to note here that the solubility of this freshly precipitated $Al(OH)_3$ is much higher than that of gibbsite.

Assuming the hydrolysis of the $Al^{+3}$ to proceed according to the three-stage hydrolysis mechanism, there must be in solution an extremely low equilibrium concentration of molecular $Al(OH)_3$ as given by

$$[Al(OH)_3] = \frac{K_1K_2K_3[Al]_t}{[H^+]^3}$$

in which $[Al]_t$ is the total concentration of $AlCl_3$ in solution, and $K_1$, $K_2$, and $K_3$ are the three-stage hydrolysis constants. It can be shown that, like the ion activity product, $(Al^{+3})(OH^-)^3$, the concentration of molecular $Al(OH)_3$ also should increase with dilution, pass through a maximum value, and then should decrease upon further dilution of the $AlCl_3$ solution. As the total concentration of $AlCl_3$ is decreased to about $10^{-5}$ $M$, the degree of supersaturation of the solution with respect to molecular $Al(OH)_3$ reaches a critical value and $Al(OH)_3$ begins to precipitate. This precipitation of $Al(OH)_3$ will cause further hydrolysis of $AlCl_3$ as the equilibrium concentrations of the hydrolysis products will tend to be restored. Consequently, the observed pH values will be lower than those predicted by the first stage hydrolysis reaction, which, in turn, will lead to a slightly higher value for the monomeric first stage hydrolysis constant, $K_m$, calculated with the assumptions that $[H^+] = [AlOH^{+2}]$ and that all the aluminum has remained in solution. This increase in the apparent value of $K_m$, upon dilution or addition of base to an aluminum salt solution, has been interpreted[11] as failure of the classical monomeric hydrolysis mechanism to describe the hydrolysis reaction, whereas it actually is due to precipitation of $Al(OH)_3$ when the degree of supersaturation of the diluted aluminum salt solution has reached a critical level. Thus, the behavior of an aluminum salt solution resembles to some extent that of a ferric chloride solution[30] which also becomes supersaturated with respect to $Fe(OH)_3$ upon dilution but from which $Fe(OH)_3$ begins to precipitate immediately. On the other hand, an aluminum salt solution tends to remain metastable, upon dilution, over a wide range of supersaturation with respect to $Al(OH)_3$. Although the presence of a variety of polymeric basic ions in partially neutralized solutions has been postulated, such solutions are obviously not at equilibrium and it seems quite likely that any polymeric complexes that may be present in such solutions represent transient stages in the aggregation of molecular $Al(OH)_3$ and its ultimate precipitation.

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# The Kinetics of Ammonia Exchange between Nickel Ammine Complexes and Ammonia in Aqueous and Anhydrous Ammonia Solutions Measured by Nuclear Magnetic Resonance of $N^{14}$[1]

BY JOHN P. HUNT,[2] HAROLD W. DODGEN, AND FRANK KLANBERG

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Rate data are reported on the exchange of $NH_3$ with $Ni(NH_3)_6^{++}$ in aqueous and anhydrous ammonia solutions. The aqueous exchange is represented by the rate law, $R = 6k_1[Ni(NH_3)_6^{++}]$, where $k_1$ is $5.6 \pm 0.5 \times 10^4$ sec.$^{-1}$ at 25° and the activation parameters are $\Delta H^* = 9.5 \pm 1.1$ kcal./mole and $\Delta S^* = -5 \pm 4$ e.u. Addition of $NH_4^+$ and some other ions had no effect on the rate. The limited data in anhydrous ammonia can be represented by the same rate law and the rate parameters are essentially the same; $k_1$ at 25° is $4.7 \pm 0.5 \times 10^4$ sec.$^{-1}$, $\Delta H^* = 10 \pm 1$ kcal./mole and $\Delta S^* = -3 \pm 4$ e.u. Possible mechanisms are discussed and comparisons with related reactions are given. No chemical shift in the $N^{14}$ resonance in $NH_3$ was produced by $Ni^{++}$.

## Introduction

Preliminary results have been reported for $NH_3$ exchange with nickel ammine complexes employing both tracer[3] and n.m.r.[4] line broadening techniques. This report represents an extension and improvement of the n.m.r. data to yield more detailed results on the kinetics of the fast exchange reactions. Very little work has been done on the kinetics of complex ion reactions in liquid ammonia (especially little at room temperature). Studies of the present sort may serve to aid in obtaining a start on a more detailed understanding of kinetic behavior in anhydrous ammonia. The exchange results reported here also should be useful in correlating the kinetic behavior of metal complexes with properties of the metal ion and ligands as well as with the nature of the solvent used. In addition, it is of considerable importance to compare results of different methods for studying fast reactions in order to establish their reliability.

## Experimental

The n.m.r. spectra were obtained using a spectrometer which employed a standard marginal oscilator and a phase-sensitive detector. The $N^{14}$ resonances in the uncomplexed $NH_3$ were ob-

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(1) This work supported in part by the U. S. Atomic Energy Commission.

(2) To whom inquiries may be addressed.

(3) J. R. Sutter and J. P. Hunt, *J. Am. Chem. Soc.*, **82**, 6420 (1960).

(4) J. P. Hunt and H. W. Dodgen, *J. Chem. Phys.*, **35**, 2261 (1961).

served usually at *ca.* 1.75 Mc./sec. and *ca.* 5700 gauss; some studies also were made at *ca.* 2.85 Mc./sec. and *ca.* 9300 gauss and the results agreed well with those obtained at the lower field. Derivatives of the absorption lines were displayed on a recorder. The line width ($W$) was taken as the peak-to-peak separation of the derivative curve. Calibration of the recorder chart was effected by using the $N^{14}$ n.m.r. lines in aqueous $NH_4NO_3$; the separation of the $NH_4^+$ and $NO_3^-$ resonances being taken as 347 p.p.m.[5,6] The modulation frequencies used varied from 150 to 30 c./sec. and the modulation amplitudes from 0.1 to 0.5 gauss. The radiofrequency power was kept well below the saturation level. A constant radiofrequency was used and the field strength was swept by changing the regulated current of the electromagnet. Usually four such sweeps were made for each sample, two with increasing field and two with decreasing field. The average line widths obtained were reproducible to within ±5 to 10%, depending on the apparent intensity and width of the line observed. Aqueous solutions were run in 18-mm. Pyrex test tubes, while the liquid $NH_3$ samples were contained in sealed thick-walled Pyrex ampoules. The sample probe temperatures were controlled to ±0.2° by means of a simple gas flow thermostatic device. Temperatures of the aqueous solutions were measured by immersing a small glass-protected thermocouple in the solution during the measurements and for the liquid $NH_3$ solutions by placing the thermocouple as close as possible to the ampoule. The uncertainty in the temperature for the liquid ammonia runs may be as much as ±1°. The observed line widths for the $NH_3$ solutions in the absence of metal ion were considerably larger than the natural widths due in part to field inhomogeneity but mainly to the modulation parameters used. The results obtained depend, however, only on differences in line widths and these differences were shown to be independent of these parameters. The aqueous solutions were prepared from A.R. grade $Ni(NO_3)_2 \cdot 6H_2O$ or $NiSO_4 \cdot 7H_2O$ using A.R. grade concentrated $NH_4OH$ and distilled water. $Ni(NH_3)_6(ClO_4)_2$ was used for the liquid $NH_3$ work because of its relatively high solubility over the temperature range studied. This salt was prepared by dissolving A.R. $NiCO_3$ in excess dilute $HClO_4$ and then passing $NH_3$ gas into the solution. The light blue precipitate which formed on cooling was filtered off, washed with ethanol and diethyl ether, and dried over NaOH for several days.

*Anal.* Calcd. for $Ni(NH_3)_6(ClO_4)_2$: Ni, 16.32; $ClO_4^-$, 55.27. Found: Ni, 16.20; $ClO_4^-$, 55.07. The infrared spectrum also confirmed the absence of water.

The liquid $NH_3$ was purified and dried in the standard way. The solutions were made by distilling the $NH_3$ onto the dry salt using a vacuum line.

## Treatment of Data and Results

In order to interpret the effect of temperature on the line broadenings produced by $Ni^{++}$ ions, it first was necessary to study the effects of temperature on the pure aqueous and anhydrous ammonia line widths. The observed widths for aqueous $NH_3$ increased with decreasing temperature while those for liquid $NH_3$ appeared to be independent of temperature over a wide range (−64 to 30°), probably because the natural width in liquid ammonia is small compared to the instrumental broadening and thus changes are hidden.

The aqueous $NH_3$ results can be interpreted in terms of a correlation time for "tumbling" of the species involved. The artificial broadening was estimated from the apparent width of the $NH_4^+$ line, which has a very small natural width. The apparent widths then were corrected by subtracting the estimated artificial broadening (*ca.* 0.4 gauss). We obtain a corrected value at 25° of 0.30 ± 0.03 gauss, which can be compared with the result of Schmidt, *et al.*,[5] of 0.320 ± 0.05 gauss (presumably at room temperature). A characteristic time for the assumed tumbling ($\tau$) is given by the relation $1/\tau = (\sqrt{3}/2)\gamma W$, where $\gamma$ is the magnetogyric ratio for $N^{14}$ (1934 gauss$^{-1}$ sec.$^{-1}$) and $W$ is the line width in gauss. We set $1/\tau = k$, where $k$ is the apparent first-order rate constant for tumbling. A plot of log $k$ *vs.* $1/T$ is given in Fig. 1. The data shown include a variation of $NH_3$ concentration from 7 to 14 $M$. The results are not very precise but there appears to be no effect due to change of $NH_3$ concentration in the range used. An apparent "activation energy" for tumbling was calculated to *ca.* −4 kcal./mole, which is a reasonable value.[7] It seems likely[5] that the line width in aqueous $NH_3$ is due to interactions with the nuclear quadrupole moment of $N^{14}$.

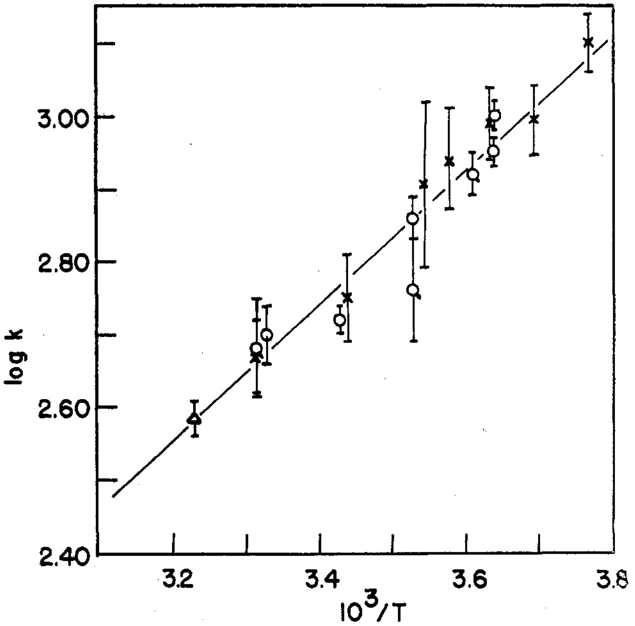

Fig. 1.—Log $k$ *vs.* $1/T$ for aqueous $NH_3$: ×, *ca.* 6000 gauss field, 14 $M$ $NH_3$; ⊙, *ca.* 9000 gauss field, 14 $M$ $NH_3$; Q, *ca.* 9000 gauss field, 7 $M$ $NH_3$; △, *ca.* 9000 gauss field, 12.2 $M$ $NH_3$.

Line broadening effects due to paramagnetic ions may or may not be determined by the rate of chemical exchange.[6] The main criterion for deciding whether the chemical exchange rate is controlling or not is the behavior of the broadening ($\Delta$) as a function of temperature. If chemical exchange is predominantly involved then a plot of log $\Delta$ *vs.* $1/T$ should show the familiar Arrhenius behavior, while if other factors control the line broadening, the negative of the Arrhenius slope may be expected. Intermediate cases can (of course) exist. Our data do fit the Arrhenius criterion, and we have proceeded to interpret our results in terms of chemical exchange.

The $Ni^{++}$ ion solution data were treated following

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(5) B. M. Schmidt, L. C. Brown, and D. Williams, *J. Mol. Spectry.*, **2**, 539 (1958).

(6) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York, N. Y., 1959, Chapters 10 and 12.

(7) P. F. Cox and L. O. Morgan, *J. Am. Chem. Soc.*, **81**, 6409 (1959).

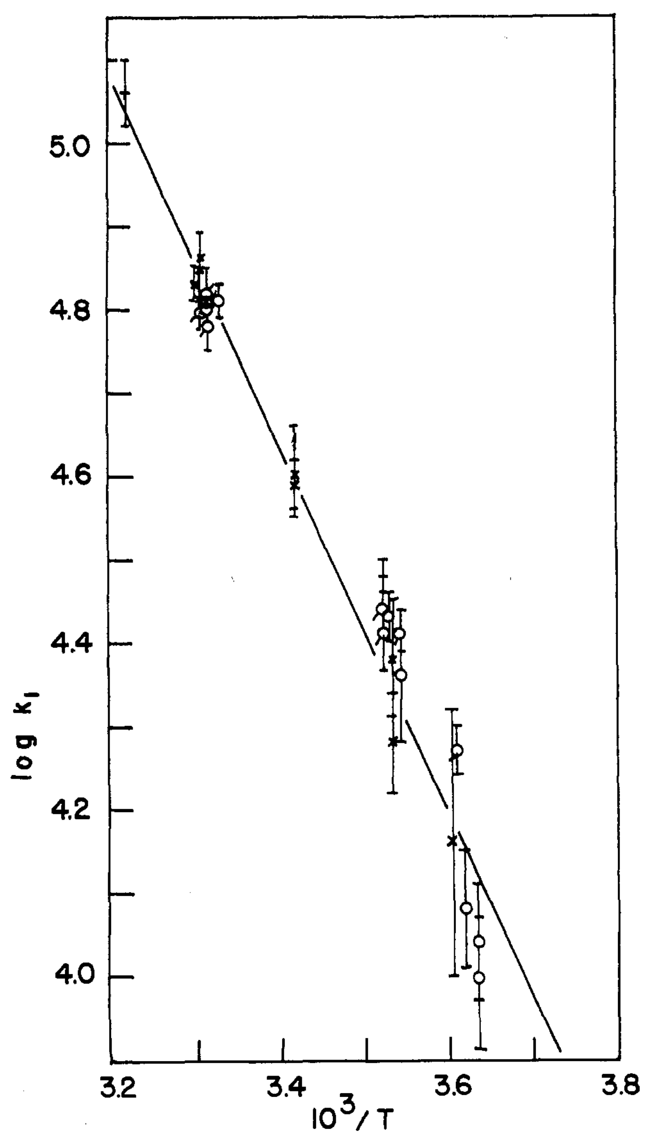

Fig. 2.—Arrhenius plot for aqueous $NH_3$ exchange data: ×, *ca.* 6000 gauss field, 14.3 *M* $NH_3$; ⊙, *ca.* 9000 gauss field, 14.3 *M* $NH_3$; ♂, *ca.* 9000 gauss field, 10.8 *M* $NH_3$; ρ, *ca.* 9000 gauss field, 7.15 *M* $NH_3$; +, *ca.* 9000 gauss field, 12.2 *M* $NH_3$.

the procedures outlined by McConnell and Weaver[8] and Connick and Poulson.[9] The essential equations are: $1/T_2 = 1/T_{2A} + 1/\tau_A$, where $T_2$ is the observed transverse relaxation time of $N^{14}$ in "free" $NH_3$ in a $Ni^{++}$ solution, $T_{2A}$ is the same relaxation time in the absence of $Ni^{++}$, and $\tau_A$ is the mean lifetime of a $N^{14}$ nucleus in free $NH_3$; $\tau_B = \tau_A P_B/P_A$, where $\tau_B$ is the mean lifetime of a $N^{14}$ nucleus in the nickel complex and $P_B$ and $P_A$ refer to the atom fractions of $N^{14}$ in the complex and free state, respectively; and $\tau_B = C/R$, where $C$ is the total concentration of $N^{14}$ in the complex and $R$ the chemical rate of exchange of $N^{14}$ nuclei between the complex and free $NH_3$ (assumed due to $NH_3$ exchange). One obtains finally the relation $R = C(P_A/P_B)(\sqrt{3}/2)\gamma\Delta$, where $\Delta$ is the difference in line widths for the pure $NH_3$ and $Ni^{++}$–$NH_3$ solutions and the other symbols have been defined previously.

Table I

Line Broadening Data for Aqueous Ammonia Solutions

| $NH_3$, *M* | Ni, *M* | *t*, °C. | Δ, gauss | $k_1 \times 10^{-4}$, sec.$^{-1}$ | Remarks |
|---|---|---|---|---|---|
| 14.3 | 0.10 | 29.5 | 1.70 | 6.8 ± 0.2 | |
| 14.3 | .10 | 28.8 | 1.75 | 7.0 ± 0.6 | |
| 14.3 | .10 | 28.0 | 1.60 | 6.4 ± 0.3 | 0.50 *M* $NaC_2H_3O_2$ present |
| 14.3 | .10 | 27.8 | 1.60 | 6.4 ± 0.3 | 4 *M* $NH_4C_2H_3O_2$ present |
| 14.3 | .10 | 27.3 | 1.60 | 6.4 ± 0.3 | $SO_4^{-2}$ anion present |
| 14.3 | .10 | 19.1 | 0.99 | 4.0 ± 0.4 | |
| 14.3 | .10 | 10.0 | .67 | 2.7 ± 0.2 | |
| 14.3 | .10 | 9.6 | .60 | 2.4 ± 0.4 | |
| 14.3 | .080 | 3.1 | .24 | 1.2 ± 0.2 | |
| 14.3 | .080 | 2.0 | .22 | 1.1 ± 0.2 | |
| 14.3 | .075 | 27.0 | 1.22 | 6.5 ± 0.2 | |
| 14.3 | .075 | 1.8 | 0.18 | 0.96 ± 0.2 | |
| 14.3 | .050 | 28.8 | .81 | 6.5 ± 0.3 | |
| 14.3 | .050 | 28.0 | .75 | 6.0 ± 0.3 | 0.50 *M* $NaC_2H_3O_2$ present |
| 14.3 | .050 | 27.8 | .81 | 6.5 ± 0.3 | 4 *M* $NH_4C_2H_3O_2$ present |
| 14.3 | .050 | 19.1 | .50 | 4.0 ± 0.4 | |
| 14.3 | .050 | 10.2 | .24 | 1.9 ± 0.3 | |
| 14.3 | .050 | 9.0 | .29 | 2.3 ± 0.5 | |
| 14.3 | .025 | 28.7 | .45 | 7.2 ± 0.7 | |
| 14.3 | .025 | 28.3 | .42 | 6.7 ± 0.5 | 4 *M* $NH_4C_2H_3O_2$ present |
| 14.3 | .025 | 28.0 | .41 | 6.6 ± 0.5 | 0.50 *M* $NaC_2H_3O_2$ present |
| 14.3 | .025 | 19.2 | .25 | 4.0 ± 0.6 | |
| 14.3 | .025 | 4.2 | .09 | 1.4 ± 0.6 | |
| 12.2 | .025 | 37.3 | .83 | 11.4 ± 1.1 | |
| 10.8 | .10 | 28.3 | 2.08 | 6.3 ± 0.9 | |
| 10.8 | .05 | 28.3 | 1.08 | 6.5 ± 0.5 | |
| 10.8 | .025 | 28.3 | 0.54 | 6.5 ± 0.8 | |
| 7.2 | .10 | 8.8 | 1.27 | 2.5 ± 0.2 | |
| 7.2 | .050 | 28.3 | 1.50 | 6.0 ± 0.3 | |
| 7.2 | .050 | 10.6 | 0.69 | 2.8 ± 0.4 | |
| 7.2 | .050 | 3.9 | .46 | 1.8 ± 0.1 | |
| 7.2 | .025 | 28.9 | .77 | 6.2 ± 0.5 | |
| 7.2 | .025 | 10.6 | .32 | 2.5 ± 0.5 | |

The rate law is determined in the usual way for exchange reactions by trying various functions for $R$ until one is found which fits the data.

No chemical shifts (>50 p.p.m.) were found to be produced by the addition of $Ni^{++}$ ion, which result also supports the assumption that a chemical exchange rate is being measured.

The line broadenings were studied as a function of nickel and ammonia concentrations, added salts, and temperature. The results for aqueous ammonia are shown in Table I. The concentration ranges used represent practical limits imposed by the sensitivity and signal-to-noise ratio of the instrument used.

In order to obtain a rate law from the data some assumption must be made regarding the nickel species involved. Bjerrum[10] has given equilibrium constants for the six aqueous ammine complexes of nickel at different ionic strengths. We estimate that at the lowest $NH_3$ concentration used (7 *M*) at least 85% of the nickel is present as $Ni(NH_3)_6^{++}$ ion. It is conceivable that the major species present might not be responsible for the observed line broadenings. The dependence of the broadening on $NH_3$ concentration is, however, most simply consistent with the reasonable assumption that we are observing the $Ni(NH_3)_6^{++}$ complex. The data are fitted within experimental error by the rate law, $R = 6k_1[Ni(NH_3)_6^{++}]$, where $k_1$ is the specific rate constant for exchange of a *particular* $NH_3$ ($k_1$ should be multiplied by 6 if the rate constant for exchange of *any one* of the six is desired). Calculated values for $k_1$ are given in Table I. In Fig. 2 is shown an Arrhenius

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(8) H. M. McConnell and H. E. Weaver, *J. Chem. Phys.*, **25**, 308 (1956).

(9) R. E. Connick and R. E. Poulson, *ibid.*, **30**, 759 (1959).

(10) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Sons, Copenhagen, 1957.

plot of log $k_1$ *vs.* $1/T$. The data were treated by the method of least squares, which gives the equation

$$k_1 = 10^{12.144}e^{-(10.09 \times 10^3)/RT}$$

and leads to values for $\Delta H^*$ and $\Delta S^*$ of 9.5 ± 1.2 kcal./mole and −5 ± 4 cal./mole deg., respectively.

The results for liquid $NH_3$ are limited due to the experimental difficulties in handling the samples at room temperature and the rather low solubility of nickel salts. The data obtained are shown in Table II and Fig. 3. The same treatment was given these results as was used for the aqueous solutions. It seems reasonable that the $Ni(NH_3)_6^{++}$ species again predominates in liquid $NH_3$. The $\Delta H^*$ and $\Delta S^*$ values calculated are 10.2 ± 1 kcal./mole and −3 ± 4 cal./mole deg., respectively. The estimated errors are taken to be the same as for the aqueous case.

TABLE II

LINE BROADENING DATA FOR LIQUID AMMONIA SOLUTIONS CONTAINING 0.10 *M* $Ni(NH_3)_6(ClO_4)_2$

| $t$, °C. | $\Delta$, gauss | $k_1 \times 10^{-4}$, sec.$^{-1}$ |
|---|---|---|
| 30 | 0.53 | 6.0 ± 0.5 |
| 20 | 0.29 | 3.3 ± 0.4 |
| 10 | 0.15 | 1.7 ± 0.4 |

## Discussion

The line broadening data in the aqueous ammonia solutions are consistent with the simple rate law $R = 6k_1[Ni(NH_3)_6^{++}]$, but not with rate laws involving the concentration of free $NH_3$, in the range 7 to 14 *M* $NH_3$ and 0.025 to 0.10 *M* $Ni^{++}$. The concentration of water varies *ca.* 30% between 7 and 14 *M* $NH_3$ solutions and shows no effect within the 10% error assigned to the rate constants which suggests (though not strongly) that water is not directly involved in the $NH_3$ exchange. Several attempts were made to vary the ionic strength by the addition of various salts. Salts such as $LiClO_4$, $NaClO_4$, $(CH_3)_4NCl$, and $(C_4H_9)_4NI$ either salted-out the nickel complex or were not soluble themselves. Neither 0.05 *M* $NaC_2H_3O_2$ nor 4 *M* $NH_4C_2H_3O_2$ produced any effect on the rate observed. The use of $SO_4^{-2}$ rather than $NO_3^-$ as the anion present likewise showed no effect. We conclude that salt effects are small in this system as might be expected if the neutral $NH_3$ species were being exchanged. The absence of an effect due to 4 *M* $NH_4^+$ also supports this view. The close similarity of the aqueous and anhydrous $NH_3$ results suggests again that water does not play a specific role in the exchange. In the liquid ammonia case the order with respect to solvent cannot, of course, be obtained. Two simple mechanisms for the aqueous ammonia exchange which might be considered are first, a dissociation mechanism of the type $Ni(NH_3)_6^{++} \rightarrow Ni(NH_3)_5^{++} + NH_3$, and second, a bimolecular mechanism involving water such as $Ni(NH_3)_6^{++} + H_2O \rightarrow Ni(NH_3)_5(H_2O)^{++} + NH_3$. As is well known, it is very difficult to distinguish between such mechanisms in aqueous solution. The rate of water exchange with $Ni(H_2O)_6^{++}$[11] has a pseudo-first-order rate constant of $2.7 \times 10^4$ sec.$^{-1}$ and a $\Delta H^*$ value of 11.6 kcal./mole, being slower than the ammonia exchange by a factor of *ca.* 2 to 3. If the water and ammonia exchange reactions both proceed by bimolecular processes involving $H_2O$, the implication is that $H_2O$ replaces $NH_3$ at about the same rate (or slightly faster) than $H_2O$ in the aquo complex. This may not be unreasonable, although it is not clear why attack on the $Ni(NH_3)_6^{++}$ species by $NH_3$ itself should not be observed. Some support for the dissociation mechanism may be found in the fact that a change of *ca.* 30% in $H_2O$ concentration produced no observable effect within the ±10% error assigned to the rate constants, although a larger variation in water concentration is certainly desirable. The apparent agreement with the limited liquid ammonia results also supports a dissociation mechanism, although differences in solvation effects, etc., eventually must be considered. If the liquid ammonia exchange involves the mechanism $Ni(NH_3)_6^{++} + NH_3 \rightarrow [Ni(NH_3)_7^{++}]^*$ then this might approximately set a lower limit for the similar process in aqueous solution. Since no dependence on $NH_3$ concentration of the rate in aqueous solution is observed and the exchange rates in the two solvents are essentially equal, a dissociation type mechanism in both solvents most simply accounts

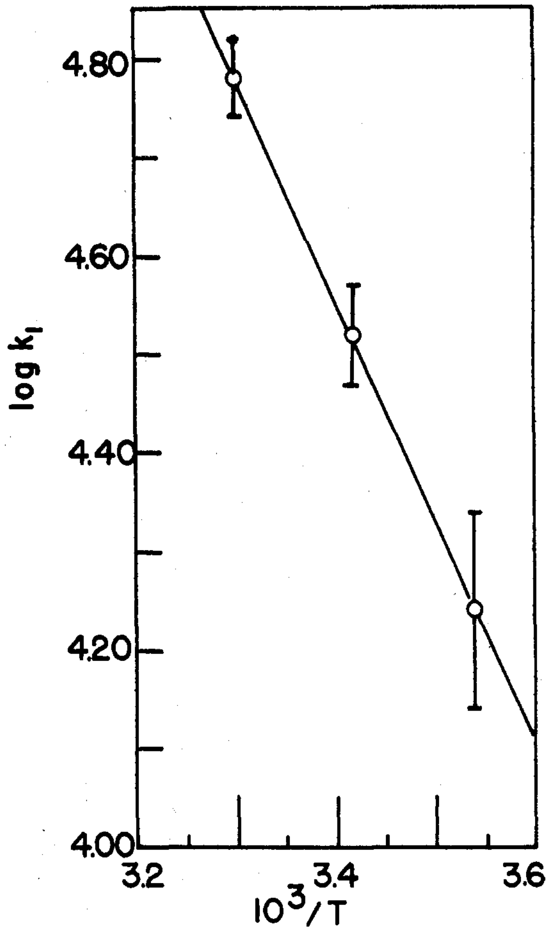

Fig. 3.—Arrhenius plot for anhydrous $NH_3$ exchange data.

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[11] T. J. Swift and R. E. Connick, *J. Chem. Phys.*, to be published.

for the observations. The theoretical calculations of Basolo and Pearson[12] based on simple crystal-field theory predict a lower activation energy for dissociation of the octahedral complex to a square pyramidal one than for association to a pentagonal bipyramidal complex. With the available data no unambiguous conclusions can be reached about alternative mechanisms. It may be profitable in such a system of two rather similar substances such as $H_2O$ and $NH_3$ to try to study both the water exchange and ammonia exchange over the entire range of composition of a mixture of the two solvents. In this way some information might be obtained regarding possible competitive processes between $H_2O$ and $NH_3$ and thus a decision as to the role of water might be reached.

Some additional rate comparisons in aqueous solution may be of interest. Additional studies on the $Cu(NH_3)_x^{++}$–$NH_3$ exchange[4] show that only a lower limit to the exchange rate can be obtained. This lower limit is *ca.* a factor of ten faster than found for the nickel system. This result is consistent with the predictions of Basolo and Pearson.[12] It is possible, however, that, because of the Jahn–Teller effect, the ammonia molecules in the copper complex are not all equivalent, which would make the comparison less straightforward. The exchange reaction $Ni(NCS)_4^{-2} + NCS^- \rightleftharpoons$ also has been studied by n.m.r. methods.[13] The relevant rate constant $k_1$ is $1.6 \times 10^5$ sec.$^{-1}$ and $\Delta H^*$ is *ca.* 5 kcal./mole. The $NCS^-$ exchange thus is faster than the $NH_3$ exchange by about a factor of two. Garner and Bjerrum[14] report a value for the first-order rate constant for dissociation of the monoammine $Ni^{++}$ complex, at $-25°$ in *ca.* 3 *M* aqueous $Mg(NO_3)_2$ solution, of $1.1 \times 10^{-2}$ sec.$^{-1}$. Extrapolating our data to $-25°$ gives a $k_1$ for the hexaammine complex of *ca.* $2 \times 10^3$ sec.$^{-1}$. The media are quite different and the extrapolation rather a long one, but it appears that the monoammine complex is considerably less labile than the hexaammine species.

The results in liquid ammonia can be compared with the approximate $N^{15}$ tracer results.[3] The tracer data give a value for $k_1$ of 28 sec.$^{-1}$ at $-50°$. Our extrapolated value is 100 sec.$^{-1}$, which is probably as good agreement as can be expected considering the errors in both sets of data.

We hope to extend the work in liquid ammonia in order to get more detailed information. There are severe limitations on such a study, particularly because of the low solubility of most salts. Addition of water should be of interest as suggested earlier.

The number of aqueous ammonia complexes of paramagnetic ions suitable for study by n.m.r. is rather limited. One additional one which might be studied by the n.m.r. method is the $Co(NH_3)_6^{++}$ complex. We plan to investigate such complexes and also to try substituted ammonias as ligands.

[12] F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," John Wiley and Sons, New York, N. Y., 1958.

[13] H. W. Dodgen, F. Klanberg, and J. P. Hunt, reported at the Northwest Regional Meeting of the American Chemical Society, Pullman, Washington, June, 1962.

[14] C. S. Garner and J. Bjerrum, *Acta Chem. Scand.*, **15**, 2055 (1961).

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CONTRIBUTION FROM THE UNITED AIRCRAFT CORPORATION
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# Ordering in Compounds of the $A(B'_{0.33}Ta_{0.67})O_3$ Type

BY FRANCIS GALASSO AND JANE PYLE

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Several compounds with the general formula $A(B'^{II}_{0.33}Ta^{V}_{0.67})O_3$, where A is a barium or strontium ion and B′ is a divalent metal ion, were prepared and studied by means of X-ray diffraction techniques. Results of this investigation show not only that the difference in the charge of the B ions causes ordering, but also that the difference in the size of these ions is an important factor in influencing the degree of long-range ordering which exists in the structure of these compounds.

## Introduction

A well known structure adopted by many $ABO_3$-type compounds is the perovskite structure in which large A ions and oxygen ions form close-packed layers with small B ions in the octahedral holes. It was postulated from a study of several compounds that if more than one ion is present in the B position it is most probable that these B ions are ordered when a large difference exists in the size or charge of the ions.[1] The first quantitative study of this hypothesis was carried out at the United Aircraft Corporation Research Laboratories using compounds with the general formula $Ba(B'^{III}_{0.5}Nb^{V}_{0.5})O_3$ which, when ordered, adopt the $(NH_4)_3FeF_6$-type structure.[2,3]

Further investigation of this hypothesis was undertaken at the Research Laboratories using compounds with the general formula $A(B'_{0.33}B''_{0.67})O_3$, although relatively few compounds of this type have been previously shown to have an ordered perovskite-type structure. There are indications, however, that some of these compounds may adopt the $(NH_4)_3FeF_6$-type struc-

[1] F. Galasso, L. Katz, and R. Ward, *J. Am. Chem. Soc.*, **81**, 820 (1959).

[2] F. Galasso and W. Darby, *J. Phys. Chem.*, **66**, 131 (1962).

[3] R. W. G. Wyckoff, "The Structure of Crystals," 2nd Ed., Reinhold Publ. Corp., New York, N. Y., 1931.