_2, K_1 << K_4$

60°C.

$K_6 << K_5$

$K_5 = 0.0085 \times 10^{10}$

$K_4 = 0.100 \times 10^{10}$

$K_3, K_2, K_1 << K_4$

DISCUSSION

Direct comparison of the measured values with data obtained by others is not possible, since all the previous work involved either different chemical systems or different physical conditions.

The curves shown in Figures 1 and 2 are in general agreement with what is known at present about the physical chemistry of the systems. Since it is not possible to measure the concentrations of the individual species present, the curves are based on gross or overall concentrations. While this type of information is usually satisfactory, in fact frequently desirable for process design, its physical interpretation is rendered difficult by the fact that the plotted functions are the resultants of many simultaneous effects. Thus the curves of Figure 1 show the expected steady increase of metal solubility with increased ammonia pressure. However the exact curvature of the lines is determined by the magnitude of the successive complex formation constants and the basis used for solution concentration. In a concentrated ammonia solution there is considerable doubt as to what constitutes a satisfactory basis, since both water and ammonia probably act as solvent. From a theoretical standpoint the mole fraction copper/(water + ammonia) would be most reasonable; however this is at present unmeasurable because of the uncertainty regarding the state of ammonia. The fact that all the curves readily extrapolate to zero metal concentration at zero ammonia pressure on an arithmetic scale is taken as an indication of the accuracy of the experimental data. As shown by the curves of Figure 1 both complexes are less stable at higher temperatures. This fact is in agreement with the negative heats of reaction found by other workers.

It was observed that the relation between the ammonia pressure over the

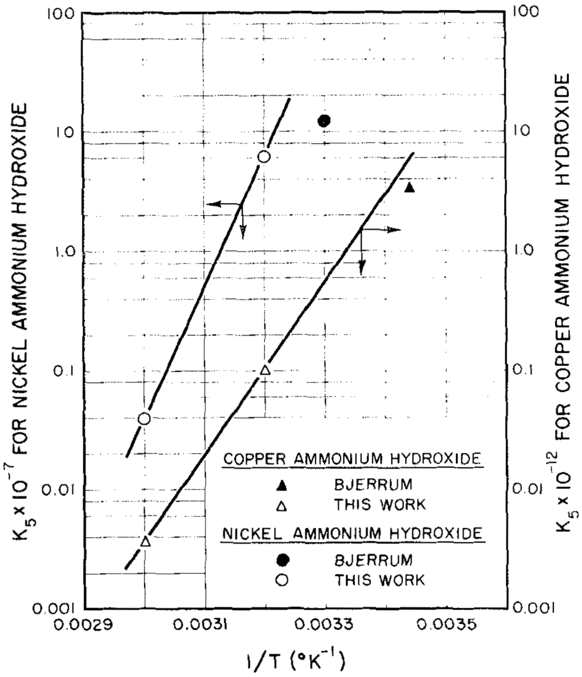

Fig. 3. K_5 for copper and nickel ammonium hydroxide.

solutions and the total ammonia in the solutions was the same for both metal systems, in fact very close to that for the ammonia-water system. As is also apparent from Figure 2 the pH of the solutions is essentially independent of whether copper or nickel is the metal ion present. Generally speaking in concentrated solutions of copper and nickel ammonium hydroxide the metals play a lesser role in the over-all properties than their concentrations would lead one to expect.

The calculated equilibrium constants have been converted to the standard states used by Bjerrum to allow comparison with his values, as shown in Table 1. Since the five coordinated complex forms dominated over the range of the measurements in both cases, it is felt that the values of K_5 are more accurately determined than those of K_4. The values for K_5 are shown in Figure 3. In both cases they have been extrapolated for comparison with Bjerrum's corresponding value. An exact check is not to be expected because differences exist in the chemical constituents of the systems and the methods used to measure the activity of the free ligands. However the fact that the measured equilibrium values could be very closely correlated by the K_4 and K_5 constants constitutes an independent check on the previous theories about coordination numbers in the copper and nickel ammonium hydroxide systems. Copper was known to be five coordinated with the fifth ligand less easily replaced, while nickel was known to be six coordinated with the fifth and sixth ligands less easily replaced. The fact that the four and five coordinated forms dominate in concentrated solutions and that the data are thus readily correlated by K_4 and K_5 is therefore very reasonable for both the copper and nickel systems.

The experimental and calculation techniques that have been illustrated are readily applicable to process design of complex systems involving volatile ligands. The requirements for such design are as follows: 1. A limited number of vapor-liquid equilibrium measurements. In contrast to earlier methods this treatment of these data does not require that the number of measurements be equal to, or in excess of, the coordination number so long as the equilibrium curve is determined to the desired accuracy over the range of interest. The coordination number need not be known. 2. If moderate temperature variations are involved, a calorimetric measurement of the heat of reaction will allow the extension of the correlation from 1. When one uses these data plus such short cuts as the independence on metal identity of the gross system properties, an equilibrium network can be quickly developed with a minimum of experimental work.

TABLE 1. EQUILIBRIUM CONSTANTS FOR COPPER AND NICKEL AMMONIUM HYDROXIDE

		Bjerrum (*1*)		This Work	
		18°C.	30°C.	40°C.	60°C.
Cu	$K_4 \times 10^{-12}$	12.2	1.07	0.0095	0.0038
Cu	$K_5 \times 10^{-12}$	3.67	–	0.101	0.0036
Ni	$K_4 \times 10^{-7}$	–	2.95	26	1.4
Ni	$K_5 \times 10^{-7}$	–	12.6	6.2	0.039

CONCLUSIONS

It has been shown how vapor pressure measurements can be used to determine free ligand activities in ammonia complex systems. This method surmounts the question of distinguishing between the ammonia and ammonium hydroxide species.

A method has been developed for the correlation of complex equilibrium data by means of the free ligand vapor pressures, the over-all metal concentration, and the free metal ion concentration. This method can be used with less than N data points and does not require a knowledge of N for the complex in question. The only requirement is a sufficient number of data points to determine the equilibrium curve to the desired accuracy.

Equilibrium measurements have been made with the copper and nickel ammonium hydroxide systems and the resulting data used to demonstrate the above correlation method.

NOTATION

Chemical Symbols

M = metal ion
A = ligand
B = ligand

Mathematical Symbols

a = activity
C_M = total concentration of a metal ion = M + MA + MA_2 + etc., (moles/kg. of water)
C'_M = total concentration of a metal ion = M + MA + MA_2 + etc., (g.moles/kg. of solution)
C'_{NH_3} = total concentration of ammonia = $NH_3 + NH_4OH + NH_4^+ + xM(NH_3)_x$, (g.moles /kg. of solution)
f = fugacity of a component in solution, (atm.)
f' = fugacity of a component in the vapor, (atm.)
f/P = fugacity coefficient
$\Delta G°$ = standard free energy change at T, (cal./mole)
k_x = individual equilibrium constant based on activities, that is for the reaction $M(NH_3)_{x-1}(H_2O)_{N-(x-1)}^{++} + NH_3 \rightleftharpoons M(NH_3)_x(H_2O)_{N-x}^{++} + H_2O$
K_x = over-all equilibrium constant based on activities, that is for the reaction $M(H_2O)_N^{++} + xNH_3 \rightleftharpoons M(NH_3)_x(H_2O)_{N-x} + xH_2O$
N = maximum coordination number
p = partial pressure, (atm. or mm. Hg)
P = total pressure, (atm.)
R = gas constant, (cal./°K.)
T = absolute temperature, (°K.)
x = ammonia coordination number in the liquid phase
y = mole fraction in the vapor
γ = stoichiometric activity coefficient

LITERATURE CITED

1. Bjerrum J., *Det Kgl. Danske Videnskabernes Selskab., Mathematisk fysiske Meddelelser*, **11**, No. 5 (1931); **11**, No. 10 (1932); **12**, No. 15 (1934); and "Metal Ammine Formation in Aqueous Solution," Haase and Son, Copenhagen (1941).
2. Rosenblatt, F., *Zeits. anorg. Chem.*, **204**, 351 (1932).
3. Lance, D., French Pat. 342,865 (1904); see *Moniteur Scientifique*, **64-65**, Patent Section 53 (1906).
4. Forward, F. A., *Trans. Can. Inst. Mining Met.*, **56**, (in *Can. Mining Met. Bull.*, **499**, 677) (1953).
5. Mackiw, V. N., R. L. Benoit, R. J. Loree, and N. Yoshida, *Chem. Eng. Progr.*, **54**, No. 3, 79 (1958).
6. Lutjen, G. P., *Eng. Mining J.*, **155**, No. 6, p. 81 (1954).
7. Caron, M. H., *Trans. Am. Inst. Mech. Engrs.*, **188**, 67, 91 (1950).
8. Konowalow, D., *J. Russ. Phys. Chem. Soc.*, **31**, 910 (1899).
9. Gaus, W., *Zeits. anorg. Chem.*, **25**, 236 (1900).
10. Bodlaender, G., and R. Fittig, *Zeits. physik. Chem.*, **39**, 597 (1902).
11. Von Euler, H., *Ber.*, **36**, 1854 (1903).
12. Locke, J., and J. Forssall, *Am. Chem. J.*, **31**, 268 (1904).
13. Bonsdorff, W., *Zeits. anorg. Chem.*, **41**, 132 (1904).
14. De Wys, H., *Rec. Trav. Chim. d. Pays-Bas*, **44**, 663 (1925).
15. Moore, T. S., and T. F. Winmill, *J. Chem. Soc.*, **101**, 1635 (1912).
16. Leden, I., Thesis, Univ. Lund, Lund (1943).
17. Froneaus, S., Thesis, Univ. Lund, Lund (1948).
18. Irving, H., and H. S. Rossotti, *J. Chem. Soc.*, 3397 (1953).
19. Rossotti, F. J. C., and H. S. Rossotti, *Acta Chem. Scand.*, **9**, 1166 (1955).
20. Sullivan, J. C., and J. C. Hindman, *J. Am. Chem. Soc.*, **74**, 6091 (1952).
21. Muendel, C. H., Thesis, Columbia Univ., New York (1959).
22. Harned, H. S., and M. A. Cook, *J. Am. Chem. Soc.*, **59**, 496 (1937).
23. Hartree, D. R., "Numerical Analysis," pp. 167 to 177, Oxford, London (1952).

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