

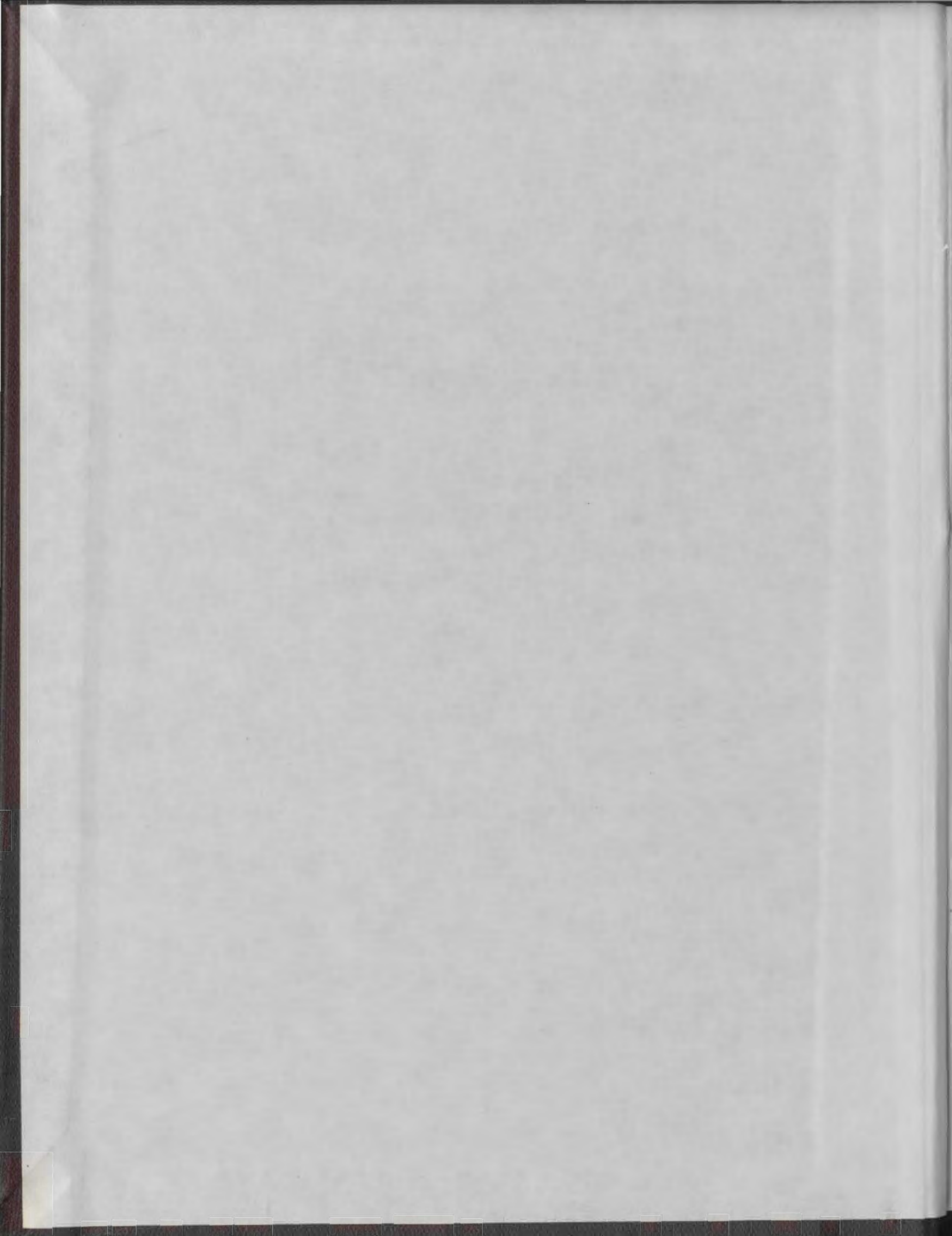
A NUCLEAR MAGNETIC  
RESONANCE STUDY: THE  
KINETICS OF HYDROGEN  
EXCHANGE REACTIONS IN  
AQUEOUS  $^{15}\text{NH}_4^+$  SOLUTION

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A NUCLEAR MAGNETIC RESONANCE STUDY:  
THE KINETICS OF HYDROGEN EXCHANGE REACTIONS IN AQUEOUS  
 $^{15}\text{NH}_4^+$  SOLUTION

by



Linda B. Thompson, B. S. in Chem.

A Thesis submitted in partial fulfillment  
of the requirements for the degree of  
Master of Science

Department of Chemistry  
Memorial University of Newfoundland

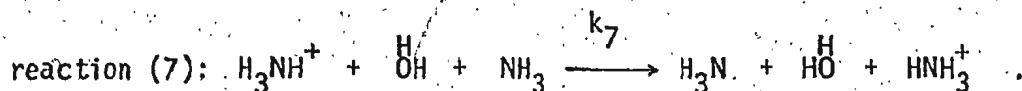
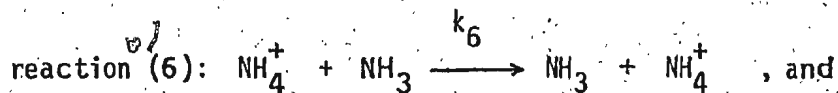
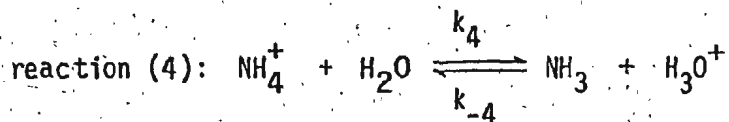
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## ABSTRACT

A study of the proton exchange reactions of  $^{15}\text{NH}_4^+$  that take place in aqueous acidic solution was conducted. Nuclear magnetic resonance methods were used to measure NH and OH line broadening resulting from exchange over the temperature range  $30^\circ\text{C}$  to  $80^\circ\text{C}$ , enabling computation of activation parameters for the reactions:



Activation energies of essentially zero for reactions (-4) and (7) have been reported in a previous study of aqueous acidic  $^{14}\text{NH}_4^+$  proton exchange reactions. Since, for the recombination reaction, any mechanism which might be associated with an activation energy of zero is inconsistent with the diffusion mechanism indicated by the bulk of data on such reactions, this study was undertaken. The  $^{15}\text{N}$  isotope was used to eliminate the possibility of a contribution to the NH linewidth by broadening due to quadrupolar relaxation.

The activation enthalpy for reaction (4) was found to be  $14.6 \text{ kcal mole}^{-1}$ . Rate constants for reaction (-4) were found to conform well to a

model for diffusion controlled reactions, with  $\Delta H_4^*$  equal to  $2.2 \pm 0.3$  kcal mole<sup>-1</sup>, and with  $P\sigma$  a constant, equal to  $(4.2 \pm 0.2) \times 10^{-8}$  cm.  $\Delta H_7^*$  was also found to have a non-zero value,  $4.3 \pm 1.6$  kcal mole<sup>-1</sup>; and  $\Delta H_6^*$  was found to equal  $5.6 \pm 1.3$  kcal mole<sup>-1</sup>.

## ACKNOWLEDGEMENTS

The author wishes to express her appreciation to Dr. E. K. Ralph for his patient supervision throughout the study.

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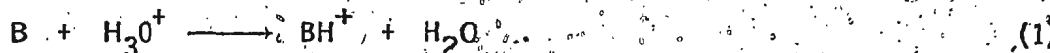
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## 1. INTRODUCTION

The conjugate bases of most acids of the type  $-OH$ ,  $-NH$ ,  $-NH^+$ , and  $-SH$ , whose  $pK_A$  values lie in the range  $-1$  to  $+15$  have rate constants for the recombination with the hydrogen ion on the order of  $10^9 \text{ sec}^{-1} \text{ M}^{-1}$  to  $10^{11} \text{ sec}^{-1} \text{ M}^{-1}$ , the generalized equation for the recombination reaction being



Conjugate bases of most  $-CH$  type acids have significantly smaller recombination constants.<sup>1</sup>

Eigen and his school have amassed rate constant data for many such inorganic and organic acids, and have been able to show that, in solution, the rate of recombination with the hydrogen ion is usually limited by the frequency of encounters of the reactants due to their thermal translational motion.\* Differences between measured reaction rates and encounter rates calculated from diffusion theory are attributed by Eigen to four factors:

\* For a tabulation of these rate constants, and a thorough discussion of the nature of the reactions with which they are associated, see references 1 and 2.

- 1) spacial symmetry and steric factors,
- 2) electrostatic interactions,
- 3) hydrogen bond structure, and
- 4) electron distribution and molecular structure.

According to Eigen, the requirements for the frequency of encounters to be rate determining are met only if the proton has free access to the reaction site via hydrogen bonding to solvent water molecules, and if the reactants are in a configuration suitable for reaction. Hence, elucidation of the mechanism of fast proton transfer processes has progressed hand in hand with elucidation of the hydrogen bond and the phenomenon of solvation.

Eigen has developed a theory correlating the kinetic constants of proton transfer reactions with the pK difference of donor and acceptor, making possible estimation of kinetic constants of acid-base systems not yet investigated.<sup>1</sup> This is a significant step toward the description of the mechanics of acid-base catalysis and of particular importance in the area of enzyme catalysis, since the properties of the active groups occurring in proteins which promote acid-base catalysis are not always known.

Of the fast reactions examined in this study, the reaction of  $\text{NH}_3$  with hydrogen ion would appear to fall into the category of reactions described by Eigen. If, however, in a study reported in 1960 by Connor and Loewenstein,<sup>3</sup> an activation energy of zero for the reaction was correctly determined, a different mechanism from that postulated by Eigen is necessitated.

Diffusion controlled reactions typically have activation energies

of about 3 kcal mole<sup>-1</sup> to 4 kcal mole<sup>-1</sup>. If, due to any of the four factors affecting reaction rates, a reaction following an encounter is not complete before reactants again separate, it could be expected to have an activation energy greater than that for a diffusion controlled reaction. The most critical of the four factors, the effect of the hydrogen bridge structure is applicable to the reaction of NH<sub>3</sub> with the hydrogen ion. It is primarily the existence of hydrogen bridges that accounts for high rates of recombination of bases with the hydrogen ion. That CH and C<sup>-</sup> groups do not readily form hydrogen bridges accounts in part for the low recombination constants of the conjugate bases of -CH type acids. It is possible that for a particular reaction, raising the temperature could cause a disruption in the hydrogen bridge system in the vicinity of the reactants, resulting in an alteration of the reaction rate. Such an effect would not be drastic enough to appear to lower the activation energy to zero, however, without warranting postulation of a different mechanism.

Also affecting the recombination rate of NH<sub>3</sub> is the lack of mutual electrostatic attraction with the hydrogen ion. Bases of the -N type show a reduction in rate of recombination with hydrogen ion from values for similar, but oppositely charged, particles.<sup>2</sup> This effect is a relatively minor one, and most likely independent of temperature.

The realm of the kinetics of fast reactions in solution was opened to the physical chemist with the advent of various spectroscopic techniques and the development of oscillographic fast-recording gear. He needed no longer label reaction rates which were fast compared to the time required for mixing and observation "immeasurable." Certain

relaxation methods and fluorescence quenching and electrochemical methods have extended the range of accessible reactions to those with halftimes as small as  $10^{-9}$  sec.<sup>4</sup>

The nuclear magnetic resonance method exploits the coexistence in solution of rapidly equilibrating species possessing different nuclear spin systems. Marked changes in corresponding spectral lines occur when lifetimes of these interchanging species are in the range of about  $10^{-1}$  sec to  $10^{-5}$  sec. In the following chapter (Chapter II, pp. 11 - 23), are presented some of the techniques which have been developed for extracting kinetic information from various types of n. m. r. data. These will be the tools of this study.

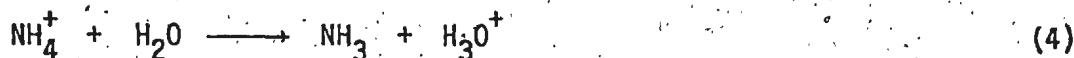
Interestingly, one of the earliest applications of the n. m. r. line shape to reaction kinetics was to the ammonia - water system. Ogg,<sup>5</sup> in 1954, observed the collapse of the triplet of intensively dried liquid ammonia to a singlet upon the introduction of water to the extent of no more than a few parts per million. He reported similar effects upon the addition of  $\text{KNH}_2$ ,  $\text{NaNH}_2$ ,  $\text{NH}_4\text{Br}$ , and  $\text{H}_3\text{NBF}_3$ . He estimated from linewidth measurements of ammonia -  $\text{NaNH}_2$  solution spectra the rate constant of the reaction



to be  $4.6 \times 10^8 \text{ sec}^{-1} \text{ M}^{-1}$  at  $0^\circ\text{C}$ , and its activation energy not to exceed a few kilocalories. Ogg suggested similar magnitudes for the reaction



Subsequently, Ogg found the spectrum of  $\text{NH}_4\text{NO}_3$  in water to be a single averaged resonance at room temperature.<sup>5</sup> The spectrum of the same solution when slightly acidified displayed the NH triplet distinct from the water line. He therefore suggested the direct transfer reaction



to be too slow to cause obliteration of spectral details, and placed an upper limit on the rate constant of  $10^3 \text{ sec}^{-1}$  for his experimental conditions.

Brodskii and Sulima,<sup>6</sup> having previously investigated the proton exchange of the aqueous ammonium ion using deuterium as a tracer, had found a halflife of exchange for  $\text{NH}_4\text{NO}_3$  in 54 percent  $\text{HNO}_3$  to be between 1 and 10 minutes at  $0^\circ\text{C}$ . The halflife was determined more precisely for the exchange with butyl alcohol by Kaplan and Wiltzback<sup>7</sup> using tritium as a tracer to be 3 minutes at  $0^\circ\text{C}$ , again in 54 percent  $\text{HNO}_3$ .

This early data illustrates the marked dependence of the rate of proton exchange on hydrogen ion concentration. The exchange in an aqueous acidic medium is known to be due primarily to a process first order in ammonium ion concentration and to at least two second order processes which are dependent on the product  $[\text{NH}_4^+][\text{NH}_3]$ .

In the pH range 1 to 4, both types of process contribute measurably to the exchange rate, the rate of the first order process being independent of pH and that of the second order processes decreasing with increasing acidity.<sup>8</sup> At very low pH the second order processes contribute



negligibly to the overall exchange. Also, in the very low pH region, the first order process shows a very marked decrease in rate. The data of Emerson, Grunwald, Kaplan, and Kromhout<sup>9</sup> presented in Table I impressively illustrate the suppression of the exchange rate.

Table I: Halflife of the Isotopic Exchange:



Halflives are given for exchange taking place at 25°C in sulfuric acid - water mixtures.

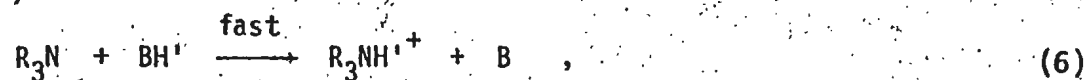
Wt. % H <sub>2</sub> SO <sub>4</sub>	t <sub>1/2</sub>
49.14	105 sec
58.37	20 min
69.38	15 hr

The work of Brodskii and Sulima and of Kaplan and Wiltzback was performed in this high acidity region of suppressed exchange rate. Also, because of deuterium and tritium isotope effects, the halflives reported by these workers are longer than would occur for exchange within undoped reaction mixtures.

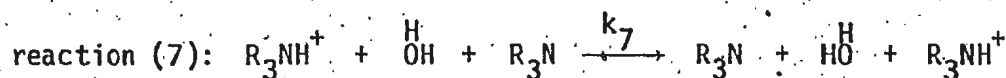
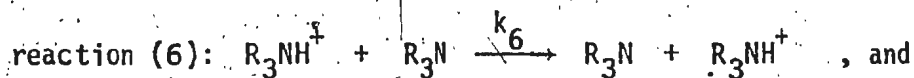
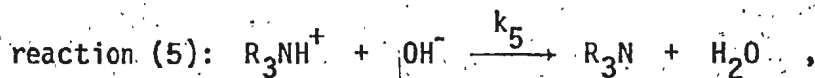
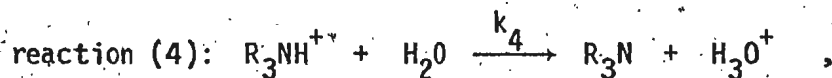
The pH range of the aqueous ammonium ion reaction mixtures from which kinetic data was obtained during this study is about 0.6 to 2.0. As will be shown in Chapter V (p. 70), the first order exchange process is to no significant extent a function of hydrogen ion concentration in

this range.

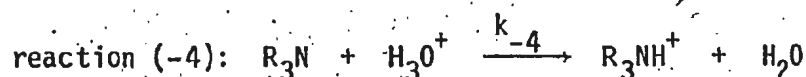
Meiboom, Grunwald, and co-workers, using the n. m. r. technique, pioneered the search for the mechanism of the protolysis of aqueous amines, investigating first the methylammonium ion.<sup>10, 11, 12, 8</sup> Primarily responsible for proton exchange of alkylammonium ions is a mechanism involving two steps:



with B a base. The specific reactions accounting for the slow step considered were:



The above notation introduced by Grunwald, Loewenstein, and Meiboom<sup>11</sup> is adopted for use in this thesis. Also adopted is the designation



An upper limit of  $0.2 \text{ sec}^{-1}$  at  $19 \pm 2^\circ\text{C}$  was placed on the rate constant for reaction (4) for the methylammonium case.<sup>11</sup> Two separate mechanisms were postulated for the slow step of the second order processes: reaction (6), involving transfer directly from  $\text{NH}_4^+$  to  $\text{NH}_3$ ; and reaction (7), involving at least one intervening water molecule. These two paths were found to be followed at comparable rates for the methylammonium case, the rate constants being  $3 \times 10^8 \text{ sec}^{-1} \text{ M}^{-1}$  at  $19 \pm 2^\circ\text{C}$ .

The investigations were extended to the protolysis reactions of the ammonium ion and to those of di- and trimethylammonium ions. Some of the results, along with more recent data, are summarized in Table II.

Emerson, Grunwald, and Kromhout<sup>13</sup> showed by application of the Debye - Smoluchowski theory of diffusion controlled reactions,\* that the values of the rate constants of reaction (-4) and reaction (6) for the ammonium ion were in agreement with those expected for a diffusion controlled reaction.

Connor and Loewenstein<sup>3</sup> put this speculation to test experimentally by doing a variable temperature study of the protolysis reactions of the ammonium and methylammonium ions. The activation energies for reaction (6) and reaction (7) were found to be essentially zero for both cases. An activation energy of  $12.2 \pm 0.5 \text{ kcal mole}^{-1}$  was found for reaction (4) for the ammonium ion case, for which Connor and Loewenstein quote the enthalpy change  $\Delta H^0$  for the acid dissociation equilibrium to be  $12.4 \text{ kcal mole}^{-1}$ , thus implying an activation energy of zero for the reverse reaction, (-4).<sup>3</sup> Current theory cannot account for these anomalously low activation

\*For a presentation of the theory, see Chapter V (pp. 81 - 83) and references 49, 50, and 51.

Table II: Rate Constants for Proton Transfer Reactions of Aqueous Alkylammonium Ions

Rate constants and acid dissociation constants are given for aqueous alkylammonium ion solutions at 25°C.

Alkyl-ammonium ion	$k_4$ (sec <sup>-1</sup> )	$10^{10} k_A$ (M)	$10^{-10} k_{-4}$ (sec <sup>-1</sup> M <sup>-1</sup> )	$10^{-10} k_5$ (sec <sup>-1</sup> M <sup>-1</sup> )	$10^{-8} k_6$ (sec <sup>-1</sup> M <sup>-1</sup> )	$10^{-8} k_7$ (sec <sup>-1</sup> M <sup>-1</sup> )	$10^{-10} k_H$ (sec <sup>-1</sup> )	References
NH <sub>4</sub> <sup>+</sup>	25	5.68	4.3	3.4	11.7	0.9	22	13, 16, 17
CH <sub>3</sub> NH <sub>3</sub> <sup>+</sup>	—	0.242	—	3.7	4.0	5.3	6.2	18, 9, 10, 17
(CH <sub>3</sub> ) <sub>2</sub> NH <sub>2</sub> <sup>+</sup>	—	0.168	—	3.1	0.5	9.0	—	11, 2, 19
(CH <sub>3</sub> ) <sub>3</sub> NH <sup>+</sup>	4.7	1.57	3.0	2.1	0.0	3.4	1.0	15, 2, 17

energies, unless perhaps the phenomenon of tunneling is involved.

Asserting that these activation energies should be no less than that for the diffusion of the reactants, Grunwald<sup>15</sup> reinvestigated the kinetics of the aqueous methylammonium ion system over the temperature range 35°C to 80°C. His data indicate reaction (-4) for the recombination of  $\text{CH}_3\text{NH}_2$  with the hydrogen ion to be a simple diffusion controlled reaction. Reaction (7) was found to have the decisively non-zero enthalpy of activation  $3.3 \text{ kcal mole}^{-1}$ .

The inconsistency of these two studies has prompted this further investigation of the aqueous ammonium ion system. It is possible that the  $^{14}\text{NH}$  resonance is influenced by a longitudinal relaxation time shortened by quadrupole relaxation of the  $^{14}\text{N}$  nucleus. This eventuality is eliminated in this work by the use of an  $^{15}\text{NH}_4^+$  salt, with which no such complication arises since  $^{15}\text{N}$  has a zero quadrupole moment.

Recent investigations have led to a remarkably detailed picture of the reaction mechanisms of reactions (4) - (7), of the nature of the solvation of the species involved, and of the making and breaking of the hydrogen bonds associated with these solvated complexes.\* ( In Table II (p. 9) are listed the values which have been determined for the rate constant  $k_H$  for the breaking of the  $\text{R}_3\text{N}\cdots\overset{\text{H}}{\text{O}}\cdots$  hydrogen bond. That  $k_H$  is very large for  $\text{NH}_3$ , by far the largest for any of the amines, lends plausibility to the theory that a breakdown in the hydrogen bond structure might occur at higher temperatures, and thus account for a low activation energy for the recombination reaction. It was hoped that this study will add clarity to this aspect of the increasing store of knowledge about proton exchange reactions.

\* See, for example, references 20, 21, 22, 23, and 17.

## II. NUCLEAR MAGNETIC RESONANCE METHODS

## Reaction rate determination from line shape\*

The n. m. r. technique of reaction rate determination from line shape is applicable to the system in which a nucleus is exchanged between two or more magnetically distinct environments. Such environments can be those of different molecules, of different sites on the same molecule, or can be the result of nuclear spin coupling.

In the extreme of very slow exchange, for the case of nuclei X exchanging between the two sites A and B, two distinct resonances with frequency separation  $\delta\omega$  are observed, one corresponding to the resonance position of X at A, the other to that of X at B. As exchange becomes faster, and the mean lifetimes  $\tau_A$  and  $\tau_B$  of X at A and at B, respectively, are no longer large compared to the frequency separation between A and B sites, the resonances are observed to broaden, merge, and finally to sharpen into a single band at a resonance frequency which is a weighted average of the resonance frequencies of X at A and at B sites.

Figure 1 illustrates this phenomenon for the case of a spin-spin doublet, with X exchanging between equally populated sites. The doublet is shown to collapse with increasing exchange rate.

The first quantitative treatment of the exchange rate - line shape phenomenon was given by Gutowsky, McCall, and Slichter<sup>25</sup> and has since been extended from their derivation of the equations describing the line shape of a spin doublet to include equations for higher multiplets and

\* A thorough treatment of this phenomenon is given in reference 24, pp. 218 - 230.

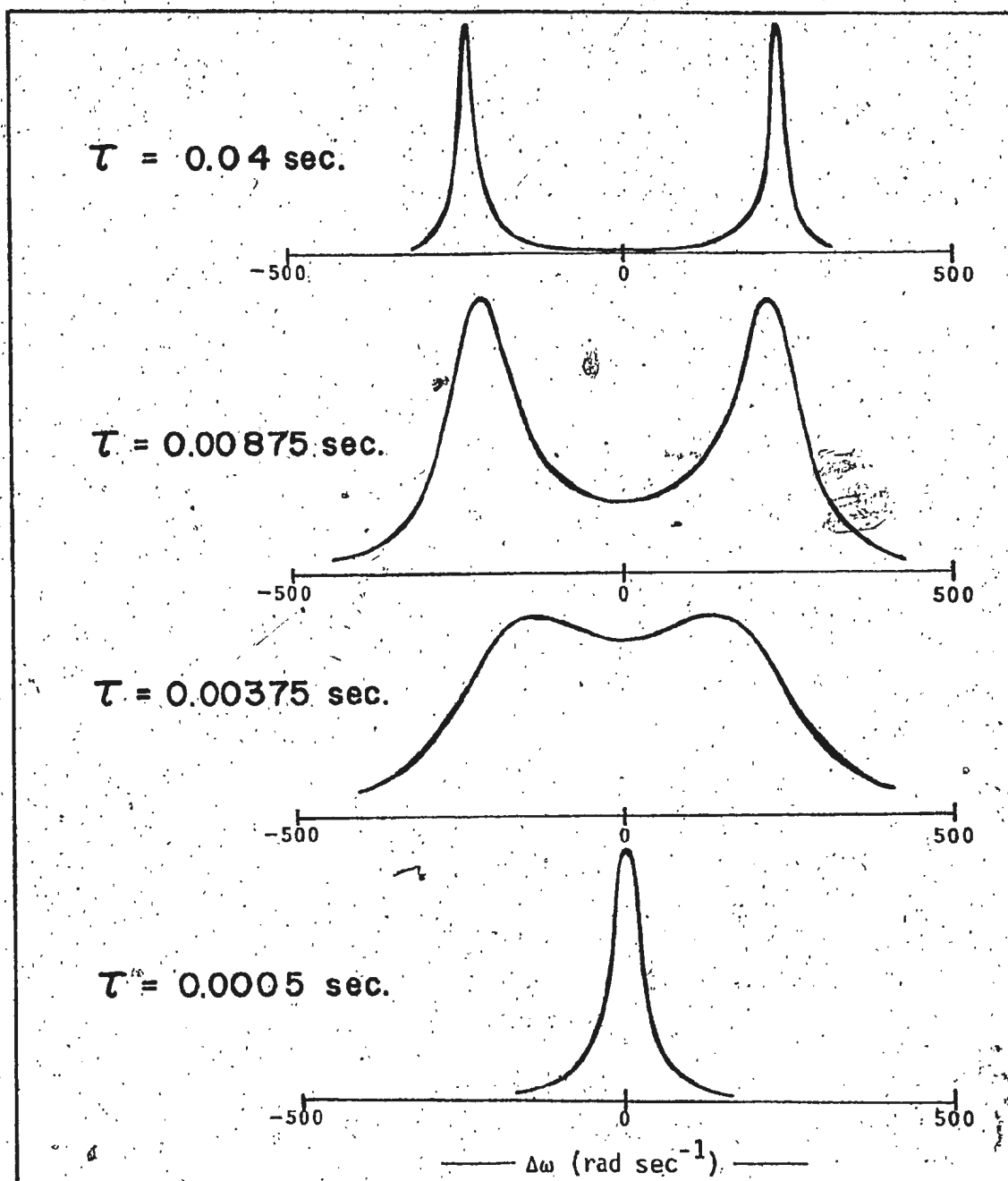


Figure 1: The Effect of Chemical Exchange on the Lineshape of the Spin Doublet

Theoretical lineshapes are computed from an expression given by Takeda and Stejskal<sup>30</sup> using the values  $J = 464 \text{ rad sec}^{-1}$  and  $T_2 = 0.5 \text{ rad sec}^{-1}$ , and allowing  $\tau$  to vary as indicated.

to cases featuring varied conditions of exchange. 11, 25, 26, 27, 28, 29

The relatively simple treatment of McConnell<sup>28</sup> is based on the familiar Bloch equations generalized to include exchange. For the process exchanging X between sites A and B, solution to the modified Bloch equations for the slow passage case gives for the absorption mode

$$\nu = \frac{\gamma H_1 M_0^A \tau_{2A} \left[ \frac{1}{T_{1A}} + \frac{\tau_{1B}}{T_{1B} \tau_A} \right] / \left[ \frac{1}{\tau_{1A}} - \frac{\tau_{1B}}{\tau_A \tau_B} \right]}{1 + \Delta\omega_A^2 \tau_{2A}^2 + \left[ \tau_{2A} \gamma^2 H_1^2 \right] / \left[ \frac{1}{\tau_{1A}} - \frac{\tau_{1B}}{\tau_A \tau_B} \right]}, \quad (7)$$

with  $\gamma$  the magnetogyric ratio of X;  $H_1$ , the applied radio frequency field;  $M_0^A$ , the equilibrium z magnetization of X at A;  $\tau_A$  and  $\tau_B$ , the mean lifetimes of X at A and at B, respectively;  $T_{1A}$  and  $T_{1B}$ , the longitudinal relaxation times of X; and  $T_{2A}$  and  $T_{2B}$ , the transverse relaxation times of X; and with

$$\frac{1}{\tau_{1A}} = \frac{1}{T_{1A}} + \frac{1}{\tau_A}, \quad \text{and} \quad (8)$$

$$\frac{1}{\tau_{2A}} = \frac{1}{T_{2A}} + \frac{1}{\tau_A}, \quad (9)$$

and similarly for  $\tau_{1B}$  and  $\tau_{2B}$ .

For the special case of slow exchange, in which the mean lifetimes  $\tau_A$  and  $\tau_B$  are large compared to the frequency separation  $\delta\omega$ , the absorption mode is given by



$$v_A = -M_0 \frac{\gamma H_1 \tau_{2A} p_A}{1 + \tau_{2A}^2 \Delta\omega_A^2} \quad (10)$$

with  $p_A$ , the fractional population of the A site

$$p_A = \frac{\tau_B}{\tau_B + \tau_A} \quad (11)$$

and similarly for  $v_B$ .  $v_A$  describes a Lorentzian curve with a linewidth at half height given by

$$\frac{1}{\tau_{2A}'} = \frac{1}{\tau_{2A}} + \frac{1}{\tau_A} \equiv \pi\Delta_A \quad (12)$$

The absorption of X at A for this case is said to be within the limit of lifetime broadening, and can be treated independently of the absorption of X at B for exchange rate determination purposes (and likewise for the absorption of X at B). For the reaction mixtures used in this study, the condition of lifetime broadening can be applied fairly well up to 50°C to the lines reflecting exchange between N and O sites and exchange between  $N(+\frac{1}{2})$  and  $N(-\frac{1}{2})$  spin states.

$T_2$  measurement from water wiggles\*

It can be seen from equation (12) that measurement of  $\pi\Delta_{NH}$  allows

\* A discussion of this method is given in reference 24, pp. 40 - 42.

determination of  $(1/\tau)_{NH}$  if  $(1/T_2)_{NH}$  can be evaluated. An additional contribution to the width of the NH line arises from broadening due to magnetic field inhomogeneity,  $(1/T_2)_{magnet}$ . Extracting  $(1/\tau)_{NH}$  values from linewidth measurements requires evaluation of both  $(1/T_2)_{NH}$  and  $(1/T_2)_{magnet}$ . The sum of these contributions will be termed  $(1/T_2)_{NH}$  for convenience. In general,  $1/T_2'$  and  $1/T_2''$  will be defined as

$$\frac{1}{T_2'} \equiv \frac{1}{T_2} + (1/T_2)_{magnet}, \text{ and} \quad (13)$$

$$\frac{1}{T_2''} \equiv \frac{1}{T_2'} + \frac{1}{\tau}. \quad (14)$$

An estimate of  $(1/T_2')_{NH}$  is obtained from the water line according to the following considerations.

During fast passage through resonance, the macroscopic moment  $M$  is unable to return to its equilibrium value at a rate comparable to the rate of passage of magnetic field  $H_0$  through resonance, as for the slow passage case.  $M$  is left in a nonequilibrium state precessing at a frequency equal to  $(H_1 - H_{res})$ , where  $H_{res}$  is small compared to  $H_1$ , until the transverse components eventually decay. The decay is exponential and depends not only upon the transverse relaxation time but upon field homogeneity, and upon such processes as chemical exchange which involve correlation times which are of comparable magnitude to  $1/\gamma H_1$ . Figure 2 shows the typical oscillatory trace obtained after fast passage through a water resonance with field homogeneity optimized.

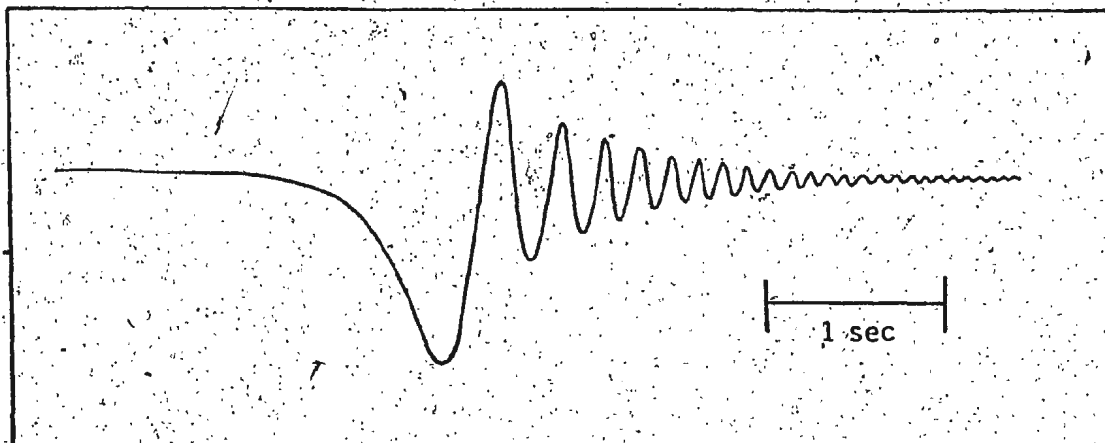


Figure 2: Decay Envelope Obtained After Fast Passage Through Water Resonance

For this trace,  $(1/T_2'')_{OH}$  is  $1.4 \text{ sec}^{-1}$ .

For aqueous ammonium ion systems, evaluation of the time constant of the exponential decay of the so called wiggles of the water line, produced by fast passage, gives  $(1/T_2'')_{OH}$ , with

$$\left(\frac{1}{T_2''}\right)_{OH} = \left(\frac{1}{T_2}\right)_{OH} + \left(\frac{1}{T_2}\right)_{\text{magnet}} + \left(\frac{1}{\tau}\right)_{OH} \quad (15)$$

$(T_2)_{OH}$  being the transverse relaxation time of an  $H_2O$  proton;  $(1/T_2)_{\text{magnet}}$ , the field inhomogeneity contribution to the water linewidth; and  $\tau_{OH}$ , the mean lifetime of a proton in the OH environment.

If broadening from field inhomogeneity is the main contribution to the linewidth of the OH resonance, and is significantly larger than the contribution  $(1/T_2)_{NH}$  of the transverse relaxation to the NH linewidth, the decay of the water wiggles serves as a measure of  $(1/T_2')_{NH}$ .

Over the temperature range 30°C to 50°C at which this technique is applied in this work, these conditions are either met by the systems being studied or are readily corrected for if not met.  $(1/T_1)_{OH}$ , to which  $(1/T_2)_{OH}$  is equal for the reaction mixtures under the conditions used in this study, as measured for air-free water by Krynicky,<sup>31</sup> ranges from a value of 0.248 sec<sup>-1</sup> at 30°C to 0.116 sec<sup>-1</sup> at 50°C. Values for  $(1/\tau)_{OH}$  may be determined by extrapolation from exchange broadening data obtained from the water line in this work at higher temperatures. At 30°C,  $(1/\tau)_{OH}$  is found to fall in the range of about 0.1 sec<sup>-1</sup> to 0.2 sec<sup>-1</sup> for the reaction mixtures studied. At 50°C,  $(1/\tau)_{OH}$  is as large as 1.0 sec<sup>-1</sup> for mixtures of low hydrogen ion concentration and of high salt concentration. The values of  $(1/T_2)_{OH}$  obtained from the water wiggles were no smaller than 1.5 sec<sup>-1</sup> for the reaction mixtures at 30°C and no smaller than 2.5 sec<sup>-1</sup> at 50°C.

Clearly, though the broadening due to field inhomogeneity is the largest of the contributions to  $(1/T_2)_{OH}$ ,  $(1/\tau)_{OH}$  contributes significantly. This is accounted for by a correction to linewidth measurements described in Chapter IV (p. 39).

$(1/T_2)_{NH}$ , which is evaluated in Chapter V (pp. 74 - 78), has a magnitude comparable to that of  $(1/T_2)_{OH}$ .

Any error introduced by approximating  $(1/T_2)_{NH}$  with  $(1/T_2)_{OH}$  is most significant at 30°C, at which temperature  $(1/\tau)_{NH}$  lies in the range 7 sec<sup>-1</sup> to 16 sec<sup>-1</sup> for the reaction mixtures studied.

#### Adiabatic half passage

A convenient method of measuring the transverse relaxation time  $T_2$

which eliminates the effect of field inhomogeneity has been described by Solomon.<sup>32, 33</sup> Termed adiabatic half passage by Meiboom,<sup>34</sup> the method involves alignment of the magnetization along the rf field  $H_1$  by an adiabatic rapid passage in the presence of  $H_1$  to the center of resonance, where the sweep is stopped. The conditions of adiabatic rapid passage must be fulfilled:

$$\frac{1}{T_2} \ll \frac{1}{H_1} \left| \frac{dH_0}{dt} \right| \ll \gamma H_1 \quad (16)$$

Since  $\gamma H_1$  is large compared to  $1/T_1$ , the magnetization remains aligned with  $H_1$  when the sweep is stopped, and decays with a time constant denoted by Meiboom as  $1/T(H_1)$ . A typical record of such a decay appears in Figure 3.

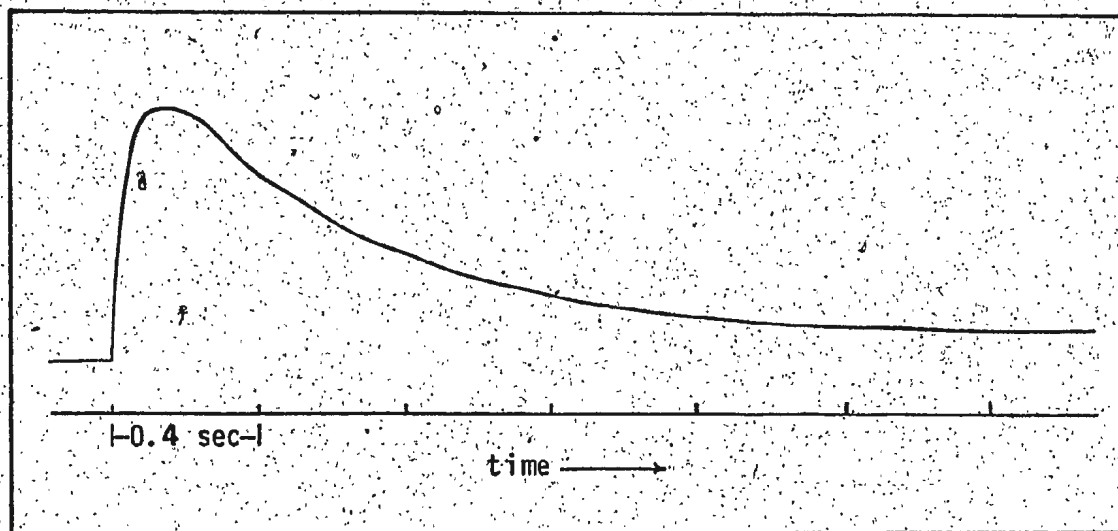


Figure 3: Typical Record Obtained After Adiabatic Half Passage Through Water Line

For this trace, recorded at  $65^{\circ}\text{C}$ ,  $1/T(H_1) = 1.5 \text{ sec}^{-1}$ .

If the inhomogeneity of the applied magnetic field  $H_0$  is small compared to  $H_1$ ,  $T(H_1)$  is not appreciably affected by it. In the coordinate system rotating with  $H_1$ ,  $1/T(H_1)$  is effectively the thermal time constant with which the magnetization decays in the applied magnetic field  $H_1$ .

$T(H_1)$  is in some instances equivalent to the ordinary transverse relaxation time  $T_2$ . However, if such processes as chemical exchange involving correlation times which are of comparable magnitude to  $1/\gamma H_1$  occur,  $T(H_1)$  reflects these additional mechanisms. Meiboom<sup>34</sup> has given a theoretical treatment of this phenomenon based on the Bloch equations generalized to include exchange.

An explicit solution of  $T(H_1)$  as a function of  $H_1$  and the exchange rate is derived for the special case in which the resonance consists of one dominant line, all other resonances being much weaker. Direct contribution of the weak lines to the observed signal is neglected; weak resonances are considered only inasmuch as they contribute to the width of the dominant line through exchange. Subject to this restriction, Meiboom gives, for a system of identical nuclei, the members of which can be in any one of  $n$  different environments which will affect its average local field,

$$\frac{1}{T(H_1)} = \frac{1}{T_1} + \sum_i^n \frac{P_i \delta_i^2}{1 + \tau^2 (\delta_i^2 + \gamma^2 H_1^2)} \quad (17)$$

with

$$P_i \gg \sum_{j \neq i}^n P_j \quad (18)$$

where  $P_i$  is the fraction of nuclei in the  $i^{\text{th}}$  environment,  $\delta_i$  is the frequency difference between the line of the nuclei in the  $i^{\text{th}}$  environment and the dominant line, and  $\tau$  is the mean lifetime of a nucleus in any one of the  $n$  environments.  $T'$  characterizes transverse relaxation due to mechanisms other than exchange.

For the water - ammonium ion systems examined in this work, the dominant line approximation is a good one, as Figure 4 illustrates. The adiabatic half passage technique proved useful in examining the broadening of the water line at temperatures sufficiently high that  $^{15}\text{NH}$  proton lines no longer satisfied the condition of lifetime broadening. For the water line of an aqueous solution of  $^{15}\text{NH}_4^+$  with  $\text{pH} < 4$ , equation (17) derived by Meiboom becomes

$$\frac{1}{T(H_1)} = \frac{1}{T'} + \frac{P_{\text{NH}}}{2} \frac{\tau (\delta_{\text{NH}} + \frac{J}{2})^2}{1 + \tau^2 (\delta_{\text{NH}} + \frac{J}{2})^2 + \gamma^2 H_1^2} + \frac{P_{\text{NH}}}{2} \frac{\tau (\delta_{\text{NH}} - \frac{J}{2})^2}{1 + \tau^2 (\delta_{\text{NH}} - \frac{J}{2})^2 + \gamma^2 H_1^2} \quad (19)$$

where  $P_{\text{NH}}$  is the fraction of NH protons, and  $J$  is the  $^{15}\text{N}$ -H coupling constant, so that  $(\delta_{\text{NH}} + \frac{J}{2})$  and  $(\delta_{\text{NH}} - \frac{J}{2})$  are the frequency differences between protons coupled to the upper spin state of  $^{15}\text{N}$  and the water line and between protons coupled to the lower spin state of  $^{15}\text{N}$  and the water line, respectively.

$T = 30^{\circ}\text{C}$   
 $[\text{NH}_4^+] = 0.4\text{ M}$   
 $[\text{H}^+] = 0.23\text{ M}$

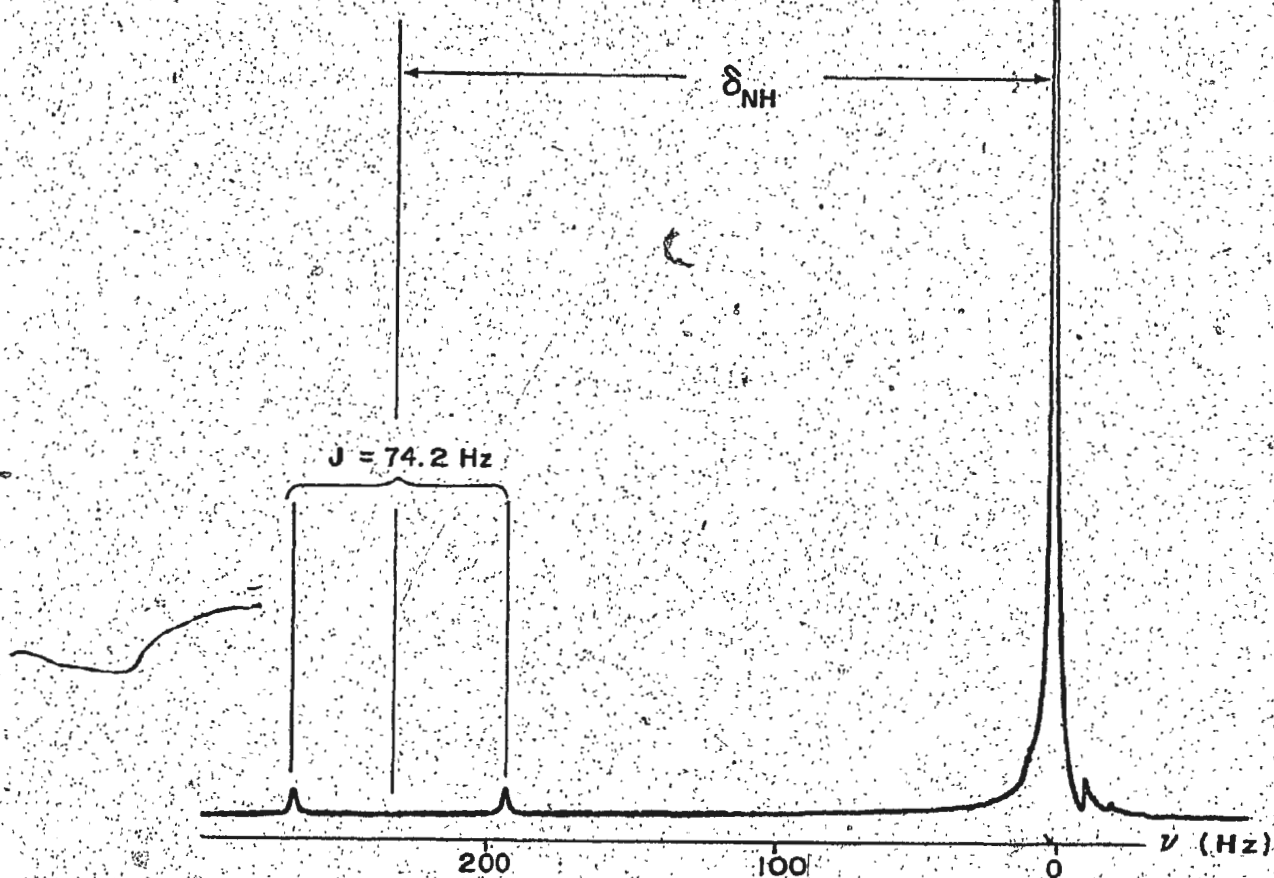


Figure 4: N. M. R. Spectrum: The  $^{15}\text{NH}$  Doublet and the Water Line



### $T_1$ measurement\*

The adiabatic half passage technique is seen to provide a route for determination of the specific rate of exchange  $1/\tau$  for the systems of interest if  $1/T'$  can be evaluated.

If all interactions contributing to transverse relaxation are characterized by short correlation times,  $T'$  will be equivalent to  $T_1$ . The method of measuring  $T_1$  used in this work employs the adiabatic fast passage conditions of equation (16). If these conditions are met during passage through resonance, the presence of the relatively large rf field  $H_1$  reverses by  $180^\circ$  the nuclear magnetization vector  $M$  of the spin system under investigation. Once the sweep through resonance is completed,  $M$  regains its original magnitude and position parallel to  $H_0$  as depicted in Figure 5. The recovery is exponential with a time constant  $1/T_1$ .

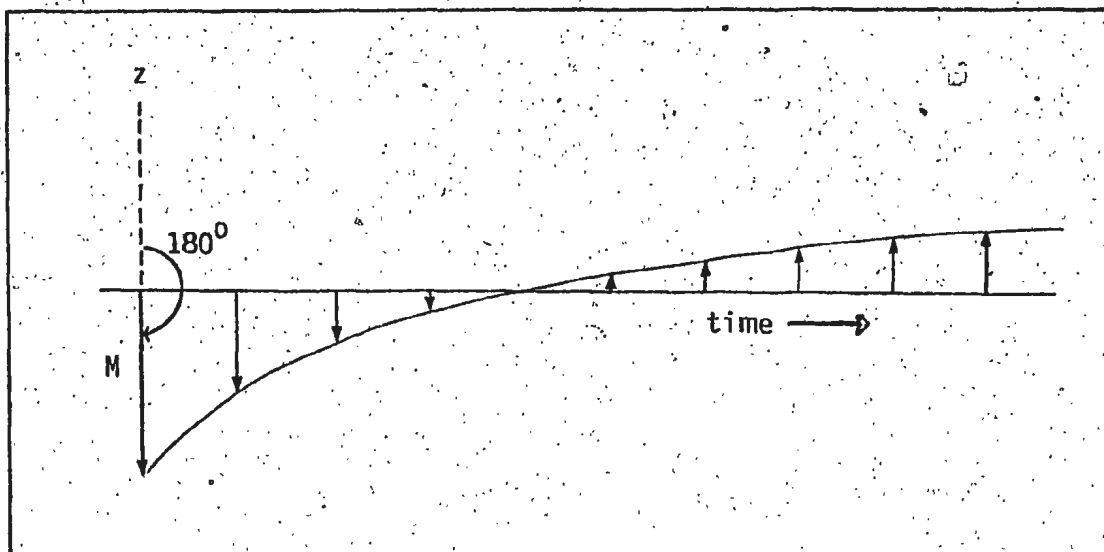


Figure 5: Adiabatic Fast Passage: Reversal and Recovery of Magnetization

\* A presentation of the method used is given in reference 35.

Experimentally, an initial adiabatic sweep through resonance is made, followed by a second sampling sweep. The relative magnitude of the magnetization observed in the second instance is a function of the time between the two sweeps. By varying this time separation in independent experiments and recording the relative magnitude of the magnetization, the recovery curve of Figure 5 (p. 22) may be obtained and  $1/T_1$  calculated.

## III. EXPERIMENTAL

## Chemicals

$^{15}\text{NH}_4\text{Cl}$  was the ammonium salt chosen to be studied in aqueous solution. It was supplied by Prochem and rated at 99.2 atom percent  $^{15}\text{N}$ . It was recrystallized from absolute ethanol and dried in vacuo. No evidence for the presence of  $^{14}\text{NH}_4^+$  was observed in n. m. r. spectra of  $^{15}\text{NH}_4\text{Cl}$  solutions.

$^{14}\text{NH}_4\text{Cl}$  was supplied by Shawinigan and was recrystallized from absolute ethanol.

Doubly distilled water was the solvent for all solutions. The second distillation was from a KOH solution.

Stock solutions of acids and bases were used in the preparation of reaction mixtures and in making acid dissociation constant measurements of the ammonium salts. HCl and NaOH solutions were prepared from concentrated reagent grade solutions and were stored in polyethylene bottles. NaOH solutions were standardized by potentiometric titration against potassium acid phthalate ( $\text{KHC}_8\text{H}_4\text{O}_4$ ) obtained from the National Bureau of Standards. HCl solutions were standardized potentiometrically against Standard NaOH solutions. Strongly acidic reaction mixtures were prepared by dilution of known weights of concentrated  $\text{H}_2\text{SO}_4$ . Density data used in the computation of solution concentrations was obtained from the International Critical Tables.<sup>36</sup>

## Reaction mixtures

Reaction mixtures were prepared from known weights of the appropriate

ammonium salt, standard acid solution, and doubly distilled water. Mixing of each solution was effected as rapidly as possible, and about 1 ml was pipeted into an ultra-precision n. m. r. tube (Wilmad Glass Co.), which had been aged in dilute HCl, washed with distilled acetone, and oven dried.

It was desired to examine the nature of exchange within reaction mixtures of the same composition over the temperature range 30°C to 80°C. Accordingly, to prevent change in composition of the solutions through evaporation, sample tubes were sealed for use throughout the study.

#### $pK_A$ measurement

$pK_A$  measurements were made by the differential potentiometric method of Bacarella, Grunwald, Marshall, and Purlee.<sup>37</sup> A solution of the appropriate ammonium salt of known composition by weight, was acidified with a known weight of HCl solution. The formal concentration of HCl was set in the range 0.004 M to 0.005 M. This is sufficiently high to insure the initial hydrogen ion concentration was due primarily to HCl, yet sufficiently low to minimize salt effects. The concentration of  $^{14}\text{NH}_4\text{Cl}$  in seven independent measurements ranged from 0.04 M to 0.50 M. The concentration of  $^{15}\text{NH}_4\text{Cl}$  in the single measurement made was 0.25 M.

A known weight of acidified  $\text{NH}_4\text{Cl}$  solution was transferred to a specially constructed cell and titrated with NaOH. The pH of the solution was measured at intervals from the initial pH of about 2.4 to a final pH of about 8.0. In the terminology of Bacarella, *et al*, this corresponded to  $\epsilon_i = 1.05$  and  $\epsilon_f = 0.95$  for  $\text{NH}_4\text{Cl} = 0.04$  M, and to  $\epsilon_i = 1.01$  and  $\epsilon_f = 0.97$  for  $\text{NH}_4\text{Cl} = 0.50$  M, with intermediate values

of  $\epsilon_i$  and  $\epsilon_f$  for intermediate  $\text{NH}_4\text{Cl}$  values.  $\epsilon$  characterizes the composition of the solution and is given by

$$\epsilon = \frac{\text{gfw NH}_4\text{Cl} + \text{gfw HCl} - \text{gfw NaOH}}{\text{gfw NH}_4\text{Cl}} \quad (20)$$

where gfw stands for gram formula weight. The concentration of NaOH for each determination was such that the amount added changed the initial volume of acidified solution by no more than 4 percent.

Solution cells were designed to prevent loss of  $\text{NH}_3$  through evaporation. A silastic cap molded to fit the glass body of each cell rendered the cell airtight when the entire assembly illustrated in Figure 6 was in place. Two ports in the cap allowed insertion of the electrode and the burette. The solution was stirred by a teflon covered magnet placed in the cell and a magnetic stirrer located underneath the bath.

The surrounding water bath was regulated by a Sargent Thermomonitor and maintained the temperature to within  $0.005^\circ\text{C}$  of  $25.000^\circ\text{C}$  for all measurements. The temperature was set with a Beckman thermometer which had been calibrated with a platinum resistance thermometer traceable to the National Bureau of Standards.

Much of the accuracy of the measurements can be attributed to the ability to deliver in increments small known volumes of base. Gilmore ultraprecision micrometer burettes, with a total capacity of either 0.25 ml or 2.5 ml, depending on the requirements of the particular measurement, were used to deliver NaOH in increments as small as

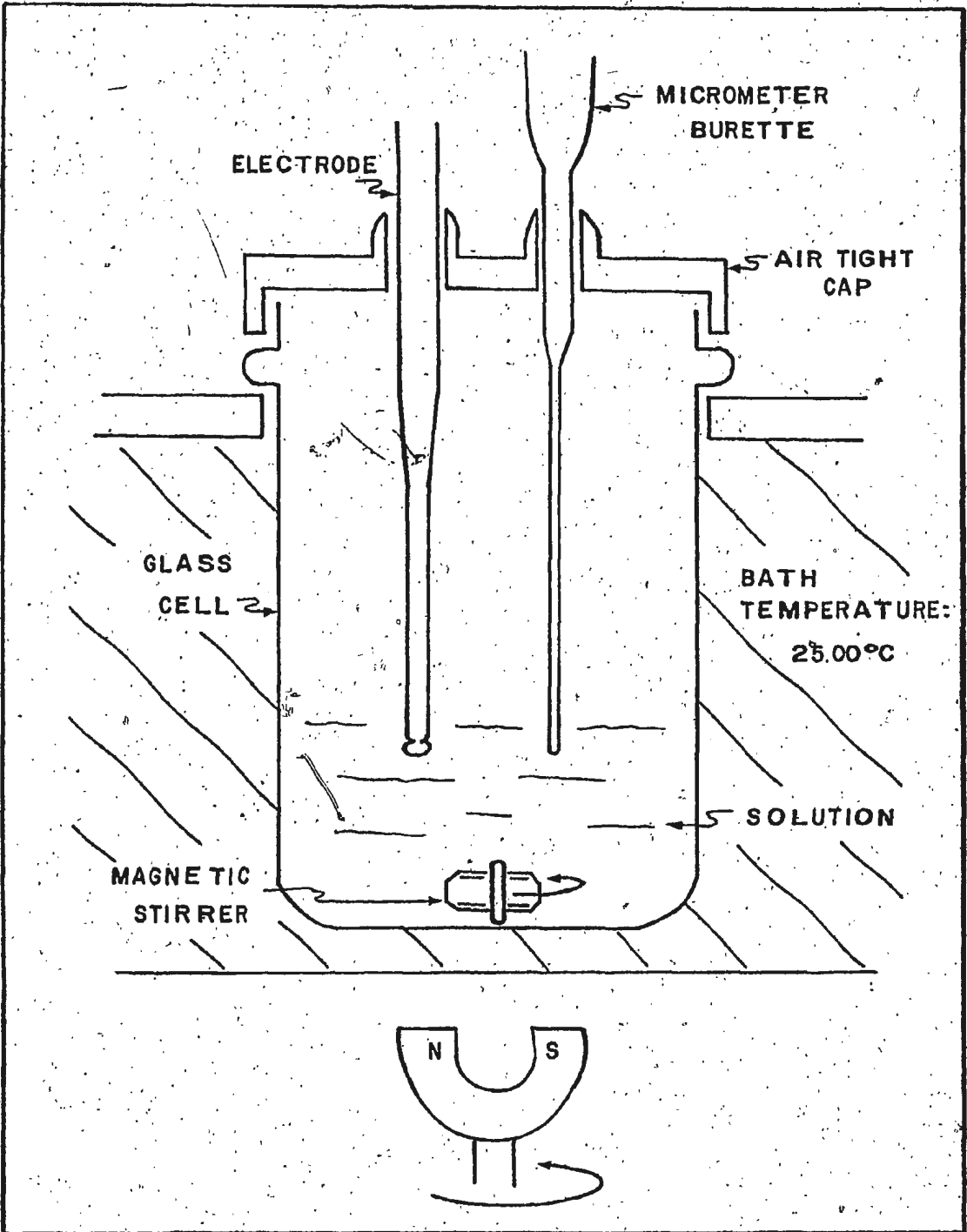


Figure 6: Solution Cell Assembly

0.00100  $\pm$  0.00002 ml. The tip of the burette was placed just beneath the surface of the solution. Diffusion from the burette could be shown to be negligible during the time of an experiment by a constant value of the measured pH of a weakly buffered solution when the burette contained 0.1 M HCl.

A Beckman 39030 Combination Electrode was used with a Beckman Research pH Meter to determine the pH during titration. pH values could be read to within 0.0005 of a pH unit.

#### N. m. r. spectra

Proton n. m. r. spectra were recorded on a Varian HA-100 Spectrometer in the frequency sweep mode at 100 MHz.

Care was taken before recording any spectrum to obtain a stable magnetic field with as high a homogeneity as possible, since the field homogeneity is an appreciable factor in determining the width of the NH resonance.

Since all reaction mixtures were aqueous solutions, it was convenient to lock on the high frequency modulation sideband of the water resonance. Thus the frequency scale for all spectra presented is calibrated with respect to the resonance position of H<sub>2</sub>O protons.

An estimate of the <sup>15</sup>NH proton linewidth in the absence of exchange for each spectrum was obtained from the decay of wiggles after fast passage through the water line, field homogeneity controls remaining unchanged from their settings during recording of the <sup>15</sup>NH spectrum.

Spectra used in linewidth determination were obtained in digital form by feeding the DC output normally applied to the graphic recorder

into an Anadex Model DF-100 DC voltage to frequency converter, and subsequently into a Hewlett Packard 5325A Universal Counter for measurement. The signal from the spectrometer was biased at the input to the voltage to frequency converter to insure that the signal plus noise was always positive. By positioning of the recorder arm, a record of spectrum amplitude could be obtained as a function of sweep frequency. A gate time of 10 seconds was allowed for each count.

#### Adiabatic half passage

Adiabatic half passage necessary for water linewidth measurements at the higher temperatures used ( $T > 50^{\circ}\text{C}$ ) was accomplished with a home-made sweep generator connected to the magnet sweep coils. The generator, with a circuit similar to that described by Meiboom,<sup>34</sup> consisted of three 1.5 V transistor radio batteries connected through a variable 50 ohm resistor to an on-off switch. In making a typical measurement, the water resonance would first be centered on the scope with the phase sensitive detector adjusted to the dispersion mode. With an rf attenuation of 80 db, the sweep generator would be switched on. A current of 10 ma to 20 ma was necessary to sit just off resonance. After having been held on for several values of  $T_1$ , the switch would be released to produce an exponential sweep back to the center of resonance with time constant characterized by the resistance and the capacitance (500, 700, 900, or 1100 mfd as desired) of the circuit. The resulting signal was recorded on a Texas Instruments oscillo/riter strip chart recorder.



### $T_1$ measurement

The longitudinal relaxation time  $T_1$  of  $H_2O$  protons was measured at the higher temperatures studied ( $T > 50^\circ C$ ) by making a series of measurements consisting of two consecutive adiabatic fast passages through the water resonance using 90 db rf power and a triangle sweep generated by a Tektronix Type 162 Waveform Generator. The time between the sweeps was varied by variation of the position of the triangular sweep with respect to the resonance position of the water line. In this way, the second of the two passages sampled the magnetization throughout its recovery from the reversal caused by the initial passage. Signals were recorded on a Texas Instruments oscillo/riter strip chart recorder.

### Temperature control

The temperature of the n. m. r. samples was controlled by passing a stream of air around the sample tube. The air was heated before the entrance to the probe by a heater whose voltage was controlled by a Honeywell Continuous Balance Unit. The temperature of the air was controlled with a copper-constantan thermocouple located in the air stream with an ice-water bath as reference. The thermocouple emf was measured with a Leeds & Northrup 7555 Type K5 Potentiometer in conjunction with a Leeds & Northrup 9834-1 Electronic DC Null Detector. The null detector in turn was used to drive the servo mechanism of the continuous balance unit. Thus the temperature of the air stream was continuously regulated to produce that emf in the thermocouple which was indicated by the potentiometer setting.

Another thermocouple with the sensing junction inserted into an n. m. r. tube was placed in the probe to measure the sample temperature. Any small difference between this temperature and that of the air stream at the base of the probe was corrected for by adjusting the emf setting of the potentiometer. The overall control and accuracy of the sample was better than  $0.1^{\circ}\text{C}$ .

Measurements made at temperatures near that of the probe (about  $28^{\circ}\text{C}$ ) or somewhat higher required no preconditioning of the air entering the probe. For measurements made above  $50^{\circ}\text{C}$ , the air was preheated.

#### Calibration of $H_1$

The radio frequency field  $H_1$  was calibrated using the adiabatic half passage technique. The decay constant  $1/T(H_1)$  was measured at probe temperature (about  $28^{\circ}\text{C}$ ) for the  $\text{H}_2\text{O}$  resonance of an aqueous acidic  $(\text{HOCH}_2\text{CH}_2)_3\text{NHCl}$  solution having a pH of approximately 2. The chemical shift  $\delta$  between the NH resonance of  $(\text{HOCH}_2\text{CH}_2)_3\text{NH}^+$  and water under the conditions used is known to be  $3512 \text{ rad sec}^{-1}$ .

The value of  $1/T(H_1)$  of the water line of an HCl solution of the same pH measured at the same temperature by the adiabatic half passage technique was used to approximate the value the decay constant  $1/T(H_1)$  of the water line of the  $(\text{HOCH}_2\text{CH}_2)_3\text{NH}^+$  solution would assume in the absence of exchange. That is,  $1/T(H_1)$  of the HCl solution is taken to be  $1/T$  of equation (17) for the salt solution. Its value was found to be constant regardless of rf field attenuation.

$H_1$  was found to be within  $500 \text{ rad sec}^{-1}$  of  $3500 \text{ rad sec}^{-1}$  at 100 db of rf power, when determined periodically throughout the experimental work.

It should be pointed out that the value of  $H_1$  is needed to compute from equation (19) the values of  $\tau$  for the exchange between  $\text{NH}_4^+$  and  $\text{H}_2\text{O}$ . The value of the term  $\gamma^2 H_1^2$  is significantly less than  $\delta_{\text{NH}}^2$ , so that even a 10 percent error in  $H_1$  does not appreciably alter computed values of  $\tau$ .

## IV. RESULTS

The  $pK_A$  of  $^{15}\text{NH}_4\text{Cl}$

The  $pK_A$  of  $^{14}\text{NH}_4\text{Cl}$  has been measured by several workers over a temperature range  $0^\circ\text{C}$  to  $50^\circ\text{C}$ .<sup>39, 40, 13</sup> Emerson, Grunwald and Kromhout,<sup>13</sup> using the differential potentiometric method of Bacarella et al.,<sup>37</sup> investigated the salt concentration dependency of the  $pK_A$  of  $^{14}\text{NH}_4\text{Cl}$  at  $25^\circ\text{C}$  over the  $\text{NH}_3\text{Cl}$  concentration range 0.25 M to 2.99M, in which falls the  $\text{NH}_4\text{Cl}$  concentration range of interest in this work. Their findings, presented graphically as a function of  $\text{NH}_4\text{Cl}$  concentration only in Figure 7, are given by the equation<sup>13</sup>

$$\log K_A = -9.246 - 0.132 [\text{NH}_4\text{Cl}] - 0.198 [\text{KCl}] \quad (21)$$

Measurement of the  $pK_A$  of  $^{14}\text{NH}_4\text{Cl}$  in a somewhat lower salt concentration range was conducted in the course of this work to determine whether such values could also be represented by equation (21). Table III contains these values. As can be seen in Figure 7 (p. 34), wherein these data also are presented, these  $pK_A$  values begin to fall off from the line given by equation (21) at  $^{14}\text{NH}_4\text{Cl}$  concentrations less than about 0.25 M.

It is of interest that Bates and Pinching<sup>40</sup> report a salt coefficient of  $-0.28$  at  $25^\circ\text{C}$ , with  $pK_A$  measurements made over the  $\text{NH}_4\text{Cl}$  concentration range 0.008 m to 0.107 m. The slope of the curve described by the  $pK_A$  values obtained in this work has a value of  $-0.28$  at an  $\text{NH}_4\text{Cl}$  concentration of about 0.13 M. A similar plot for  $\text{CH}_3\text{NH}_3\text{Cl}$  has also been found to be non-linear, with a large initial slope.<sup>18</sup>

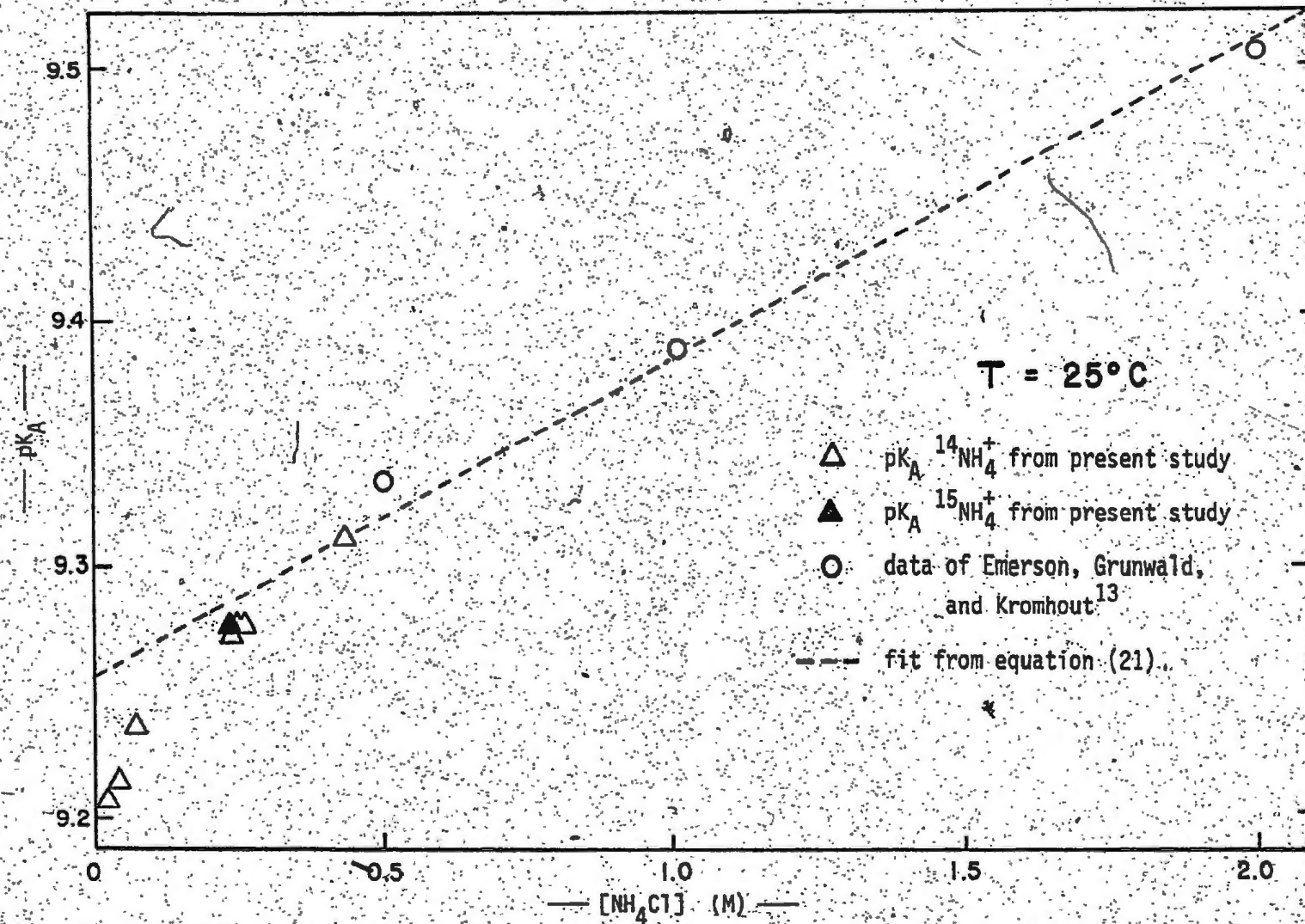


Figure 7: The  $pK_A$  of  $^{14}, ^{15}\text{NH}_4^+(\text{aq})$  as a Function of Salt Concentration

Table III: The  $pK_A$  of  $^{14}\text{NH}_4\text{Cl}$  and  $^{15}\text{NH}_4\text{Cl}$  at  $25.00^\circ\text{C}$ 

$[\text{NH}_4\text{Cl}]$ (M)	$pK_A$	isotope	$[\text{NH}_4\text{Cl}]$ (M)	$pK_A$	isotope
0.03974	9.207	$^{14}\text{N}$	0.2475	9.278	$^{15}\text{N}$
0.04393	9.215	$^{14}\text{N}$	0.2482	9.277	$^{14}\text{N}$
0.07833	9.234	$^{14}\text{N}$	0.2518	9.273	$^{14}\text{N}$
0.2468	9.272	$^{14}\text{N}$	0.4420	9.309	$^{14}\text{N}$

It was desired to obtain the ratio of the acid dissociation constants of the isotopic salts  $^{15}\text{NH}_4\text{Cl}$  and  $^{14}\text{NH}_4\text{Cl}$ :  $^{15}K_A/^{14}K_A$ .  $pK_A$  values measured at  $25^\circ\text{C}$  for the isotopic salts were, within experimental error, indistinguishable at an  $\text{NH}_4\text{Cl}$  concentration of 0.25 M. Reproducibility of the results is demonstrated by the three determinations at the  $^{14}\text{NH}_4\text{Cl}$  concentration 0.25 M.

Had the desired ratio differed greatly from 1.0, measurements at other temperatures would have been considered necessary. Since it did not, the ratio is assumed to differ only insignificantly from 1.0 over both the concentration range of  $\text{NH}_4\text{Cl}$  spanned in this work and the temperature range investigated.

Infinite dilution values of  $pK_A$  reported by Bates and Pinching<sup>40</sup> for  $^{14}\text{NH}_4\text{Cl}$  are best fit by the empirical equation

$$\log K_A^0 = \frac{-2835.76}{T} + 0.6322 - 0.001225 T, \quad (22)$$

over the temperature range 0°C to 50°C. Upon conversion of their measurements from molal to corresponding molar quantities, equation (22) becomes

$$\log K_A^0 = \frac{-2820.34}{T} + 0.5676 - 0.001172 T \quad (23)$$

Since the acid dissociation equilibrium of  $^{14}\text{NH}_4\text{Cl}$  has been established as an adequate model for that of  $^{15}\text{NH}_4\text{Cl}$  at 25°C, equation (23) is adopted as a description of the temperature dependency of the acid dissociation equilibrium constant of  $^{15}\text{NH}_4\text{Cl}$  for use in this work.

#### Spectral features

The exchange reactions of interest were studied over a hydrogen ion concentration range of from 0.01 M to 0.23 M, and at  $\text{NH}_4\text{Cl}$  concentrations of 0.4 M, 0.6 M, and 0.8 M.

Spectra, in general, consisted of the NH doublet resonance, for which the coupling constant is 74.2 Hz, approximately 240 Hz downfield from the singlet water resonance of much greater intensity, as can be seen in Figure 4 (p. 21). The frequency difference  $\delta_{\text{NH}}$  between the NH resonance and the water resonance was influenced by the several variables of the experiment, most markedly by the hydrogen ion concentration. In the spectra of strongly acidic  $\text{NH}_4\text{Cl}$  solutions used to look at line broadening in the absence of exchange (see Chapter V, pp. 74 - 78), the NH resonances observed lie upfield from the water resonance.

Reactant concentrations and sample temperatures were such that measureable variations were introduced into the n. m. r. spectral features



reflecting proton exchange. Figure 8 shows the variation in the NH resonance with temperature.

Exchange rate measurements were made over the temperature range 30°C to 80°C. Below 30°C, the lines of the NH doublet for the reaction mixtures studied are distinct and narrow. The natural linewidth plus broadening due to field inhomogeneity is of comparable magnitude to the exchange broadening, rendering accurate measurement of exchange broadening difficult. Above 30°C, as exchange becomes faster,  $(1/\tau)_{\text{NH}}$  becomes appreciably greater than  $(1/T_2')_{\text{NH}}$ . The error introduced by the assumption that  $(1/T_2')_{\text{NH}}$  is equal to  $(1/T_2'')_{\text{OH}}$  becomes insignificant compared to  $\pi\Delta_{\text{NH}}$ , so that  $(1/\tau)_{\text{NH}}$  may be extracted from the linewidth by using a value for  $(1/T_2')_{\text{NH}}$  obtained from  $(1/T_2'')_{\text{OH}}$  of the water wiggles.

Such a procedure was used in the range 30°C to 50°C where, thanks to the large  $^{15}\text{N}$ -H coupling constant, the conditions of lifetime broadening are met by the members of the NH doublet resonance for most reaction mixtures studied. Overlap becomes significant at  $\tau_{\text{NH}} < 0.04$  sec, a condition applicable to reaction mixtures at 50°C and to mixtures of low hydrogen ion concentration at 40°C. Merging of the lines increases the apparent width at half height and makes baseline determination difficult. The artificial increase in  $(1/\tau)_{\text{NH}}$  as a result of overlap was compensated for by subtraction from the measured linewidth a correction term  $(1/T)_{\text{corr}}$ , with

$$\pi\Delta_{\text{NH}} = \left(\frac{1}{T_2'}\right)_{\text{NH}} + \left(\frac{1}{\tau}\right)_{\text{NH}} + \left(\frac{1}{T}\right)_{\text{corr}} \quad (24)$$

$(1/T)_{\text{corr}}$  was found by applying linewidth computation procedures to



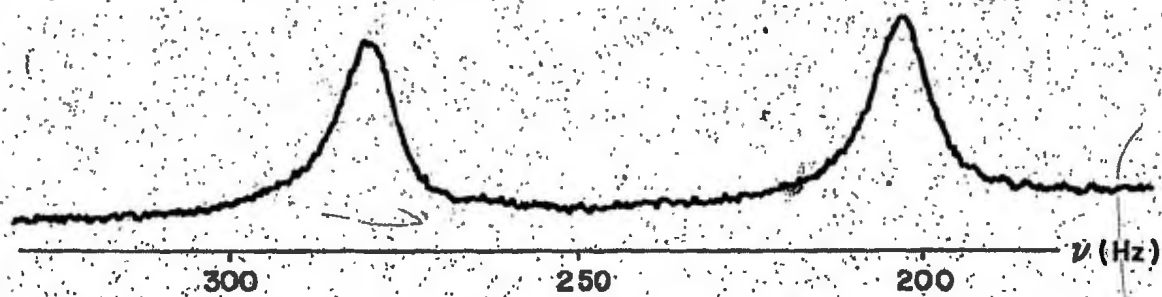
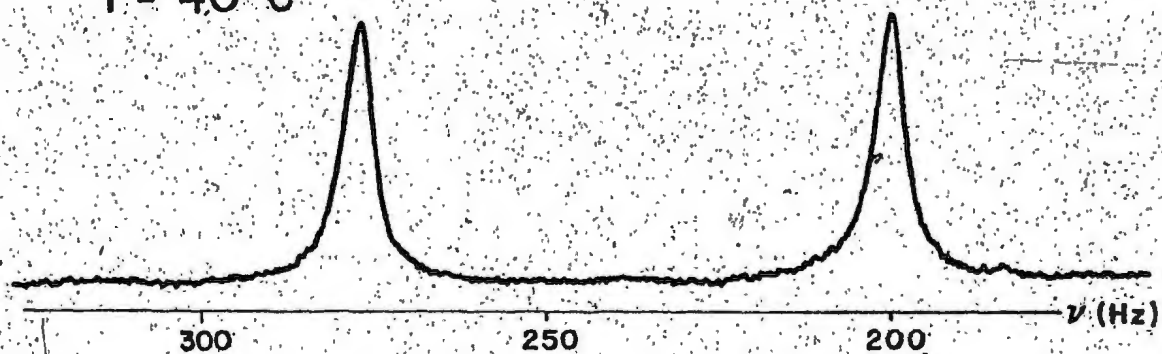
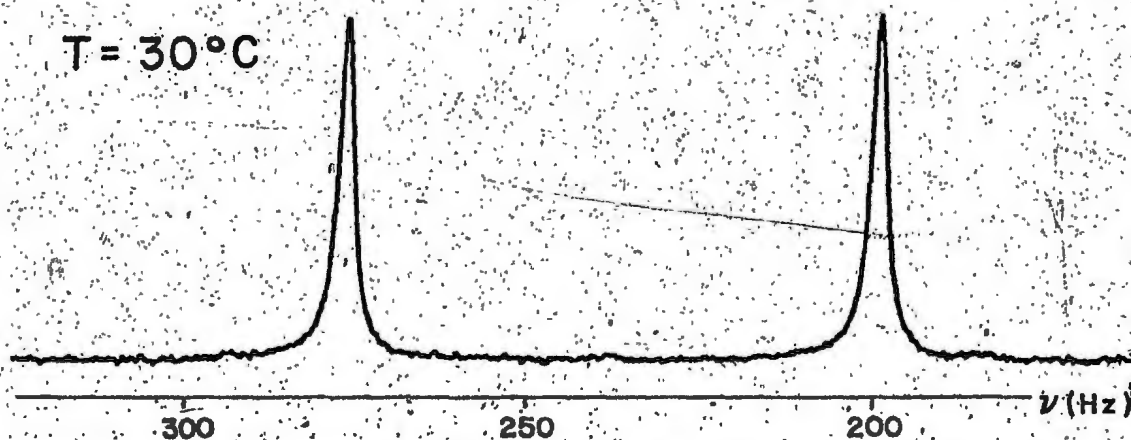
$T = 50^{\circ}\text{C}$  $T = 40^{\circ}\text{C}$  $T = 30^{\circ}\text{C}$ 

Figure 8: Spectra of  $^{15}\text{NH}$  Doublet: Change in Lineshape with Temperature

Spectra are of a reaction mixture for which  $[\text{NH}_4^+] = 0.050 \text{ M}$ ,  $[\text{H}^+] = 0.6 \text{ M}$ .

theoretical spectra computed from an expression given by Takeda and Stejskal,<sup>30</sup> such as presented in Figure 1 (p. 12), with J equal to 74.2 Hz, and the variables  $(1/T_2)_{\text{NH}}$  and  $(1/\tau)_{\text{NH}}$  assigned appropriate values. The difference in the linewidth computed and the sum  $(1/T_2)_{\text{NH}} + (1/\tau)_{\text{NH}}$  gives  $(1/T)_{\text{corr}}$ . Its value ranged from less than  $0.1 \text{ sec}^{-1}$  at  $\tau_{\text{NH}} = 0.04 \text{ sec}$  to  $1.6 \text{ sec}^{-1}$  at  $\tau_{\text{NH}} = 0.0125 \text{ sec}$ .

At faster exchange rates, it also became evident that the observable  $(1/T_2)_{\text{OH}}$  from water wiggles was no longer primarily a measure of the transverse relaxation and inhomogeneity broadening, but included a significant contribution from exchange broadening. The extent of this broadening was estimated by extrapolation of the  $(1/\tau)_{\text{OH}} = [1/T(H_1) - 1/T']$  values from water line broadening measurements made at higher temperatures, thus allowing the linewidth in the absence of exchange alone to be extracted from  $(1/T_2)_{\text{OH}}$  values obtained from the water wiggles. The correction was made at  $40^\circ\text{C}$  and at  $50^\circ\text{C}$ . Table IV gives extrapolated values of  $(1/\tau)_{\text{OH}}$ .

Table IV: Extrapolated Values of Water Line Exchange Broadening

T	$(1/\tau)_{\text{OH}}$ in $\text{sec}^{-1}$ for $[\text{NH}_4^+]$ equal to		
	0.4 M	0.6 M	0.8 M
$30^\circ\text{C}$	$0.089 + \frac{0.0001}{[\text{H}^+]}$	$0.14 + \frac{0.0003}{[\text{H}^+]}$	$0.17 + \frac{0.0006}{[\text{H}^+]}$
$40^\circ\text{C}$	$0.20 + \frac{0.0003}{[\text{H}^+]}$	$0.30 + \frac{0.0006}{[\text{H}^+]}$	$0.37 + \frac{0.0011}{[\text{H}^+]}$
$50^\circ\text{C}$	$0.41 + \frac{0.0005}{[\text{H}^+]}$	$0.63 + \frac{0.0012}{[\text{H}^+]}$	$0.76 + \frac{0.0020}{[\text{H}^+]}$

The NH resonance occurs on the wing of the water line. This produces a baseline for the NH resonance of non-zero, non-linear intensity, becoming more pronounced with faster exchange. To account for this, the wing of the water line was assumed to be able to be described by a parabolic curve. Baseline intensity on or near the NH resonance was then found by parabolic interpolation of intensities measured where the NH resonance was negligible.

To summarize, correction was made to digitized spectral data to account for (1) overlap of the peaks of the NH doublet, (2) a contribution from OH - NH proton exchange to the magnitude of the decay constant of the water wiggles, and (3) non-zero baseline intensity due to the water line. Factors (1) and (3) tend to increase apparent halfwidths of NH resonances. Factor (2) if left unaccounted for would cause  $(1/\tau)_{\text{NH}}$  values to appear to be too small. All three factors are more important at 50°C than at the lower temperatures.

Above 50°C, merging of the lines of the NH doublet made it necessary to abandon direct measurement of the NH linewidth. Since above 50°C exchange broadening of the water line becomes significantly greater than  $(1/T_2)_{\text{OH}}$ , the adiabatic half passage technique became useful.

#### NH line broadening measurements

The exchange broadening of NH proton lines was used to determine the mean lifetime  $\tau_{\text{NH}}$  of a proton in the  $\text{NH}_4^+$  environment.  $\tau_{\text{NH}}$  is related to the specific rate of exchange  $R_{\text{NH}}$  of any NH proton by the expression

$$4 \times \left(\frac{1}{\tau}\right)_{\text{NH}} = \frac{R_{\text{NH}}}{[\text{NH}_4^+]} \quad (25)$$

The specific rate is four times greater than  $(1/\tau)_{\text{NH}}$  since there are four hydrogen atoms bonded to each nitrogen atom in the  $\text{NH}_4^+$  species.

In terms of the variables describing the rates of the reactions responsible for proton exchange,

$$\left(\frac{1}{\tau}\right)_{\text{NH}} = \frac{k_4}{4} + \left(\frac{k_6}{8} + \frac{k_7}{4}\right) [\text{NH}_3] + \frac{k_5}{4} [\text{OH}^-] \quad (26)$$

where  $[\text{NH}_3]$  may be replaced by  $K_A[\text{NH}_4^+]/[\text{H}^+]$ . For any reaction mixture examined, the  $\text{NH}_4^+$  concentration may be considered to be the formal concentration of  $\text{NH}_4\text{Cl}$ ; the hydrogen ion concentration is equal to the formal concentration of  $\text{HCl}$ . The rate constant  $k_6$  has been multiplied by a factor of  $\frac{1}{2}$  because, for reaction (6), transfer of protons between the environments of  $^{15}\text{N}$  nuclei of different spin states only results in line broadening. Therefore, for  $^{15}\text{N}$  with spin  $\frac{1}{2}$ , only half of the transfers described by reaction (6) are evidenced by  $(1/\tau)_{\text{NH}}$ .

Values of  $(1/\tau)_{\text{NH}}$  computed from linewidth measurements are recorded in Table V.  $(1/\tau)_{\text{NH}}$  is shown plotted as a function of reciprocal hydrogen ion concentration in Figures 9, 10, and 11 for  $\text{NH}_4^+$  concentrations of 0.4 M, 0.6 M, and 0.8 M, at each of the temperatures  $30^\circ\text{C}$ ,  $40^\circ\text{C}$ , and  $50^\circ\text{C}$ . The contribution of reaction (5) to the linewidth is neglected, as is to be discussed in this chapter (pp. 53 - 54). As required by equation (26) when rewritten as follows:

$$\left(\frac{1}{\tau}\right)_{\text{NH}} = \frac{k_4}{4} + \left(\frac{k_6}{8} + \frac{k_7}{4}\right) \frac{K_A[\text{NH}_4^+]}{[\text{H}^+]} \quad (27)$$

the plots  $(1/\tau)_{\text{NH}}$  versus  $1/[\text{H}^+]$  are linear. They enable the determination

Table V:  $(1/\tau)_{\text{NH}}$  from NH Line Broadening Measurements

Values of  $(1/\tau)_{\text{NH}}$  are given in  $\text{sec}^{-1}$ . The number of significant figures is greater than the accuracy of the measurements and are given to avoid truncating errors in calculating rate constants.

$[\text{H}^+]$	$(1/\tau)_{\text{NH}}$ for $[\text{NH}_4^+]$ equal to		
	0.399 M	0.598 M	0.799 M
at 30°C:			
0.010	—	13.65	16.07
0.014	10.96	—	—
0.019	9.68	10.51	10.69
0.036	9.08	8.92	9.34
0.067	7.78	7.70	8.04
0.125	7.70	7.75	7.58
0.230	7.89	7.09	7.40
at 40°C:			
0.010	—	32.99	34.86
0.014	23.71	27.00	29.4
0.019	21.81	23.65	23.66
0.025	19.41	20.34	21.9
0.036	17.68	19.45	18.50
0.050	18.54, 19.05	18.68	—
0.067	16.43	17.13	14.83
0.092	17.51	15.49	—
0.125	—	15.91	13.33
0.168	14.14	14.58	—
0.230	14.47	13.69	13.55
at 50°C:			
0.010	—	68.25	77.13
0.014	52.82	58.82	64.39
0.019	42.45	41.85	47.33
0.025	41.08	38.20	41.84
0.036	34.69	37.80	37.69
0.050	—	—	38.36
0.067	36.13	34.02	32.33
0.092	—	—	29.37
0.125	32.00	33.92	—
0.168	—	—	28.73
0.230	30.51	29.48	27.45

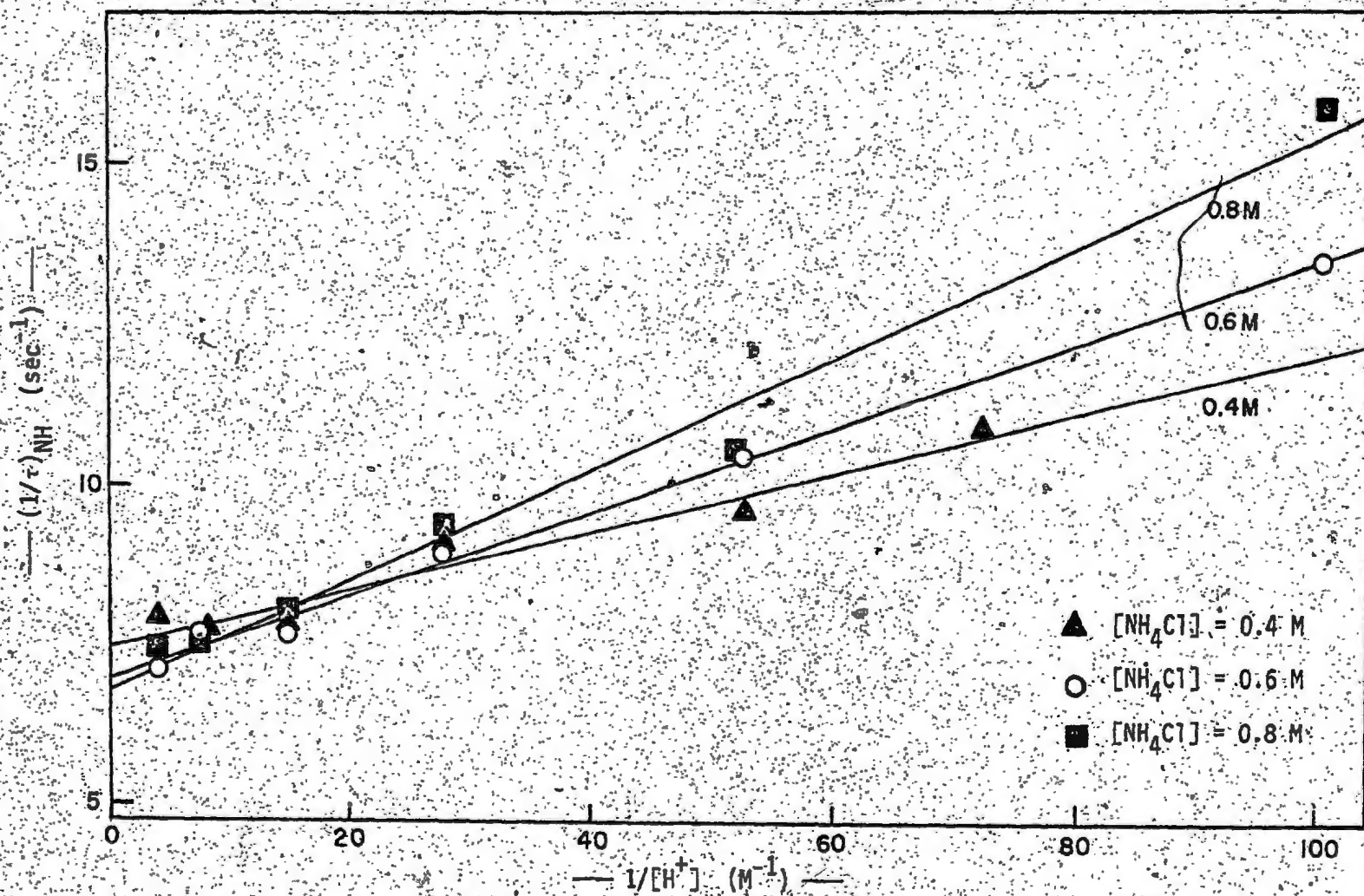


Figure 9:  $(1/\tau)_{\text{NH}}$  v.  $1/[\text{H}^+]$ , from NH Linewidth Measurements at  $30^\circ\text{C}$ .



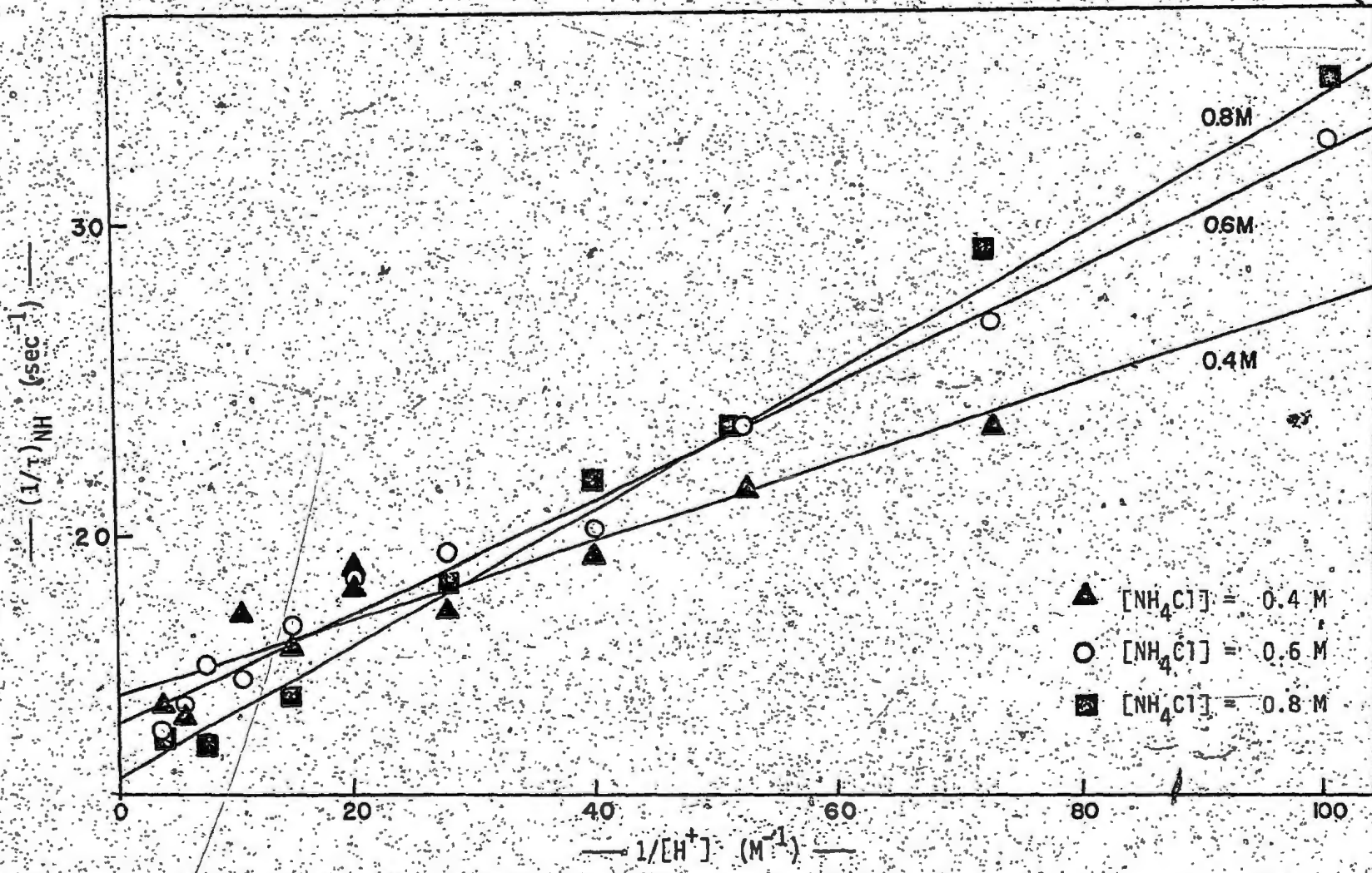


Figure 10:  $(1/\tau)_{\text{NH}}$  v.  $1/[\text{H}^+]$ , from  $\text{NH}$  Linewidth Measurements at  $40^\circ\text{C}$

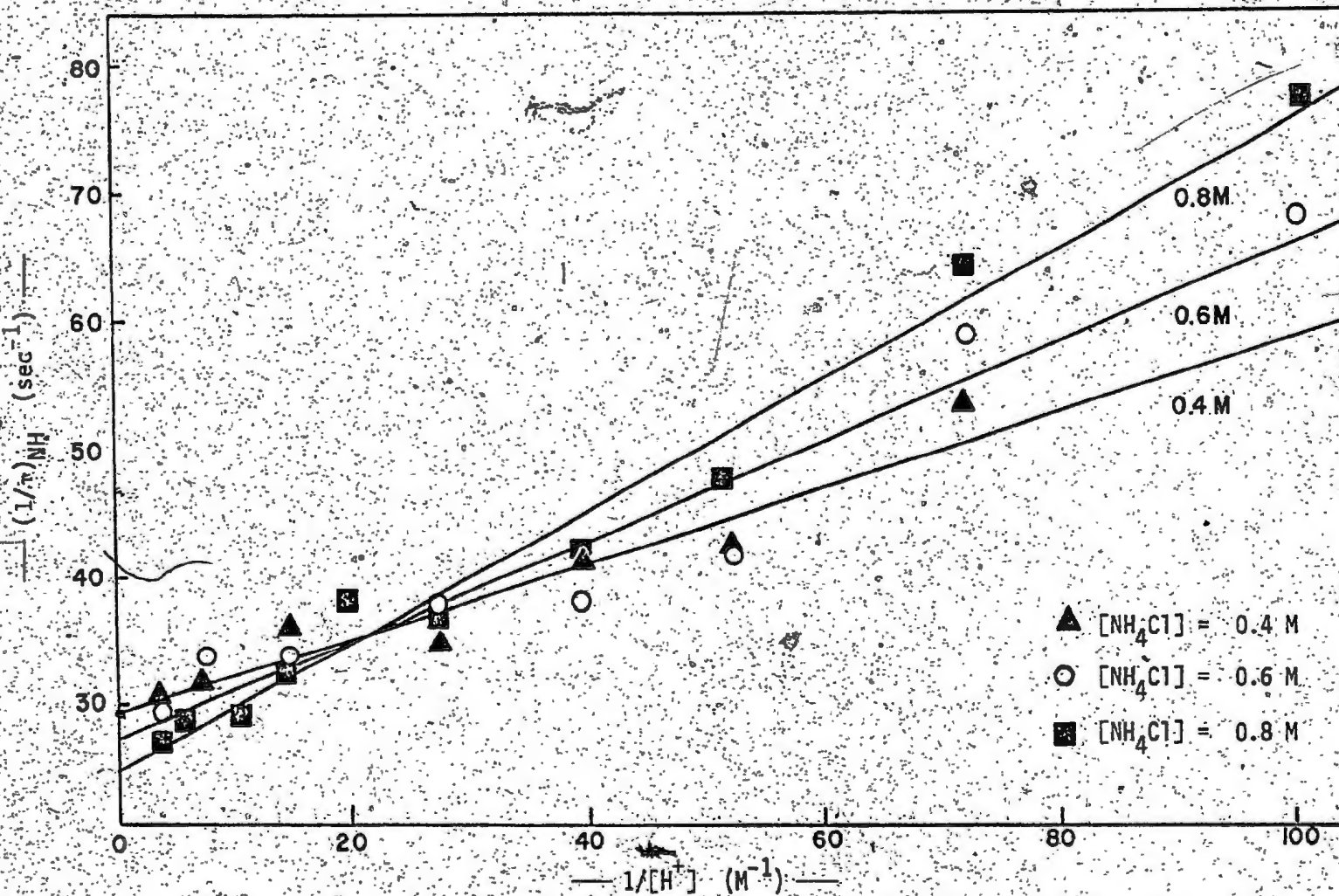


Figure 11:  $(1/\tau)_{NH}$  v.  $1/[H^+]$ , from NH Linewidth Measurements at 50°C



of  $k_4$  and the quantity  $k_2 K_A \equiv (k_6/8 + k_7/4) K_A$  for each  $\text{NH}_4^+$  concentration and temperature investigated.

Recorded in Table VI are the values of  $k_4$  and  $k_2 K_A$  determined from linear fits to these data.

Table VI: Rate Constants from NH Line Exchange Broadening Measurements

Values of  $k_4$  and  $k_2 K_A$  are given in  $\text{sec}^{-1}$ .

[ $\text{NH}_4\text{Cl}$ ]	at 30°C:		at 40°C:		at 50°C:	
	$k_4$	$k_2 K_A$	$k_4$	$k_2 K_A$	$k_4$	$k_2 K_A$
0.4 M	29.7 ± 0.8	0.118 ± 0.013	58.7 ± 2.3	0.324 ± 0.042	117 ± 6	0.739 ± 0.090
0.6 M	27.8 ± 0.5	0.112 ± 0.004	55.2 ± 1.2	0.314 ± 0.012	109 ± 8	0.650 ± 0.069
0.8 M	27.1 ± 0.9	0.112 ± 0.006	47.9 ± 1.4	0.289 ± 0.009	98.4 ± 4.8	0.641 ± 0.032

#### Water line broadening measurements

The quantity  $(1/T_1)_{\text{OH}}$  was measured at several temperatures for one reaction mixture, which was 0.6 M in  $^{15}\text{NH}_4\text{Cl}$  and 0.050 M in HCl. The values obtained are given in Table VII.

Table VII:  $1/\tau_1$  of Water

Values of  $(1/\tau_1)_{OH}$  are given in  $\text{sec}^{-1}$ .

T	$(1/\tau_1)_{OH}$ , experimental	T	$(1/\tau_1)_{OH}$ , interpolated
44.1°C	0.15 <sub>0</sub>	50.0°C	0.14 <sub>0</sub>
54.7°C	0.12 <sub>9</sub>	65.0°C	0.11 <sub>3</sub>
69.0°C	0.11 <sub>6</sub>	80.0°C	0.093 <sub>5</sub>
85.8°C	0.083 <sub>6</sub>		

Interpolated values of  $(1/\tau_1)_{OH}$  for the reaction mixtures at the temperatures 50°C, 65°C, and 80°C, also given in Table VII (this page), were found by fitting the data to an equation of the form

$$\log \left( \frac{1}{\tau_1} \right) = A + \frac{B}{T} \quad (28)$$

to give

$$\log \left( \frac{1}{\tau_1} \right)_{OH} = (-2.91 \pm 0.30) + \frac{664 \pm 100}{T} \quad (29)$$

with an activation energy of about 3 kcal mole<sup>-1</sup>. These values of  $(1/\tau_1)_{OH}$  are somewhat smaller than those of Krynicky<sup>31</sup> for air-free water.

Since the viscosity of all reaction mixtures is essentially equal,  $(1/\tau_1)_{OH}$  was considered to vary insignificantly over the acid and salt

concentration ranges of these mixtures. For each temperature the values obtained for the one reaction mixture on which measurements were made was assumed to equal the value of  $(1/\tau_1)_{OH}$  for the other reaction mixtures.

These values of  $(1/\tau_1)_{OH}$  were then subtracted from  $1/T(H_1)$  values obtained from water line broadening measurements to allow computation of  $(1/\tau')_{NH}$  at 50°C, 65°C, and 80°C. The quantity  $(1/\tau')_{NH}$  is related to the specific rate of proton transfer between N and O environments only:

$$4 \times \left(\frac{1}{\tau'}\right)_{NH} = \frac{R_{NH-OH}}{[NH_4^+]} \quad (30)$$

In terms of the rate constants describing reactions (4) through (7),

$$\left(\frac{1}{\tau'}\right)_{NH} = \frac{k_4}{4} + \left(\frac{k_7}{4}\right) \frac{K_A [NH_4^+]}{[H^+]} \quad (31)$$

where the contribution of reaction (5) has been neglected.

Values of  $(1/\tau')_{NH}$  are recorded in Table VIII and shown plotted against reciprocal hydrogen ion concentration in Figures 12, 13, and 14 for  $NH_4^+$  concentrations of 0.4 M, 0.6 M, and 0.8 M at each of the temperatures 50°C, 65°C, and 80°C. As required by equation (31), the plots approximate a straight line. Table IX records values of  $k_4$  and  $(k_7/4)K_A$  determined from linear fits to the data.

Table VIII:  $(1/\tau')_{\text{NH}}$  from Water Line Broadening Measurements

Values of  $(1/\tau')_{\text{NH}}$  are given in  $\text{sec}^{-1}$ . The number of significant figures is greater than the accuracy of the measurements and are given to avoid truncating errors in calculating rate constants.

$[\text{H}^+]$	$(1/\tau')_{\text{NH}}$ for $[\text{NH}_4^+]$ equal to		
	0.399 M	0.598 M	0.799 M
at 50°C:			
0.010		42.6, 40.9	42.4
0.014		40.2, 42.3	39.1, 39.5
0.019		39.9, 41.2	37.7
0.025	—	39.1	38.3
0.050		39.0	36.6
0.092		38.1	35.8, 36.6
0.168		35.1, 38.5	34.6, 35.3
0.230		36.8	34.0
at 65°C:			
0.010	—	99.94	92.69, 93.70
0.014	106.2, 108.8	99.97, 100.4	93.67, 95.97
0.019	103.0	86.44	92.70, 83.84
0.025	97.00	91.31	90.86
0.036	102.5	93.67	83.01
0.050	99.94, 105.6	96.99	81.78
0.067	99.94, 101.4	—	—
0.092	100.9, 101.4	88.62	84.26
0.168	93.67, 105.6	86.87	78.58
0.230	97.48, 103.5	—	81.37
at 80°C:			
0.010	—	238.4	226.6
0.014	240.4	229.4	215.4
0.019	244.5	222.8	208.4
0.025	241.4	222.8	202.5
0.050	236.4	217.2	198.4
0.168	224.7	212.8	—
0.230	234.3	—	196.0

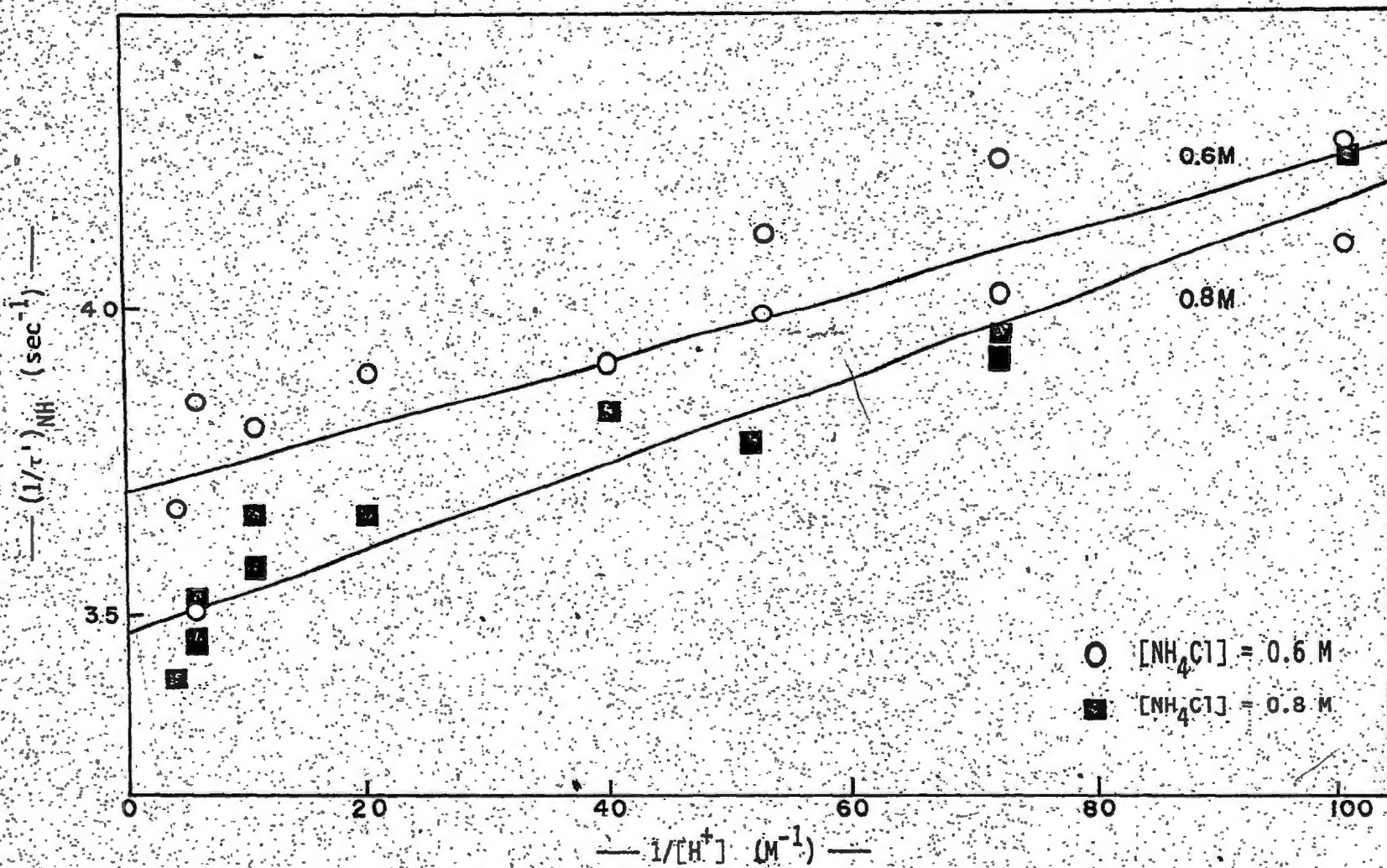


Figure 12:  $(1/\tau')_{\text{NH}}$  v.  $1/[\text{H}^+]$ , from Water Linewidth Measurements at 50°C



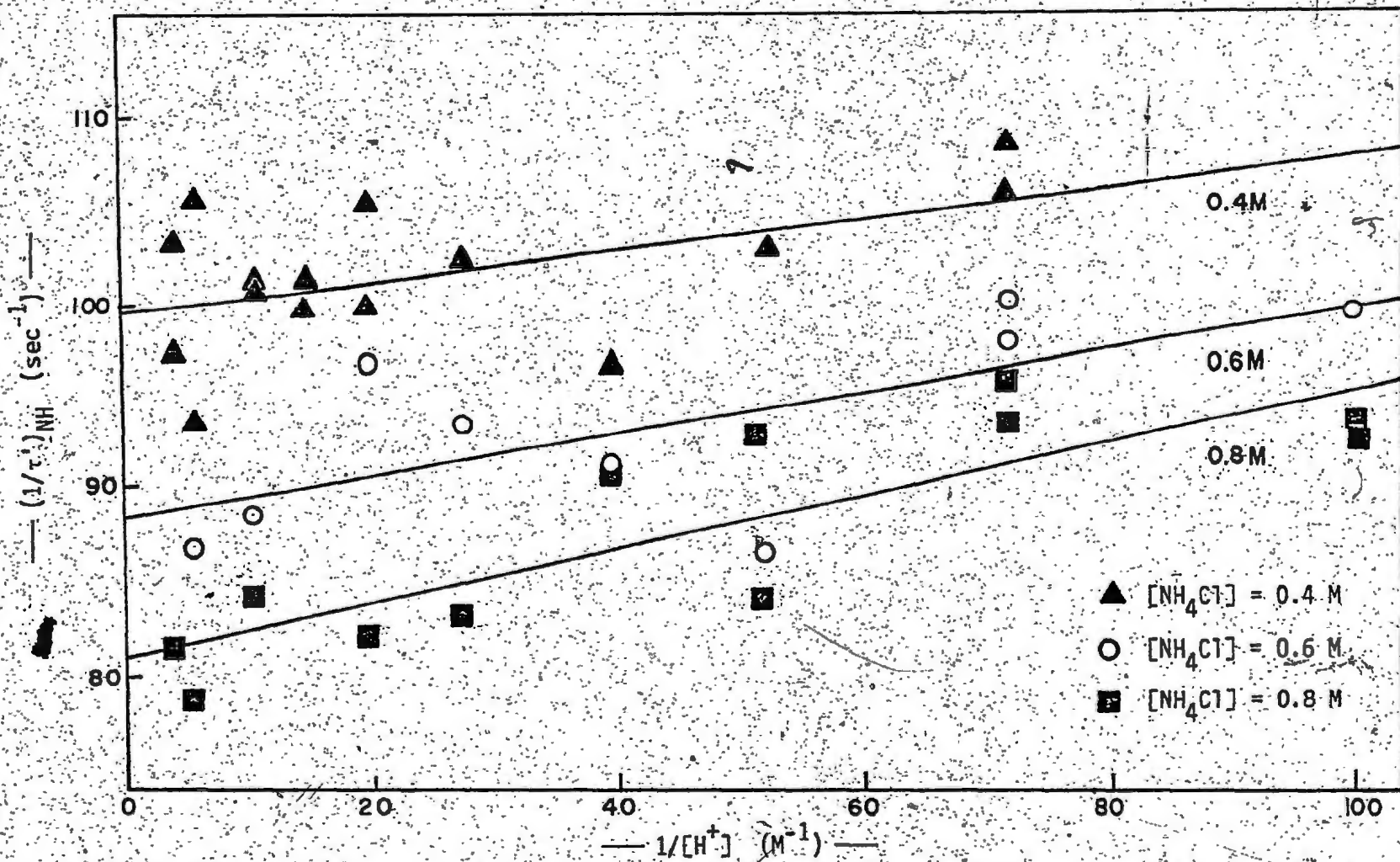


Figure 13:  $(1/\tau')_{\text{NH}}$  v.  $1/[\text{H}^+]$ , from Water Linewidth Measurements at  $65^\circ\text{C}$

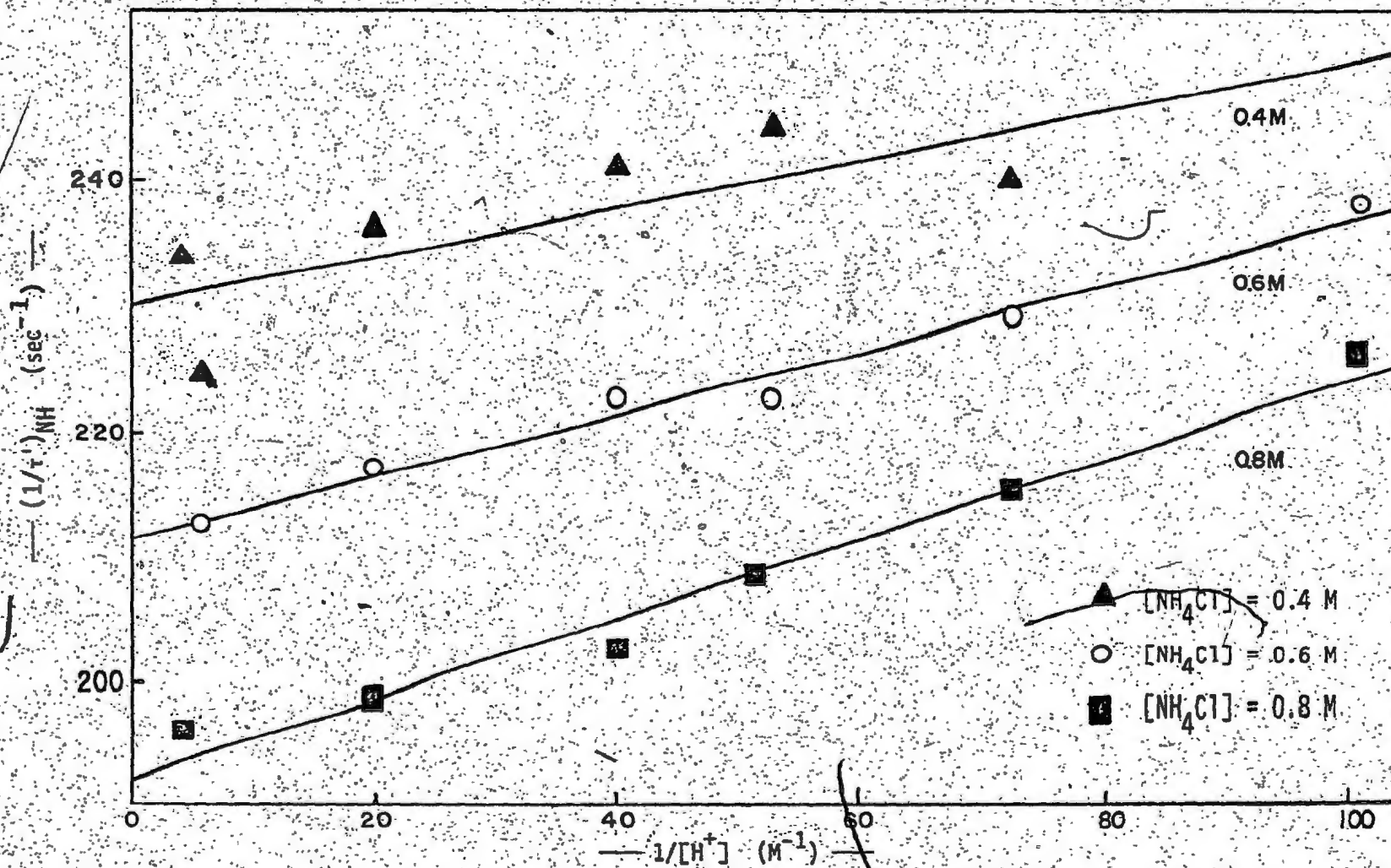


Figure 14:  $(1/\tau')_{\text{NH}}$  v.  $1/[\text{H}^+]$ , from Water Linewidth Measurements at 80°C

Table IX: Rate Constants from Water Line Exchange Broadening Measurements

Values of  $k_4$  and  $(k_7/4)K_A$  are given in  $\text{sec}^{-1}$ .

[NH <sub>4</sub> Cl]	at 50°C:		at 65°C:		at 80°C:	
	$k_4$	$(k_7/4)K_A$	$k_4$	$(k_7/4)K_A$	$k_4$	$(k_7/4)K_A$
0.4 M	—	—	398 ± 5	0.226 ± 0.099	922 ± 14	0.494 ± 0.021
0.6 M	148 ± 2	0.09 ± 0.015	354 ± 10	0.194 ± 0.079	845 ± 4	0.433 ± 0.030
0.8 M	139 ± 2	0.0877 ± 0.0090	323 ± 7	0.187 ± 0.037	769 ± 6	0.407 ± 0.033

The reaction with OH<sup>-</sup>

In extracting kinetic constants from NH and water linewidths, the contribution of reaction (5) was neglected. This reaction has a rate constant reported to be  $3.0 \times 10^{10} \text{ sec}^{-1} \text{ M}^{-1}$  at 20°C.<sup>16</sup> The concentration of hydroxyl ion in the reaction mixtures examined is, however, so small that the contribution of reaction (5) to the observed rate of exchange may be neglected. This is demonstrated by an estimation of the term  $(k_5/4) [\text{OH}^-]$  in equation (26).

The hydroxyl ion concentration may be obtained from the expression for the ion dissociation constant  $K_w$  of water in a salt solution:



$$K_w = \left( \frac{\gamma_{H^+} \gamma_{OH^-}}{a_{H_2O}} \right) m_{H^+} m_{OH^-} \quad (32)$$

where  $(\gamma_{H^+} \gamma_{OH^-} / a_{H_2O})$  is the activity coefficient function for water, and  $m_{H^+}$  and  $m_{OH^-}$  are the respective molalities of solvated protons and hydroxyl ions.  $K_w$  is well known over the temperature range investigated.<sup>41</sup> The hydrogen ion concentration of the reaction mixtures is predominately due to HCl. Since the ionic activity coefficient of  $H_2O$  is similar for most chloride solutions,<sup>41</sup> KCl may satisfactorily be adopted as a model for  $NH_4Cl$ , and values of the activity coefficient function in  $NH_4Cl$  solution may be obtained by interpolating activity coefficient function data for water in KCl solution.\*

If  $k_5$  is assigned an energy of activation of 4 kcal/mole<sup>-1</sup>, a reasonable upper limit value for diffusion controlled reactions,<sup>1</sup> the greatest contribution of reaction (5) to the observed linewidth of the NH resonance of the reaction mixtures studied is estimated to be 0.29 rad sec<sup>-1</sup>, or about 0.12 percent of the total exchange<sup>o</sup> broadening  $(1/\tau)_{NH}$  for the particular case. This computation applies to the mixture at 80°C for which the  $NH_4^+$  concentration is 0.6 M, and the HCl concentration is 0.01 M. For all other cases, the value of the term would be smaller.

#### Infinite dilution rate constants

Because exchange is monitored at dynamic equilibrium,

$$K_A = \frac{k_a}{k_{-a}} \quad (33)$$

\* Values of the activity coefficient function for KCl were obtained from H. S. Harned and W. J. Hamer in reference 41, p. 752.

where  $k_a$  is the rate constant for the acid dissociation process, and  $k_{-a}$  the rate constant for the recombination process. As is to be shown in Chapter V (p. 70), for the ammonium ion, the observed rate constant  $k_4$  is approximately equal to  $k_a$ , and  $k_{-4}$  can be identified with  $k_{-a}$ , so that

$$k_4 = \frac{K_A}{k_{-4}} \quad (34)$$

Experimentally, isothermal values of  $\log k_4$  have been found to be a linear function of salt concentration for the acid dissociation of  $\text{NH}_4^+$ ,  $\text{CH}_3\text{NH}_3^+$ , and  $(\text{CH}_3)_3\text{NH}^+$ .<sup>13, 18, 20</sup> Thus is the case with the present data (refer to Figure 15, p. 57). If the position of the transition state for the acid dissociation along the reaction coordinate is assumed to be close to that of the products,  $k_a$ , and thus  $k_4$ , may be shown to vary as does  $K_A$  with ionic strength.<sup>42</sup>

Medium effects on isothermal values of  $K_A$  can be approximated by the following equation:

$$\log \frac{K_A}{K_A^0} = B_A [\text{NH}_4\text{Cl}] + B'_A [\text{HCl}] \quad (35)$$

Isothermal values of  $k_4$  should then show the same linear dependence on ionic strength. That is,

$$\log \frac{k_4}{k_4^0} = b_4 [\text{NH}_4\text{Cl}] + b'_4 [\text{HCl}] \quad (36)$$

The salt coefficient  $b_4$  should have the same numerical value as  $B_A$ .

$b_4'$  should equal  $B_A$ . Accordingly, linear least square fits to plots of  $\log k_4$  versus  $[\text{NH}_4\text{Cl}]$ , shown in Figure 15, are used to find values of  $k_4^0$  and  $b_4$ . Dependence of  $k_4$  on acid concentration has already been accounted for by previous extrapolation of  $(1/\tau)_{\text{NH}}$  and  $(1/\tau')_{\text{NH}}$  values to infinite dilution with respect to  $[\text{H}^+]$ . Values of  $k_4^0$  and  $b_4$  are presented in Table X. The equality of  $b_4$  and  $B_A$  would justify assuming the transition state to resemble the product, and would thus be consistent with the theory that the reverse reaction (-4) is diffusion controlled.

Table X: Infinite Dilution Rate Constants, Salt Coefficients

	T	$k_4^0$ (sec <sup>-1</sup> )	$b_4$	$k_2^0 k_A^0$ (sec <sup>-1</sup> )	$(b_2 + B_A)$	$k_7^0 k_A^0$ (sec <sup>-1</sup> )	$(b_7 + B_A)$
from NH exchange date	30°C	32.4	-0.10	0.124	-0.06	—	—
	40°C	72.8	-0.22	0.366	-0.12	—	—
	50°C	139	-0.18	0.84	-0.15	—	—
from NH-OH exchange date	50°C	179	-0.14	—	—	0.0955	-0.05
	65°C	489	-0.23	—	—	0.251	-0.17
	80°C	1106	-0.20	—	—	0.592	-0.21

Bates and Pinching<sup>40</sup> report values of  $B_A$  for  $\text{NH}_4\text{Cl}$  over the concentration range 0.008 m to 0.107 m, for temperatures between 0°C and 50°C:

$$\begin{aligned} \text{at } T = 0^\circ\text{C}, & \quad B_A = -0.22, \\ \text{" } = 5^\circ\text{C}, & \quad \text{" } = -0.27, \end{aligned}$$

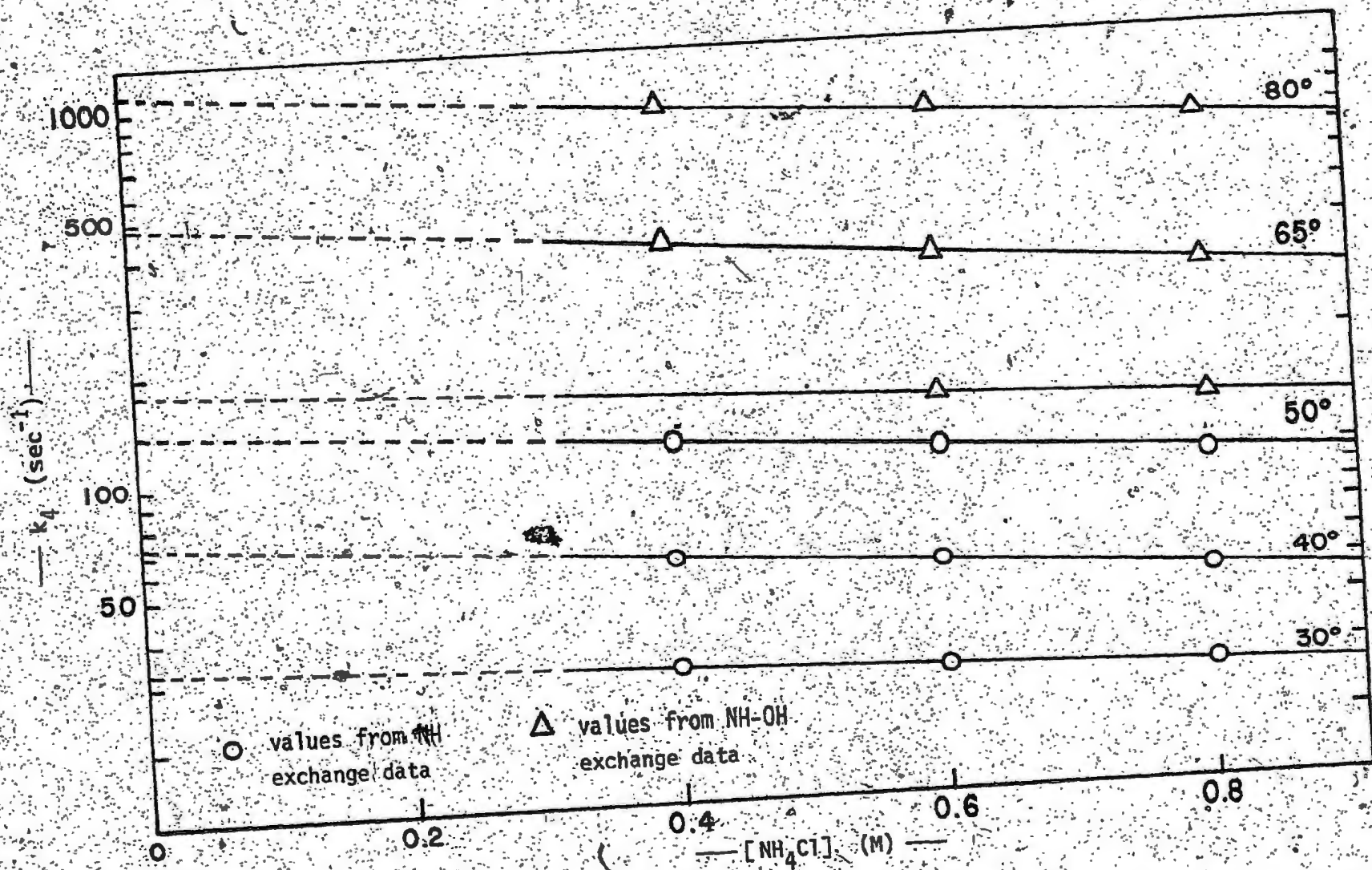


Figure 15: Extrapolation of  $k_4$  to Infinite Dilution

$$\begin{aligned}
 \text{at } T &= 10^{\circ}\text{C} - 40^{\circ}\text{C}, & B_A &= -0.28, \\
 &= 45^{\circ}\text{C}, & &= -0.30, \text{ and} \\
 &= 50^{\circ}\text{C}, & &= -0.31.
 \end{aligned}$$

The  $pK_A$  appears to increase more rapidly with salt concentration in this low concentration range than it does in the concentration range of this work.  $B_A$  measured by Emerson, Grunwald, and Kromhout<sup>13</sup> for the  $\text{NH}_4\text{Cl}$  concentration range 0.25 M to 2.0 M is  $-0.132$  at  $25^{\circ}\text{C}$ , compared to a  $B_A$  value of  $-0.28$  at  $25^{\circ}\text{C}$  reported by Bates and Pinching.

$B_A$  has not been measured as a function of temperature over the salt concentration range used in this work. It can, however, be assumed, by adopting the behavior of the low concentration values reported by Bates and Pinching, to differ little from its value at  $25^{\circ}\text{C}$  of  $-0.132$ .

Rate constants  $k_6$  and  $k_7$  have previously been found experimentally to be independent of ionic strength except for a slight dependence on viscosity.<sup>18</sup> Solutions 0.4 M, 0.6 M, and 0.8 M in  $\text{NH}_4\text{Cl}$  as were used in this study have values of relative viscosity  $\eta/\eta_0$  very close to unity. Experimental values of  $k_6$  and  $k_7$  (and, as well,  $k_2$ , which includes a  $k_6$  term and a  $k_7$  term) would then be expected to exhibit no variation with ionic strength. The experimentally determined values of  $k_2K_A$  and  $k_7K_A$  should vary as does  $K_A$  with ionic strength, so that

$$\log \frac{k_2K_A}{k_2^0K_A^0} = (b_2 + B_A) [\text{NH}_4\text{Cl}], \quad \text{and} \quad (37)$$

$$\log \frac{k_7K_A}{k_7^0K_A^0} = (b_7 + B_A) [\text{NH}_4\text{Cl}], \quad (38)$$

where  $B_A$  is the constant in equation (35), and  $b_2$  and  $b_7$  are very small.

Accordingly, least squares analyses of  $\log k_2 K_A$  versus  $[\text{NH}_4\text{Cl}]$  and of  $\log k_7 K_A$  versus  $[\text{NH}_4\text{Cl}]$  were used to find  $k_2^0 K_A^0$  and  $k_7^0 K_A^0$  values and respective salt coefficients  $(b_2 + B_A)$  and  $(b_7 + B_A)$ . Results for each temperature are recorded in Table X (p. ).

The acid dissociation reaction

$\log k_4^0$  values are shown plotted as a function of reciprocal temperature in Figure .  $\log (k_4^0/T)$  values can be fit to an equation of the form

$$\log \left( \frac{k}{T} \right) = \frac{A}{T} + B \quad (39)$$

to give

$$\log \left( \frac{k_4^0}{T} \right) = - \frac{3180 \pm 69}{T} + (9.35 \pm 0.21) \quad (40)$$

In obtaining this fit, the two data points at  $50^\circ\text{C}$  were each weighted half as heavily as any other data point, so as not to overemphasize the two least reliable data points merely because  $k_4^0(50^\circ\text{C})$  alone was determined by both of the methods used. This practice was applied also to computing equations (42) and (44) and to computing the root mean square deviation of  $\log (k_4^0/T)$  for equations (40) and (42).

Fitting the data to a three parameter equation improves the root mean square deviation of calculated values from data points by about 9 percent. It was difficult to decide which course to follow: to assign a heat capacity of activation to the recombination or to assume there is none. A fit of data is frequently improved by the use of an additional



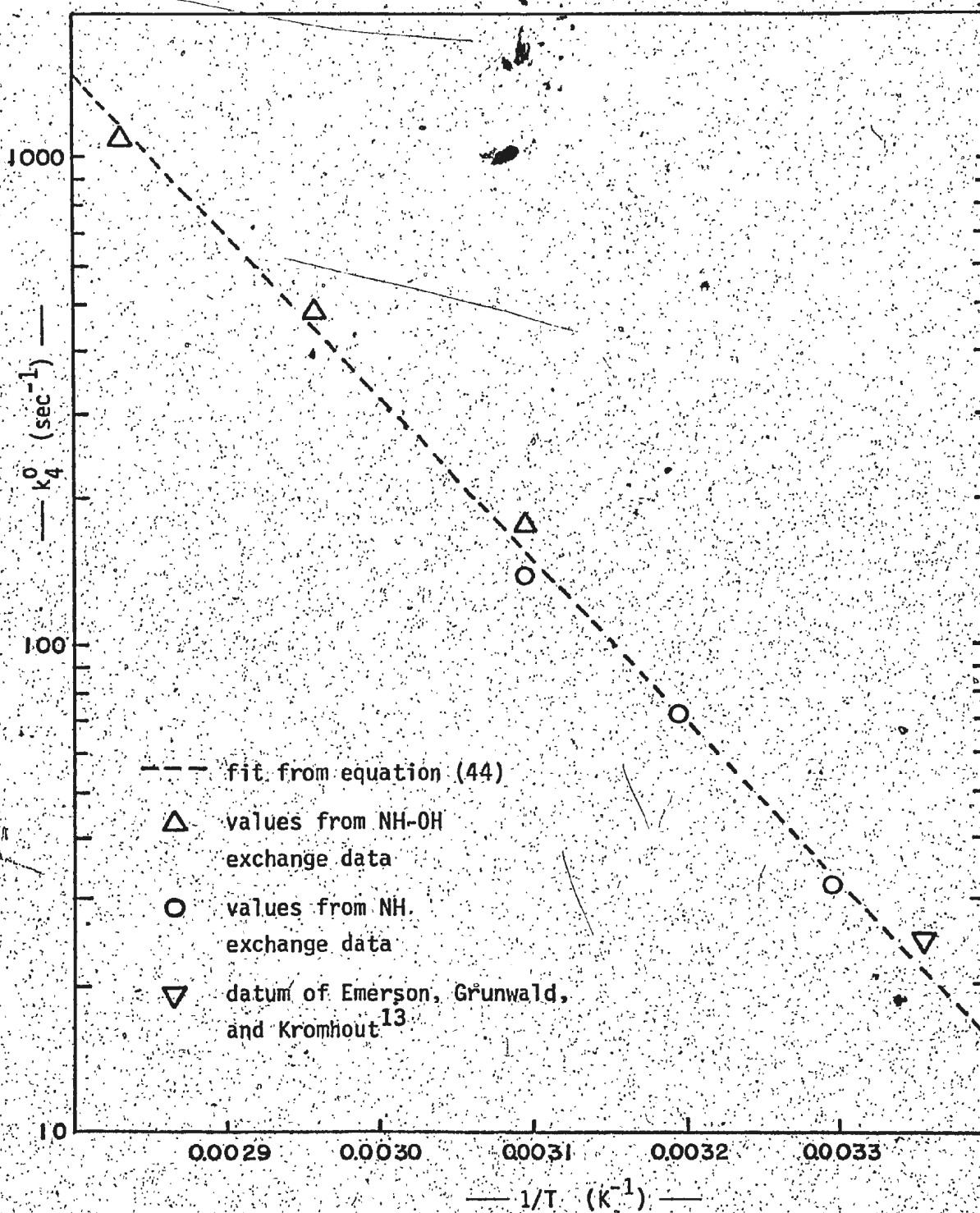


Figure 16:  $\log k_4^0$  as a Function of Reciprocal Temperature

parameter. Since the scatter of the data about the line described by equation (40) does not seem to be particularly methodical, and since temperature dependence of activation enthalpies is difficult to ascertain, it seems best not to claim observation of a  $\Delta C_p^*$ .

As a matter of record, the three parameter fit of the form

$$\log \left( \frac{k}{T} \right) = \frac{A}{T} + B + CT \quad (41)$$

will be given here:

$$\log \left( \frac{k_4^0}{T} \right) = - \frac{5105.51}{T} + 21.32 - 0.01799 T \quad (42)$$

This form, suggested by Harned and Robinson,<sup>43</sup> requires  $\Delta C_p^*$  be directly proportional to  $T$ .

The enthalpy of activation  $\Delta H_4^*$  for the acid dissociation reaction is determined by equation (40) to be  $14.6 \pm 0.3$  kcal mole<sup>-1</sup>. The entropy of activation  $\Delta S_4^*$  is -3.6 e.u.

Equation (23) is of the same form as equation (41), and gives the  $\log K_A^0$  values of Bates and Pinching as a function of  $1/T$  and  $T$ . The parameters analogous to  $\Delta H_4^*$  and  $\Delta S_4^*$  for the acid dissociation equilibrium change with temperature, according to equation (23), and are presented in Table XI for three temperatures.  $\Delta C_p^0$  is approximately -3 cal mole<sup>-1</sup> at 25°C.

Everett and Wynne-Jones<sup>39</sup> report  $\Delta C_p^0$  to be essentially zero, and  $\Delta H^0$  to be a constant equal to 12.40 kcal mole<sup>-1</sup>.



Table XI: Enthalpy and Entropy Changes for the Acid  
Dissociation Equilibrium

T	H <sup>0</sup> (kcal mole <sup>-1</sup> )	S <sup>0</sup> (e.u.)
30°C	12.41	- 0.65
40°C	12.35	- 0.85
50°C	12.24	- 1.19

The recombination reaction

Rearrangement of equation (34) gives the following definition  
of  $k_{-4}$ :

$$k_{-4} = \frac{k_4}{K_A} \quad (43)$$

which is used to calculate  $k_{-4}^0$  values from experimental values of  $k_4^0$   
and from values of  $K_A^0$  given by equation (23). Results are recorded in  
Table XII.

Log ( $k_{-4}^0/T$ ) values are fit to the equation

$$\log \left( \frac{k_{-4}^0}{T} \right) = - \frac{481 \pm 65}{T} + (9.7 \pm 0.2) \quad (44)$$

$\Delta H_{-4}^*$  is then equal to  $2.2 \pm 0.3$  kcal mole<sup>-1</sup>.  $\Delta S_{-4}^*$  is equal to  $-2.8$  e.u.

Error in  $k_{-4}^0$  values is derived primarily from  $k_4^0$  data, since  $K_A^0$  is known accurately.

Table XIII: Rate Constants for the Recombination Reaction

	T	$k_4^0$ ( $\text{sec}^{-1}$ )	$10^9 K_A^0$ (M)	$10^{-10} k_{-4}^0$ ( $\text{sec}^{-1} \text{M}^{-1}$ )
from NH exchange data	30°C	32.4	0.80247	4.04
	40°C	72.8	1.5491	4.70
	50°C	139	2.8664	4.85
from NH-OH exchange data	50°C	179	"	6.24
	65°C	489	6.7184	7.28
	80°C	1106	14.5966	7.58

The symmetrical exchange reaction via  $\text{H}_2\text{O}$

Grunwald and Ku<sup>22</sup> have measured the rate constant for the symmetrical exchange process through water for aqueous ammonium ion at 30°C using a spin-echo technique, and report a value of  $(5.0 \pm 0.4) \times 10^7 \text{ sec}^{-1} \text{M}^{-1}$ .

The values of  $k_7^0$  extracted from water line broadening measurements in this work are not expected to be as accurate as those of Grunwald and Ku, which were made at lower hydrogen ion concentrations. Taken, however, in conjunction with their value at 30°C, the rate constant data presented in Table XIII approximate a picture of the temperature dependency of the

exchange reaction through water.

Table XIII: Rate Constants for Symmetrical Exchange Reactions

T	$10^{-8} k_7^0$ ( $\text{sec}^{-1} \text{M}^{-1}$ ) experimental	$10^{-8} k_7^0$ ( $\text{sec}^{-1} \text{M}^{-1}$ ) computed from eqn. (45)	$10^{-8} k_6^0$ ( $\text{sec}^{-1} \text{M}^{-1}$ )
30°C	$0.50 \pm 0.04^*$	0.58	11
40°C	—	0.76	17
50°C	1.33	1.0	21
65°C	1.49	1.4	—
80°C	1.62	1.9	—

\* datum of Grunwald and Ku<sup>22</sup>

Log  $(k_7^0/T)$  values are best fit by the two parameter equation

$$\log \left( \frac{k_7^0}{T} \right) = - \frac{940 \pm 340}{T} + (8.4 \pm 1.0) \quad (45)$$

The enthalpy of activation  $\Delta H_7^*$  for the reaction is then  $4.3 \pm 1.6$  kcal mole<sup>-1</sup>, and the entropy of activation  $\Delta S_7^*$  is -8.8 e.u.

The direct symmetrical exchange reaction

From equation (45) may be calculated  $k_7^0$  values for the temperatures at which  $k_2^0$  was obtained from NH linewidth measurements. This allows

separation of  $k_6^0$  from the quantity  $k_2^0 \equiv (k_6^0/8 + k_7^0/4)$ . Values of  $k_6^0$  obtained thus are recorded in Table XIII (p. 64). The ratio  $k_7^0/k_6^0$  has an average value of 0.05, and to within the accuracy limits of the data, does not vary with temperature.

Log  $(k_6^0/T)$  values are best fit by the two parameter equation

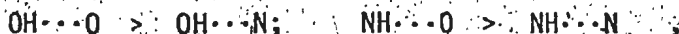
$$\log \left( \frac{k_6^0}{T} \right) = - \frac{1220 \pm 270}{T} + (12.6 \pm 0.9) \quad (46)$$

$\Delta H_6^*$  is then  $5.6 \pm 1.3$  kcal mole<sup>-1</sup>, and  $\Delta S_6^*$  is 1.3 e.u.

## V. DISCUSSION

For the general case, amine B and its conjugate acid  $BH^+$  may be regarded to exist in aqueous solution in various rapidly equilibrating solvated forms,  $B \cdots (HO)_n^H$  and  $BH^+ \cdots (OH)_m^H$ . Of the amines, the size and structure of  $NH_3$  and its conjugate acid,  $NH_4^+$ , resemble most closely those of the corresponding species of water,  $H_2O$  and  $H_3O^+$ . In aqueous solution, minimum disruption of the liquid water structure is thought to occur in the vicinity of these solute species.<sup>13</sup> The extent to which nonpolar organic groups in water are solvated and the nature of solvent-solute interaction has been under recent scrutiny.<sup>17, 23</sup>

It is the existence of hydrogen bridges that allows proton transfer from a donor to an acceptor species, which can in solution be separated by one or more solvent molecules. Transfer across a single hydrogen bridge is known to be very fast. Proton mobility in ice crystals has been determined to give values for the lifetime of  $H_3O^+$  of  $0.8 \times 10^{-13}$  sec to  $1 \times 10^{-13}$  sec.<sup>44</sup> Of reactions in solution, the recombination of the hydrogen ion with  $OH^-$  with a rate constant of  $1.4 \times 10^{11}$  sec<sup>-1</sup> is one of the fastest known.<sup>45</sup> Following the tendency to hydrogen bonding, the rate of proton transfer between species of interest in this study would parallel the series:



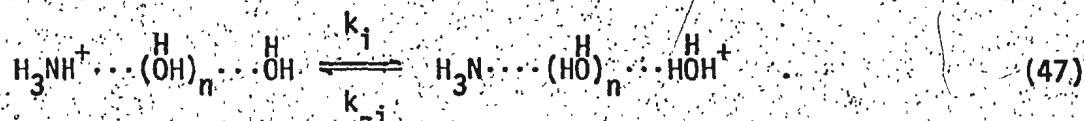
subject to distortion caused by charge, steric, and other effects as outlined in Chapter I (pp. 1 - 3). The rate of proton transfer along a

number of hydrogen bridges comprising the framework of a hydrate complex is determined by the extent and nature of the solvation.

Obviously there are many variables to consider when examining the kinetic properties of proton exchange reactions. Much is now understood about the mechanisms of the reactions under study. These mechanisms will be presented in the following discussion, and the results of this work examined in their light.

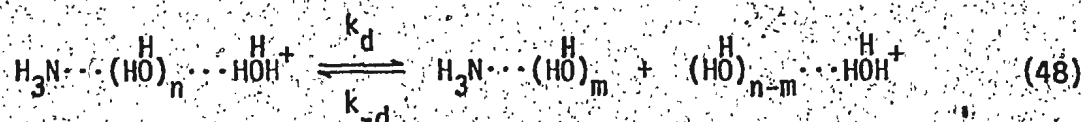
#### The acid dissociation reaction

The first step in the acid dissociation\* of the  $\text{NH}_4^+$  complex, as for the general case of the  $\text{BH}^+$  complex, is a shift of the proton  $\text{H}^+$  along the framework of the complex:



This is a one-to-one transformation so that the atoms to which each atom is bonded remain the same, although the bonding sequence has shifted.

Acid dissociation occurs if any one of the hydrogen bonds in the ionized species is broken:



\*The kinetic scheme presented in this section is discussed in reference 20.



The rate constant  $k_a$  for the acid dissociation process is then given by

$$k_a = \frac{k_i k_d}{(k_{-i} + k_d)}, \quad (49)$$

with  $k_i$ ,  $k_{-i}$ ,  $k_d$ , and consequently  $k_a$  each a function of  $n$ . The rate constant for the reverse process is

$$k_{-a} = \frac{k_{-d} k_{-i}}{(k_d + k_{-i})}, \quad (50)$$

and the equilibrium constant  $K_A$  is equal to  $k_{-a}/k_a$ .

Hydrogen exchange occurs only if the  $\text{H}_3\text{N}\cdots\overset{\text{H}}{\text{HO}}$  hydrogen bond is broken:



and the site at  $\text{H}_3\text{N}$  is attacked to ultimately form  $\text{H}_3\text{NH}^+\cdots(\overset{\text{H}}{\text{OH}})_n$ .

The rate constant  $k_4$  for the exchange, which is the process reflected by n. m. r. linewidths, is then

$$k_4 = \frac{k_a}{1 + \frac{k_{-a}[\text{H}^+]}{k_H}}, \quad (52)$$

That the proton transfer proceeds by the loss of a hydrogen ion by the amine complex to the bulk solvent was first postulated by Swain and Laves<sup>46</sup> for the proton exchange between ammonium ion and methanol. The

body of data that has since been collected on the exchange between alkylammonium ions and water indicates that the Swain mechanism is applicable to these systems<sup>9, 23</sup> and that the integers  $n$  and  $m$  are both greater than zero.<sup>20</sup>

As illustrated in Chapter I (p. 6), proton exchange between alkylammonium ions and water or methanol is greatly suppressed in strongly acidic media. The rationale for the apparently anomalous suppression of reaction rate, presented by Grunwald,<sup>20</sup> is that upon dissociation of the alkylammonium ion  $BH^+$ , the amine  $B$  retains its contact with the previously covalent proton, and that exchange is effected only by the breaking of this bond. In other words, the integer  $m$  is greater than zero. At high hydrogen ion concentrations, the term  $k_a[H^+]/k_H$  of equation (52) becomes large, and therefore  $k_4$  becomes small.

The rate constant  $k_H$  for the breaking of the  $NH_3 \cdots H-O$  hydrogen bond has been evaluated at 25°C. to be  $22 \times 10^{10} \text{ sec}^{-1}$ , and is the largest value of  $k_H$  for an amine<sup>17</sup> (refer to Table II, p. 9). In the present work, the breaking of this bond was taken to be sufficiently rapid that for the pH range used, the observed rate constant for the exchange could be identified with that for the acid dissociation:

$$k_4 = \frac{k_a}{1 + \frac{k_{-a}[H^+]}{k_H}} = k_a \quad (53)$$

for the dissociation of  $NH_4^+$ . If the value obtained for the rate constant  $k_{-4}$  for the recombination when extrapolated to 25°C is taken to be  $k_{-a}$  at that temperature, then the term  $k_{-a}[H^+]/k_H$  assumes the values:



$$\frac{k_{-a} [H^+]}{k_H} = 0.0017 \text{ for } [H^+] = 0.01, \text{ at } 25^\circ\text{C}, \text{ and}$$

$$= 0.038 \text{ for } [H^+] = 0.23, \text{ at } 25^\circ\text{C}.$$

Thus the assumption  $k_4 = k_a$  is justified.

A first inspection of the plot  $k_4^0$  versus  $1/T$  might lead one to the conclusion that the two methods used to measure the exchange rate for reaction (4) are incompatible. The overlap at  $50^\circ\text{C}$  of the rate constant  $k_4^0$  determined from the NH linewidth measurements with those from the water line measurements is not smooth. It is nevertheless believed that the remaining  $k_4^0$  values present a reliable picture of the variation of  $k_4^0$  with temperature.

The accuracy of  $k_4^0(50^\circ\text{C})$  derived from NH linewidth measurements depends to a much greater extent on the methods of correction for overlap of the NH doublet peaks with one another and with the waterline than does that of  $k_4^0(40^\circ\text{C})$  and of  $k_4^0(30^\circ\text{C})$ . Of the high temperature determinations also,  $k_4^0(50^\circ\text{C})$  is the least reliable. The magnitudes of  $1/T(H_1)$  and  $(1/T_1)_{OH}$  are of the same order. Their difference, which approximates  $P_{NH}(1/\tau)_{NH}$ , is subject to error contributions from both terms.

The data do not appear to warrant assignment of a heat capacity of activation to the acid dissociation reaction. Nor has the acid dissociation equilibrium been reported to have a heat capacity change differing greatly from zero. Everett and Wynne-Jones<sup>39</sup> report a  $\Delta C_p^0$  of zero. Bates and Pinching<sup>40</sup> report a  $\Delta C_p^0$  of zero in one instance and  $-3 \text{ cal K}^{-1} \text{ mole}^{-1}$  in another. By contrast, studies of other alkylamines have yielded positive values of  $\Delta C_p^0$ :  $8.0 \text{ cal K}^{-1} \text{ mole}^{-1}$ ,  $23.1 \text{ cal K}^{-1} \text{ mole}^{-1}$ , and  $43.8 \text{ cal K}^{-1} \text{ mole}^{-1}$  for mono-, di-, and trimethylamines,

respectively.<sup>47</sup> The acid dissociation reaction of trimethylammonium ion has been reported to have a heat capacity of activation estimated to be  $80 \pm 60 \text{ cal} \cdot \text{K}^{-1} \text{ mole}^{-1}$ .<sup>20</sup>

A critical examination of the data

Before examining the implications of the activation parameters determined for the recombination reaction, acceptance of the results of this work in favor of the results of Connor and Loewenstein should be justified. The results, after all, imply two entirely different mechanisms for the reaction; (f, that is, an activation energy of essentially zero can be said to imply any understood mechanism. Unless tunneling through the potential barrier by the proton contributes significantly to the process, the activation enthalpy of the protonation should be at least as large as the activation enthalpy for the diffusion of the reacting species to one another. In order for tunneling to give a zero activation energy, the species  $\text{H}_3\text{O}^+$  and  $\text{NH}_3$  must be continually connected by hydrogen bonds such as would be found in a solvent cage so that proton transfer could occur without the requirement of diffusion. Such a situation implies an abnormal attraction between  $\text{H}_3\text{O}^+$  and  $\text{NH}_3$  or a very stable network of hydrogen bonded water molecules in the complex  $\text{H}_3\text{N} \cdots (\text{HO})_n \cdots \text{HOH}^+$ . Neither possibility is likely, particularly the latter, since the magnitude of  $k_H$  indicates that the hydrogen bonding is weak. Should the recombination reaction be better represented by a type of concerted mechanism than by the Eigen mechanism, the enthalpy of activation would still be on the order of or greater than that for the diffusion of the reacting species.

slight and almost encompassed by the error in the  $\Delta H_4^*$  values, but could, nevertheless, contribute to the anomalously low activation energy reported by Connor and Loewenstein.

The Connor and Loewenstein study was conducted on a 60 Mc instrument,<sup>3</sup> which produces signals with amplitude 0.36 of the signal amplitude produced on the 100 Mc machine used in this work. Already, given equal concentrations of  $\text{NH}_4\text{Cl}$  in solution, any one member of the  $^{14}\text{NH}$  triplet is less intense than a peak of the  $^{15}\text{NH}$  doublet by a factor of about one third. The chemical shift  $\delta$  of any resonance observed on the 60 Mc instrument is 0.6 of the chemical shift observed in a 100 Mc magnetic field. This becomes important at higher temperatures where the wing of the water resonance increasingly encroaches upon NH territory, necessitating baseline corrections to linewidth measurements.

It is not obvious from the Connor and Loewenstein paper how such baseline corrections were made, nor whether correction was made for partial collapse of the  $^{14}\text{NH}$  multiplet, or for contribution from exchange broadening to the decay constant of the water wiggles, from which their estimate of  $(1/T_2)_{\text{NH}}$  was taken. Their measurements were made using solutions with hydrogen ion concentrations as low as 0.01 M, and at as high a temperature as  $56^\circ\text{C}$ . Under these conditions, the above effects require consideration. The data of Connor and Loewenstein should be appraised keeping in mind the magnitude of such effects. Although no one effect mentioned above is in itself large, their sum might be sufficient to account for the discrepancy between the activation energies of zero for reactions (4) and (6) reported by Connor and Loewenstein and the non-zero activation energies indicated by these data.

Also, in the present study, greater field/frequency stability was

In the previous study done by Connor and Loewenstein with  $^{14}\text{NH}_4\text{Cl}$ , rate measurements were made at only one salt concentration, 1.0 M.<sup>3</sup> In the present study, measurements were made at three salt concentrations, 0.4 M, 0.6 M, and 0.8 M, then extrapolated to infinite dilution. The activation parameters obtained from infinite dilution data are not necessarily represented accurately by data taken at 1.0 M salt concentration. There is a slight tendency in the salt coefficient  $b_4$ , as determined in this study (see Table X, p. 56) to become more negative with temperature. Consequently rate constants  $k_4$  determined at 1.0 M  $\text{NH}_4\text{Cl}$  would show less of an increase with temperature than do  $k_4^0$  values.

To illustrate this effect,  $\Delta H_4^*$  has been calculated from the values of  $k_4(T)$  determined in this work for each of the  $\text{NH}_4^+$  concentrations 0.4 M, 0.6 M, and 0.8 M, and is reported in Table XIV.

Table XIV:  $\Delta H_4^*$  as a Function of Salt Concentration

$[\text{NH}_4\text{Cl}]$	$\Delta H_4^*$ (kcal mole <sup>-1</sup> )
(0)	$14.55 \pm 0.32$
0.4 M	$14.29 \pm 0.49$
0.6 M	$14.09 \pm 0.34$
0.8 M	$13.93 \pm 0.44$

The tendency to become smaller with increasing salt concentration is

achieved on the 100 Mc machine because of the internal lock system it employs, and the signal-to-noise ratio of the spectra obtained was increased by use of the voltage to frequency conversion technique.

Finally, in comparing the two studies, is the matter of quadrupole relaxation. Although contribution of  $^{14}\text{N}$  quadrupole relaxation to the NH linewidth seems justifiably negligible,<sup>3</sup> the possibility of such a contribution is eliminated entirely with the use of  $^{15}\text{N}$ , which has a zero quadrupole moment. The ammonium ion is a spherically symmetrical ion. Electric fields with which the nuclear quadrupole can interact may, however, be set up with species Coulombically attracted to it. Figure 16 shows the spectrum of a strongly acidic aqueous solution equal in  $^{14}\text{NH}_4\text{Cl}$  and  $^{15}\text{NH}_4\text{Cl}$  concentration. Note the difference in the widths at half height of the two absorptions. Proton exchange is greatly suppressed;  $(1/\tau)_{\text{NH}}$  is estimated to equal  $0.0460 \text{ sec}^{-1}$ , corresponding to a broadening of only 0.01 Hz at half height. The difference in the halfwidths of the two lines is then due primarily to the difference in the transverse relaxation of the two species, the broadening due to magnetic field inhomogeneity being the same for each.

Equation (54) gives the factors contributing to the linewidth of the NH absorptions:

$$\pi\Delta_{\text{NH}} = \frac{k_4}{4} + \left(\frac{1}{T_2}\right)_{\text{magnet}} + \left(\frac{1}{T_2}\right)_{\text{DIP}} + \left(\frac{1}{T_2}\right)_{\text{QUAD}} \quad (54)$$

If the dipolar relaxation term  $(1/T_2)_{\text{DIP}}$  may be shown to be equal for the two species as well as are the first two terms of the right hand side of the equation, then the difference in the halfwidths must be attributed to

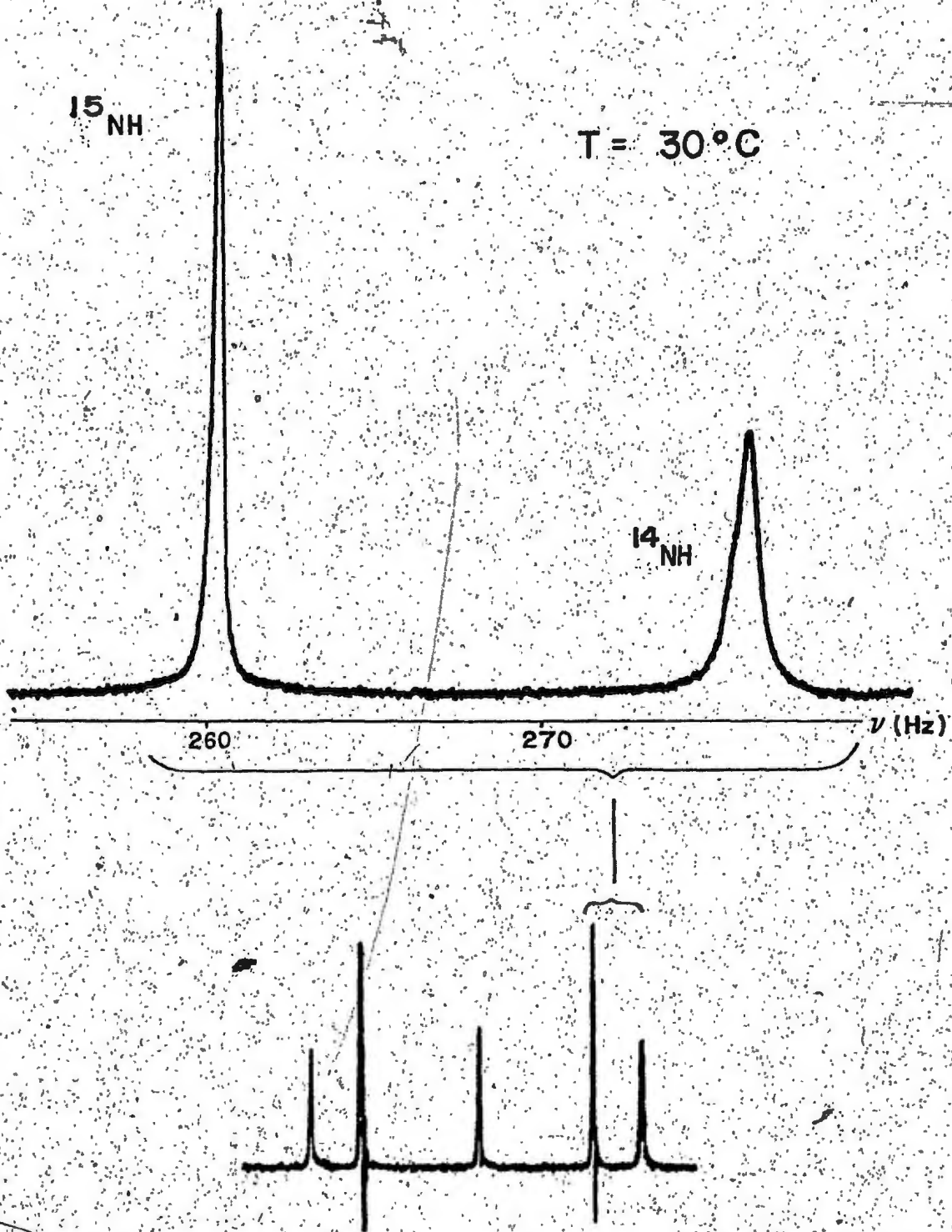


Figure 17: Comparison of Linewidths in Strongly Acidic Solution

The spectrum shown is of a reaction mixture 58.9% by weight  $\text{H}_2\text{SO}_4$

the quadrupole relaxation of the  $^{14}\text{N}$  nucleus.

Spectra similar to that shown in Figure 16 (p. 74) were run at  $30^\circ\text{C}$  for three concentrations of  $\text{H}_2\text{SO}_4$ . Solutions were in each case 0.6 M in  $^{15}\text{NH}_4\text{Cl}$  and in  $^{14}\text{NH}_4\text{Cl}$ . Data obtained from these spectra in conjunction with  $(1/T_2)_{^{14}\text{NH}}$  values reported by Emerson, Grunwald, and Kromhout<sup>13</sup> for  $^{14}\text{NH}_4\text{Cl}$  solutions at  $25^\circ\text{C}$  are used to give an estimate of the magnitude of  $(1/T_2)_{^{15}\text{NH}}$  in the following manner.

The difference in the halfwidth of the  $^{14}\text{NH}$  peak and that of the  $^{15}\text{NH}$  peak is due to the difference in the broadening of the two caused by dipole - dipole interaction plus the additional broadening of the  $^{14}\text{NH}$  line due to quadrupole relaxation:

$$^{14}(\pi\Delta) - ^{15}(\pi\Delta) = ^{14}\left(\frac{1}{T_2}\right)_{\text{DIP}} - ^{15}\left(\frac{1}{T_2}\right)_{\text{DIP}} + ^{14}\left(\frac{1}{T_2}\right)_{\text{QUAD}} \quad (55)$$

The values of  $(1/T_2)_{^{14}\text{NH}}$  reported by Emerson, Grunwald, and Kromhout contain a dipolar contribution and a quadrupolar contribution:

$$\left(\frac{1}{T_2}\right)_{^{14}\text{NH}} = ^{14}\left(\frac{1}{T_2}\right)_{\text{DIP}} + ^{14}\left(\frac{1}{T_2}\right)_{\text{QUAD}} \quad (56)$$

A simple subtraction gives  $^{15}(1/T_2)_{\text{DIP}}$ :

$$\left(\frac{1}{T_2}\right)_{^{14}\text{NH}} - \left[ ^{14}(\pi\Delta) - ^{15}(\pi\Delta) \right] = ^{15}\left(\frac{1}{T_2}\right)_{\text{DIP}} \quad (57)$$

Table XV gives the values of  $^{14}(\pi\Delta) - ^{15}(\pi\Delta)$  for the three  $\text{H}_2\text{SO}_4$



Table XV: Computation of  $^{15}(1/T_2)_{DIP}$

Wt. % $H_2SO_4$	$^{14}(\pi\Delta)$ (rad sec <sup>-1</sup> )	$^{15}(\pi\Delta)$ (rad sec <sup>-1</sup> )	$^{14}(\pi\Delta) - ^{15}(\pi\Delta)$ (rad sec <sup>-1</sup> )	* $(\frac{1}{T_2})_{NH}^{25^\circ C}$ (sec <sup>-1</sup> )	$\frac{\eta}{\eta_0}(25^\circ C)$ ***	$\frac{\eta}{\eta_0}(30^\circ C)$ ***	$^{15}(\frac{1}{T_2})_{DIP}^{30^\circ C}$ (sec <sup>-1</sup> )
80	—	—	—	5.3	—	—	—
65.2	—	—	—	2.48	—	—	—
58.9	2.29	1.31	0.98	** 2.03	5.69	5.59	0.18 <sub>1</sub>
52.8	2.07	1.16	0.91	** 1.78	4.35	4.28	0.19 <sub>6</sub>
49.6	—	—	—	1.70	—	—	—
44.0	2.19	1.28	0.81	** 1.51	3.07	3.07	0.22 <sub>8</sub>
34.2	—	—	—	1.43	—	—	—
28.9	—	—	—	1.15	—	—	—
0	—	—	—	(0.8)	— extrapolated —	—	(0.37)

\*\* data of Emerson, Grunwald, and Kromhout<sup>13</sup>

\*\*\* interpolated values

Values are interpolated from data obtained from reference 36.



concentrations at which it was determined and values of  $(1/T_2)_{14\text{NH}}$  at these acidities interpolated from the data of Emerson, Grunwald, and Kromhout, reported at 25°C, corrected to 30°C by assuming direct variation with viscosity. The correction factor for each acidity is the ratio of the relative viscosity of an  $\text{H}_2\text{SO}_4$  solution of the appropriate concentration at 30°C to that at 25°C.

The last column of Table XV (p. 77) gives  $^{15}(1/T_2)_{\text{DIP}}$  corrected to a relative viscosity of 1.00, which is very nearly the relative viscosity of all reaction mixtures in the pH range 0.6 to 2.0 studied. These values are not a constant over the acidity range examined. Although correction of  $^{15}(1/T_2)_{\text{DIP}}$  to a relative viscosity of 1.00 accounts for a change in the correlation time with concentration, the electric field gradient of the  $^{14}\text{N}$  environment, which also may vary with concentration, and upon which  $^{14}(1/T_2)_{\text{QUAD}}$  is dependent, remains unaccounted for. Consequently,  $^{15}(1/T_2)_{\text{DIP}}$  was extrapolated using a linear least squares fit to give a value of  $0.37 \text{ sec}^{-1}$  at a relative viscosity of 1.00.

This estimate of  $^{15}(1/T_2)_{\text{DIP}}$  is rough, and probably very generous, because of the compounding of error with each interpolation, correction, and extrapolation. Nevertheless, it is decidedly less than the value of  $0.8 \text{ sec}^{-1}$  to which  $(1/T_2)_{14\text{NH}}$  reported by Emerson, Grunwald, and Kromhout tends at 0.0 weight percent  $\text{H}_2\text{SO}_4$ .<sup>13</sup> The difference is attributable only to broadening due to quadrupole relaxation.

Even a value of  $^{14}(1/T_2)_{\text{QUAD}}$  as small as  $0.4 \text{ sec}^{-1}$  at 30°C that decreases with increasing temperature is sufficient to distort the apparent behavior of the rate constant  $k_4$  with temperature.

### Acid dissociation constants

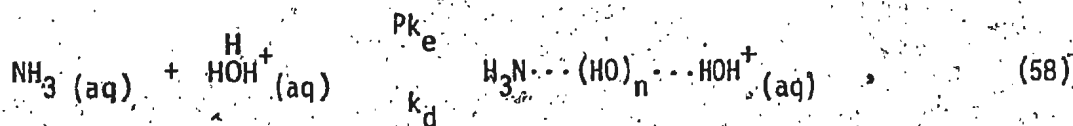
Vibrational data on  $^{14}\text{NH}_4^+$  and  $^{15}\text{NH}_4^+$  and their conjugate bases is not sufficiently adequate to do a statistical thermodynamic calculation of the ratio of their  $K_A$  values. To find our measurement of the  $\text{p}K_A$  of  $^{15}\text{NH}_4^+$  at one temperature and concentration chosen arbitrarily was gratifying.

Although isotope effects may reverse and become equal to zero at a particular temperature,<sup>48</sup> the relative differences in the masses of the isotopic species concerned is small enough that error incurred by assuming  $^{15}K_A$  to equal  $^{14}K_A$  (p. 36) are insignificant compared with errors in the measurement of rate constants. It should be mentioned that the data of Bates and Pinching<sup>40</sup> extend only as high as  $50^\circ\text{C}$ ; and that adopting equation (23) for use over the temperature range  $30^\circ\text{C}$  to  $80^\circ\text{C}$  means incurring some error in the extrapolated values at the higher temperatures. This error is subsequently incorporated into values of  $k_{-4}^0$  calculated from  $k_4^0$  and  $K_A^0$ .

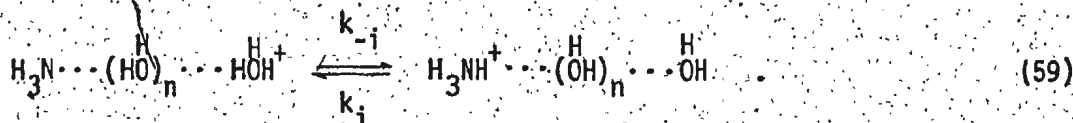
### The recombination reaction

The bulk of data that has been accumulated for the recombination of bases with the hydrogen ion indicate that these reactions are of a diffusion controlled nature.<sup>1</sup> The values of the rate constant determined in this study for the recombination of  $\text{NH}_3$  with the hydrogen ion are of the appropriate magnitude for a diffusion controlled reaction; for which rate constants at  $25^\circ\text{C}$  range down from  $1.4 \times 10^{11} \text{ sec}^{-1}$  for  $\text{OH}^-(\text{aq})$ <sup>44</sup> by a couple of orders of magnitude.

The Eigen mechanism<sup>1</sup> for the recombination reaction is a diffusion controlled encounter:



followed by a rapid transfer within the hydrogen bonded complex:



The rate constant for the overall process is given by

$$k_{-a} = \frac{Pk_e k_{-i}}{(k_d + k_{-i})} \quad (60)$$

where  $P$  is a steric factor giving the probability that an encounter will result in reaction. If the proton transfer along the hydrogen bonded network is fast compared to the rate of diffusion of the species away from one another such that  $k_{-i} \gg k_d$ , then the observed rate constant, which may be identified with  $k_{-a}$ , is given by

$$k_{-4} = Pk_e \quad (61)$$

and the energetics of the recombination should parallel those for the diffusion of the species to one another.

Should the proton transfer be the slow step, the observed rate constant becomes

$$k_{-4} = \frac{Pk_e}{k_d} k_{-i} = K_e k_{-i} \quad (62)$$

The activation energy of the recombination reaction would then be

$$\Delta E_{-4}^* = \Delta H_e^0 + \Delta E_{-i}^* \quad (63)$$

The Debye - Schmolukowski treatment<sup>49, 50, 51</sup> of a diffusion controlled process between two species A and B gives for the rate constant of the process

$$k = \frac{4\pi N_0}{1000} P\sigma (D_A + D_B) \quad (64)$$

where  $k$  is in  $\text{sec}^{-1} \text{M}^{-1}$ ,  $N_0$  is Avagadro's number,  $\sigma$  is the effective collision diameter,  $D$  is the diffusion coefficient of the specified reacting species, and  $P$  is as defined for equation (60).

Equation (64) assumes the spherical symmetry of both reacting species, and assumes an electrostatic potential of zero between them. It is then applicable to the recombination of  $\text{NH}_3$  with the hydrogen ion. To test how well it holds for reaction (-4),  $P\sigma$  is treated as a parameter and calculated using the experimentally determined values of  $k_{-4}^0$ . The diffusion coefficients used in the calculation are given in Table XVI.  $D_{\text{H}^+}$  values were obtained from ionic equivalent conductance data<sup>52</sup> using the relationship<sup>53</sup>

$$D_i = 0.893 \times 10^{-9} T \Lambda_i \quad (65)$$

$D_{\text{NH}_3}$  has been measured over a small range ( $0^\circ\text{C}$  to  $17^\circ\text{C}$ ) by various workers<sup>54</sup> and is found to vary roughly with  $T/\eta_{\text{H}_2\text{O}}$ . Their data have been extended in proportion to  $T/\eta_{\text{H}_2\text{O}}$  into the temperature range of this work to give the values for  $D_{\text{NH}_3}$  shown in Table XVI (p. 82).  $P\sigma$  values

calculated are reported in Table XVI (this page).

Table XVI: Diffusion Parameters for the Recombination Reaction

T	$10^5 D_{H^+}$ ( $\text{cm}^2 \text{sec}^{-1}$ )	$10^5 D_{NH_3}$ ( $\text{cm}^2 \text{sec}^{-1}$ )	$\cdot 10^8 P$ (cm)
30°C	2.61	9.892	4.26
40°C	3.30	11.55	4.18
50°C	4.06	13.27	4.23*
65°C	5.34	15.92	4.52
80°C	6.82	18.24	4.00

\* computed from the average of the two experimental  $k_{-4}^0$  values

$P\sigma$  is found not to vary significantly with temperature, which should be the case for a diffusion controlled reaction, unless the constraints themselves reflected in the term  $P\sigma$  vary with temperature.

In his investigation of the aqueous trimethylamine system, Grunwald<sup>15</sup> chose for the intermolecular distance between reactants a value of 5 Å, corresponding to at least one solvent water molecule intervening between the amine and  $H_3O^+$ . Using this value, he then found  $P$  to be equal to 0.6 over a temperature range 35°C to 80°C. Use of the same value for  $\sigma$  yields  $P$  for the recombination reaction of  $NH_3$  equal to  $0.85 \pm 0.04$  over the temperature range 30°C to 80°C.

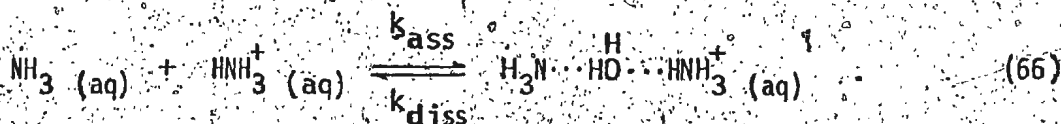
Another approach can be taken. If only  $1/4$  of the molecular surface of  $\text{NH}_3$ , corresponding to the N orbital containing the unshared pair of electrons, is considered to be reactive, and if  $3/4$  of the surface of  $\text{H}_3\text{O}^+$  is capable of proton donation, then  $P$  could be assigned a lower limit of  $(1/4)(3/4) = 3/16$ , assuming a random distribution of the line of approach of the two ions. Using a value of  $3/16$  for  $P$ ,  $\sigma$  is then found to equal  $24 \text{ \AA}$ , corresponding to a large number of intervening molecules. Of course, cooperation of solvent molecules to this extent is a farfetched expectation. Even tertiary hydration of the hydrogen ion is considered to exhibit properties of relatively weak bonding.<sup>1</sup> As is discussed by Grunwald,<sup>55</sup> the species  $\text{NH}_3$  and  $\text{H}_3\text{O}^+$  approaching one another in solution would tend to be oriented, not randomly, but so that a proton has free access to the reactive site via hydrogen bonding, thus favoring the formation of an encounter complex. It is quite likely that  $P$  is close to the upper limit lying between 0.8 and 0.9 determined by assigning a value of  $5 \text{ \AA}$  to  $\sigma$ .

The average value of  $P\sigma$  calculated for the recombination reaction of  $\text{NH}_3$  is around 35 percent larger than  $P\sigma$  for that of  $(\text{CH}_3)_3\text{N}$ : 4.2 compared to 3.1. This is probably due to the  $\text{CH}_3$  groups occupying so extensively the molecular surface of  $(\text{CH}_3)_3\text{N}$  as to impose stricter orientation limits on the reactant species  $(\text{CH}_3)_3\text{N}(\text{aq})$  and  $\text{H}_3\text{O}^+(\text{aq})$ , so that the steric factor  $P$  has a value substantially less than 1.0 for the recombination reaction of trimethylamine.

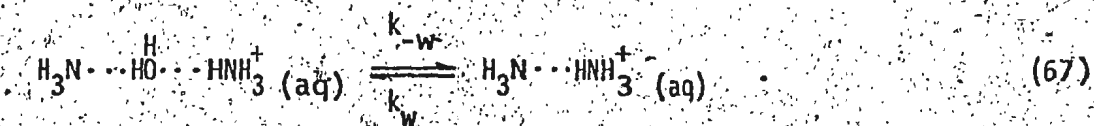
Direct second order exchange reaction

The mechanism for the direct second order exchange presented by

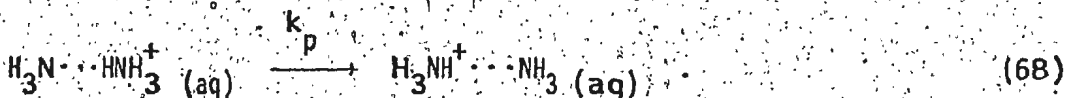
Grunwald and Ku,<sup>22</sup> when applied to the aqueous ammonium ion system, consists first of a diffusion controlled encounter to form a solvent-separated complex:



The solvent-separated complex then converts to a nearest neighbor complex:



Within this complex the proton transfer is thought to be rapid:



It has been shown that the dehydration step with rate constant  $k_{-w}$  is probably rate determining.<sup>22</sup> The observed rate constant  $k_6$  is then given by

$$k_6 = \frac{1}{2} \frac{k_{\text{ass}} k_{-w}}{(k_{\text{diss}} + k_{-w})} \quad (69)$$

The factor  $\frac{1}{2}$  is the probability that proton exchange will have occurred upon the dissociation of the complex  $\text{H}_3\text{NH}^+ \cdots \text{NH}_3$ . Since  $k_{-w} \ll k_{\text{diss}}$ , then

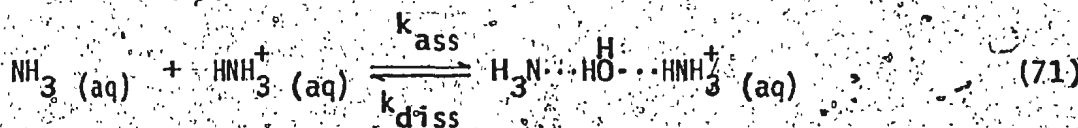
$$k_6 = \frac{1}{2} K_{\text{ass}} k_{-w} \quad (70)$$

The extrapolated value of  $k_6 = 1.1 \times 10^9 \text{ sec}^{-1} \text{ M}^{-1}$  at  $25^\circ\text{C}$  (computed from data obtained in this study using equation (46)), is in good agreement with the value reported by Emerson, Grunwald, and Kromhout<sup>13</sup> of  $(1.17 \pm 0.04) \times 10^9 \text{ sec}^{-1} \text{ M}^{-1}$  at  $25^\circ\text{C}$ . It is somewhat lower than the value reported by Connor and Loewenstein,<sup>3</sup>  $k_6 = 1.32 \times 10^9 \text{ sec}^{-1} \text{ M}^{-1}$ , independent of temperature. Both of the latter values were found by assuming the ratio  $k_7/k_6$  to be equal to 0.08, and to be independent of temperature and concentration. The ratio  $k_7/k_6$  computed from the data of this study is 0.05, experimental error being too large to detect variation with temperature.

The entropy of activation for the symmetrical exchange through water has a relatively large negative value, -8.8 e.u.; when compared to the small positive entropy of activation, 1.3 e.u., of reaction (6), in which the solvent-separated complex loses the intermediate water molecule before exchange occurs. This might be expected since the cooperation of at least one additional molecule is required for reaction (7) to proceed.

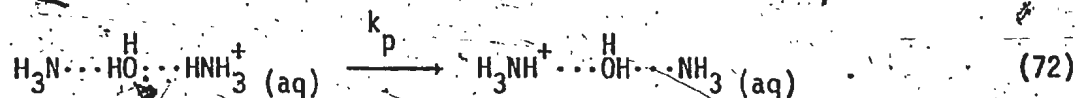
#### Symmetrical exchange through water

The mechanism of the symmetrical exchange through water has been deduced for the reaction between  $(\text{CH}_3)_3\text{NH}^+$  and  $(\text{CH}_3)_3\text{N}$ .<sup>56, 57</sup> Assuming the mechanism for the aqueous ammonium ion corresponds to that for the aqueous trimethylammonium ion, it may be represented by a diffusion controlled encounter to form a solvent-separated complex:





followed by a concerted transfer of the protons within the complex:



Luz and Meiboom have demonstrated that only one intermediate water molecule is involved in the transfer.

The rate constant for the overall process of proton transfer is given by

$$k_7 = \frac{k_{\text{ass}} k_p}{(k_{\text{diss}} + k_p)} \quad (73)$$

A study of isotope effects on the exchange processes of the trimethylammonium ion indicate that, although fast, reaction (7) is not diffusion controlled.<sup>56</sup>

It would have been desirable to have measured the symmetric exchange rates at smaller hydrogen ion concentrations in order to obtain more accurate values of the rate constants  $k_6$  and  $k_7$ . In an acidity range, however, where  $k_6$  and  $k_7$  are sufficiently large to reduce the relative size of experimental error, the buffering capacity of the hydrogen ion would be so reduced as to make estimation of  $\text{NH}_3$  concentration difficult.

Nevertheless, despite the appreciable error, activation enthalpies for the symmetrical exchange reactions, as well as that for the recombination reaction, are of theoretically plausible magnitudes substantially greater than zero.

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