spectively). A small amount of methane is also observed.

Analytical, spectroscopic, and molecular weight data[9] along with chemical characterization (Scheme I) suggest that the product is the dimer III. Solutions of III are rapidly oxidized in air but the solid may be handled briefly in air.

Thermolysis of III in toluene (Scheme I) produces mainly methane and some ethylene and ethane. Reactions which require the generation of titanocene, such as the ethylene-producing pathways, are slow and are followed by Cp–H insertion to produce "titanocene".[10] This reluctance to generate the high-energy intermediate Cp_2Ti provides a rationale for the thermal stability of III and the predominance of CH_4 in the decomposition gases. When a more viable leaving fragment is provided, the reaction proceeds as expected. For example, reaction of III with iodine (Scheme I) gives ethylene, Cp_2TiI_2, and some methane.

In this system the 1,3- rather than the 1,2-dimetallacyclobutane is favored due to polarization of the Cp_2TiCH_2 moiety and the steric bulk of the Cp ligands.

The use of II as a source of Cp_2TiCH_2 for reaction with unsaturated organic and organometallic substrates appears to be a promising pathway to other metallacyclic and bimetallic methylene bridged systems.

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(9) Anal. Calcd: C, 68.77; H, 6.30. Found: C, 68.88, H, 6.55; $^{13}C\ [^1H]$ (22.53 MHz, shifts relative to CD_2Cl_2 at δ 53.8): δ 235.2 (CH_2), 112.2 (Cp's). $^1J_{C\text{-}H}$ for the CH_2 resonance was measured from the ^{13}C satellites in the ^1H spectrum and found to be 126 Hz. IR (benzene-d_6): 2920, 2980 (m, sh). Molecular weight: calculated 384; found 396 ± 30 (cryoscopic in benzene); 427 ± 20 (Signer's method. For a description of the method, see: Clark, E. P. *Ind. Eng. Chem., Anal. Ed.* **1941**, *13*, 820).

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Some Observations Concerning the Temperature Dependence of the Reaction of Ammonia with Water

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Following Albery and Robinson,[1] we have recently shown that it is possible to account for the heat capacity of activation ($\Delta C_p^{\ddagger}$) which characterizes the temperature dependence of hydrolytic rate constants by postulating the existence of at least one intermediate between the neutral reactants and ionic products.[2] The same idea has been applied successfully to the heat capacity changes ($\Delta C_p^{\ominus}$) which characterize the ionization of carboxylic acids by invoking the Eigen intermediate between the aqueous covalent acids and the related ions.[3] In this contribution a similar model is applied to the ionogenic reaction between water and ammonia, namely,

$$NH_3 + H_2O \overset{K_1}{\rightleftharpoons} I \overset{K_2}{\rightleftharpoons} NH_4^+ + OH^- \qquad (1)$$

where I represents the intermediate.

Table I. Equilibrium Data Related to the Ionization of Ammonia in Water at Various Temperatures

T, °C	$K_b \times 10^5$,[a,e] obsd	$K_b \times 10^5$,[b] calcd	$K_b \times 10^5$,[c] calcd	$K_1 \times 10$,[d,f] calcd
0	1.374	1.374	1.374	12.3
5	1.479	1.478	1.478	10.0
10	1.570	1.570	1.570	8.3
15	1.652	1.650	1.650	6.8
20	1.710	1.717	1.717	5.7
25	1.774	1.772	1.772	4.8
30	1.820	1.814	1.814	4.0
35	1.849	1.846	1.846	3.4
40	1.862	1.868	1.868	2.9
45	1.879	1.882	1.882	2.5
50	1.892	1.889	1.889	2.2

[a] Taken from ref 18. [b] Calculated from A, B, C and D, solution a, (Table II). [c] Calculated from A, B, C and D, solution b (Table II). [d] Calculated from C and D of solution a, (Table II). [e] For the Wentworth–Deming regression ΔK_b was taken as 0.2% of the observed value of K_b (this estimate may be optimistic); ΔT was taken as 0.01 or 0.001. The differing values of ΔT made no difference to the quantities reported in Table II. [f] Khakham reports $K_1 = 0.5$ at 25 °C, whereas Moore and Winmill report $K_1 = 0.88$ (see also ref 7, p 31).

In contrast to the solvolytic reactions and the carboxylic acid equilibria mentioned above, the notion that an intermediate exists in the ammonia reaction has had a long and interesting history. Such a proposal formed the basis for the work reported by Moore and Winmill[4,5] early in this century. Their work was reviewed sympathetically in two treatises by Sidgwick[6,7] although a revised, posthumous edition[8] of one of them gives a less detailed account of Moore's work. Writing in 1973, Bell[9] is much less enthusiastic than Sidgwick and claims that Moore and Winmill's work is "based on unverifiable assumptions about the distribution coefficients of the individual species". The related work of Khakham[10] is also dismissed with the added comment that the Russian contribution is in conflict with that of the British investigators. Bell apparently overlooked an important contribution by Patterson[11] and co-workers in which all the evidence[12,13] for the existence of

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Table II. Derived Parameters from the Temperature Dependence of the Ionization Constant (K_b) for Ammonia[a]

	$\Delta H_a^\ominus$	$\Delta S_a^\ominus$	$\Delta H_1^\ominus$	$\Delta S_1^\ominus$	$\Delta H_2^\ominus$	$\Delta S_2^\ominus$	$\Omega^b \times 10^8$
			Solution a[b]				
A 507.971 ± 142.667							
B −12.2435 ± 0.3864	−1.01	−24.34	−6.10	−21.93	5.09	−2.43	4.82
C 3.067.83 ± 132.25	±0.28	±0.77	±0.26	±1.43	±0.54	±2.20	
D −11.0256 ± 0.7232							
			Solution b[b]				
A −2559.86 ± 271.27							
B 1.2278 ± 1.102	5.09	24.40	6.1	21.91	−1.01	2.49	4.82
C −3067.83 ± 132.25	±0.54	±2.26	±0.26	±1.43	±0.8	±3.63	
D 11.0256 ± 0.7232							

[a] $\Delta H^\ominus$ is in kcal mol^{-1} and $\Delta S^\ominus$ in cal mol^{-1} K^{-1}. Calculated from $\Delta H^\ominus = -RA$ or $= -RC$ and $\Delta S^\ominus = RB$ or RD, etc., with $R = 1.9872$ cal mol^{-1} K^{-1}. [b] Values of A, B, C, and D given so the K_{obsd} can be calculated to three significant digits and Ω to two. The value of Ω for the Valentiner equation, $\ln K_b = (A/T) + B \ln T + C$, is 6.58×10^{-8}. The value of B for this fit gives a real heat capacity of −46.5 cal mol^{-1} K^{-1} which is, of course, deemed as anamolous here.

an intermediate in the ammonia reaction is considered and reviewed. Patterson includes[11] evaluation of his own work on the high field conductance of ammonia solutions and offers an opinion that "By disputing the existence of a compound intermediate between completely unreacted NH_3 and NH_4^+ and OH^- writers such as Velden and Ketelaar and Davis (and by the same token Bell) find themselves in conflict with well established experimental fact". We tentatively agree with Patterson's appraisal (see also ref 16b) but add a note of caution, namely, that the various numerical facts which quantify the existence of "I" are in relatively poor agreement with each other. We now turn to an alternative approach which provides confirmatory evidence for the existence of an intermediate in the ammonia reaction.

The observed equilibrium constant (K_{obsd}) for the ammonia ionization is readily shown to be a function of the ancillary equilibrium constants K_1 and K_2 by the equation[16b,c,11b]

$$K_{obsd} = K_1K_2/(1 + K_1) = K_b/(1 + K_1) \qquad (2)$$

Following Sidgwick,[8] K_b might be described as the "true" equilibrium constant between aqueous ammonia and its ions. If K_b and K_1 are assumed to have the simple temperature dependencies

$$\ln K_b = (A/T) + B \qquad (3)$$

and

$$\ln K_1 = (C/T) + D \qquad (4)$$

respectively, then the temperature dependence of K_{obsd} is given by the equation

$$K_{obsd} = \exp[(A/T) + B]/[1 + \exp[(C/T) + D] \qquad (5)$$

The corresponding anomalous heat capacity term[2] related to the ammonia equilibrium is given by the readily derived expression

$$\Delta C_p^\ominus \text{ (anomalous)} = -\left[\frac{K_1}{(1+K_1)^2}\right]\left(\frac{RC^2}{T^2}\right) = -\left[\frac{K_1}{(1+K_1)^2}\right]\left(\frac{\Delta H_1^2}{RT^2}\right) \qquad (6)$$

where R is the gas constant and ΔH_1 is equal to $-RC$ (see eq 4 above).

Following our previous work,[2] we have fitted the data set of Bates and Pinching[17] (11 K_b–T pairs) to eq 5 using the Wentworth–Deming[18,19] algorithm and compared the result for goodness of fit with that from the Valentiner equation using the Gauss criterion (Ω).[2a] The results of these computations are given in Tables I and II. While both equations give good fits, the normalized deviations slightly favor eq 5, a result clearly consistent with the existence of an intermediate. As previously,[2a] the nonlinear analysis provides two different solutions (a and b) for A, B, C, and D, and these quantities along with the related thermodynamic parameters are detailed in Table II. Solution a appears to give values of K_1 which are closer numerically to those determined by other methods (see Table I and footnotes therein). The agreement between our value for K_1 and that of Khakham[10] at 298.16 K is reasonable but we note that the value for K_{obsd} obtained by this author is in rather poor agreement with that reported by Bates and Pinching.[17]

We now turn to the interesting problem of making some decision regarding the structure of the intermediate (I). Since solution a provides K_1 values comparable to previous estimates, our structural considerations are based on the thermodynamic parameters arising from this particular solution. While the enthalpy changes associated with K_1 and K_2 are not particularly informative, we believe that the entropy changes related to K_1 and K_2 are more revealing. Thus we observe that the change in entropy for the first stage (K_1) is large and negative (ca. −22 cal mol^{-1} K^{-1}) but that the change in the second step (K_2), while still negative, is an order of magnitude less (−2 cal mol^{-1} K^{-1}). In brief, entropy considerations favor a "product-like" intermediate. Such an observation is consistent with the existence of a bridged ion-pair intermediate of the type $H_3N^+H{-}O(H){-}H{-}OH^-$.

The hypothesis that the intermediate has considerable ionic character and hence may contribute to part of the high field conductance possibly accounts for the low values of K_1 reported by Patterson.[11] Patterson himself implies that high field measurements might perturb the relative concentrations of the species present in the absence of the field.

Although the present analysis of the temperature dependence of ammonia ionization is good numerically, it is not necessarily unique. This latter observation embraces a wider problem, namely, that there is no infallible guide as to how classical thermodynamics is to be applied to chemical systems because equilibrium constants are invariably phenomenological quantities. More specifically, equilibrium constants are formulated often without complete knowledge of the chemical system to which they refer. Thus the treatment of the ammonia ionization presented here recognizes and corrects an analytical oversight, i.e., it revises the tacit assumption that the all of the unreacted component of the ammonia system is present as a single species. The latter assumption underpins the quantitative examination of most ionogenic reactions.

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(16) (a) Portion in parentheses added to the Patterson quote. (b) It is interesting to reflect that eq 2 was first derived by Kauffman.[16c] However, the thermodynamic significance of this equation, particularly in relation to heat capacities, has been neglected by all subsequent workers. Moore and Winmill appear to have recognized the K_{obsd} could be resolved into the ancillary components K_1 and K_2 via the temperature dependence of K_{obsd}. However, their K_{obsd} values were "classical", i.e., not corrected for ionic strength effects and their analysis is further confused by combining distribution equilibria with the ionic equilibria. The latter unnecessarily complicates the exercise and in this sense Bell's comments are valid. The origin of the postulate of an intermediate in the ammonia reaction is obscure but was probably connected with the disparity observed between the basicity of the primary, secondary, and tertiary amines and the tetraalkylammonium hydroxides. Hantzsch's concept of pseudoacidity and -basicity was also involved. All of these conceptual problems were resolved when the Brönsted definitions of acidity and basicity were proposed together with the important distinction between ionogens and ionophores. (c) Kauffman, H. *Z. Phys. Chem. (Leipzig)* **1904**, *47*, 618.

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When the analytical oversight is corrected, a *new* meaning may be attached to the heat capacity function. Indeed, the meaning of the heat capacity function is contingent entirely upon how we formulate the equilibrium constant for the system. In this way the heat capacity function, either real or anomalous, provides a revealing mechanistic tool.

Nonequivalence of ^{31}P NMR Chemical Shifts of RNA Complexes

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Phosphorus-31 nuclear magnetic resonance (^{31}P NMR) spectroscopy has been used extensively in studies of nucleic acid constituents.[1-6] Recently ^{31}P NMR has been used to investigate helical complexes of larger oligonucleotides[7] and polynucleotides.[8,9] In the study of (dG-dC)$_8$[7] and poly(dG-dC),[8] an important feature of the ^{31}P NMR spectrum of the helical complex is the conversion of a single resonance in low salt into two resonances in high salt. The high salt spectrum is consistent with the results of X-ray diffraction studies of oligomers of (dG-dC),[10] which indicate two different phosphate-backbone conformations, one for ..GpC.. and another for ..CpG.. sequences (Z-DNA). Studies of the crystal structure of d-pApTpApT[11] and a variety of existing physical and chemical data on poly(dA-dT) lead to the hypothesis of an alternating B-DNA structure[12] for poly(dA-dT)·poly(dA-dT). In this model the phosphate backbone is different for ..ApT.. and ..TpA.. sequences in the helical complex. This hypothesis has received experimental support from recent ^{31}P NMR studies[9] of poly(dA-dT) where two phosphorus resonances are observed, depending on the temperature and salt concentration. These data support the general contention that base sequence can affect nucleic acid conformation.[13]

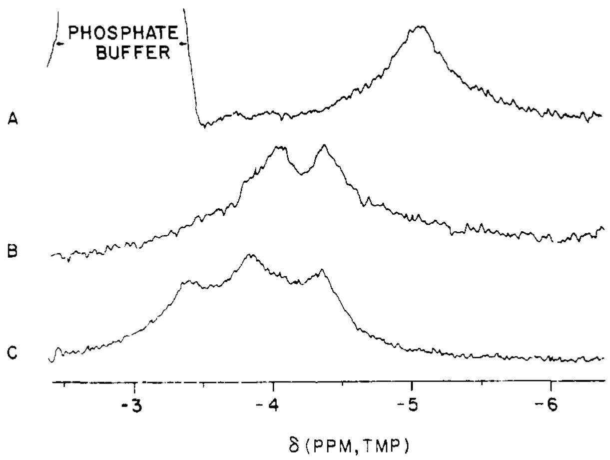

Figure 1. Phosphorus-31 NMR spectra of (A) poly(A$^+$)·poly(A$^+$), (B) poly(A)·poly(U), and (C) poly(A)·2poly(U). Conditions are those indicated in Table I.

Table I. P-31 Chemical Shifts[a] of RNA Helical Complexes

complex[b]	chemical shift, ppm
poly(A$^+$)·poly(A$^+$)	−5.10
poly(A)·poly(U)[c]	−4.10, −4.45
poly(I)·poly(C)[d]	−4.03,[e] −4.54[f]
poly(I)·poly(C$_{12}$U)	−4.03, −4.55
poly(A)·2poly(U)	−3.39,[g] −3.84, −4.36

[a] Maximum intensity position of resonance with respect to internal trimethyl phosphate, 30 °C. [b] Complex is 20–30 mM in base pair, in aqueous solution (20% D$_2$O) containing 0.003 M EDTA, 0.04 M sodium phosphate and NaCl. The solution pHs are 6.8–7.2 except for poly(A$^+$)·poly(A$^+$) (pH 5.6). Concentrations of NaCl are 0.05 M, poly(A$^+$)·poly(A$^+$); 0.1 M, poly(A)·poly(U); 0 and 0.6 M, poly(I)·poly(C); 0.6 M, poly(I)·poly(C$_{12}$U); 0.4 M, poly(A)·2poly(U). [c] Chemical shifts of noncomplexed poly(A) and poly(U) are −3.97 and −3.85, respectively. [d] Chemical shifts of noncomplexed poly(I) and poly(C) are −3.70 and −4.22, respectively. [e] Complexed phosphates of poly(I) strand. [f] Complexed phosphates of poly(C) strand. [g] Complexed phosphates of poly(U) strand involved in Hoogstein base pair with poly(A).

Variation in the structure of the phosphate backbone is also apparent in fibers of nucleic acids.[14,15] Fibers of RNA homopolynucleotide complexes have been extensively studied by X-ray diffraction to deduce their helical conformations. From these studies it is apparent that phosphate-backbone conformations may be dependent not only on the base sequence but also on the nature of the association of bases through hydrogen bonds in polynucleotide complexes. In the cases of complexes with poly(A), three types of base–base association are observed: poly(A$^+$)·poly(A$^+$),[16] poly(A)·poly(U),[17] and poly(A)·2poly(U).[18] The general feature of the phosphate-backbone conformation of the poly(A$^+$)·poly(A$^+$) and poly(A)·poly(U) complexes is that of C_2 symmetry with respect to the helical axis of the double-stranded complex (i.e., the conformation of the phosphate backbone of each strand is identical). In contrast, the fiber structure of the poly(A)·2poly(U) complex is deduced as one in which a unique phosphate-backbone conformation exists for each of the three strands.

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