needles from *n*-hexane and an X-ray study is underway. The nmr spectrum of its chloroform solution is identical with that observed for the directly prepared mixture exhibiting the same over-all composition.

Structural proofs in addition to the nmr were obtained by treating mixtures of various over-all compositions, as well as the isolated $P_4O_6 \cdot 2BH_3$ species, with an excess of nickel tetracarbonyl. First the uncoordinated phosphorus atoms were seen to react with the $Ni(CO)_4$. Then the BH_3 groups are stripped off and replaced by $Ni(CO)_3$ groups. Finally, the well-characterized $P_4O_6[Ni(CO)_3]_4$ complex[1] is obtained, proving that the basic birdcage structure of the P_4O_6 persisted throughout the reactions with diborane.

Equilibria are reached rapidly between the various $P_4O_6 \cdot xBH_3$ complexes in solution, and the distribution of species at equilibrium (see Figure 1) depends only on the over-all BH_3/P_4O_6 mole ratio in solution and has been achieved by using various combinations of starting materials to give the BH_3/P_4O_6 ratio.

When P_4O_6 dissolved in 4 moles or more of $BF_3 \cdot O(C_2H_5)_2$ (less than 4 moles gives two phases) is allowed to stand at room temperature, a slow reaction is observed which is accompanied by the evolution of gaseous products including PF_3, $(C_2H_5)_2O$, and PF_2OPF_2. New peaks also appear in both the P^{31} and F^{19} nmr spectra and have been shown tentatively to include the end and middle groups of the BF_3–B_2O_3 scrambling system. Finally, gels and glasses are obtained for a large range of composition. These data mean that, under these conditions, exchange of bridging oxygens with fluorine atoms takes place between P_4O_6 and BF_3, but an equilibrium is not reached since the PF_3 and PF_2OPF_2 are allowed to escape. Similarly, decomposition of the $P_4O_6 \cdot xBH_3$ complexes is observed at elevated temperatures or long standing.

PF_2OPF_2 is the first recorded member of the μ-oxoperfluoropolyphosphorus family of compounds. It has been isolated and exhibits a molecular weight of 154 (mass spectrometry); calculated 154. In the P^{31} nmr spectra, it was found that $\delta_P = -114.6$ ppm, $J_{P-F_1} = 1380$ cps.

Highly reactive, amorphous, insoluble compounds were immediately precipitated by mixing phosphorus trioxide with BCl_3, BBr_3, BI_3, $AlCl_3$, $AlBr_3$, $GaCl_3$, and $InCl_3$ in various unreactive solvents.

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Weak Bases in Strong Acids. I. On the Hydration of Anilinium Ions in Aqueous Sulfuric Acid[1]

Sir:

The relative base strengths of various classes of amines in dilute aqueous solution were explained a number of years ago in terms of different degrees of specific hydration of the corresponding ammonium ions[2-4] through hydrogen bonds from the acidic ammonium hydrogens to water as an acceptor. An important argument in support of this idea was the regular difference of about 5 cal/mole deg between the entropies of ionization for the methyl representatives of each class of ion: ammonium, primary, secondary, and tertiary. This observed entropy effect was taken as plausible evidence for the ion hydration concept because any ordering of the hydration water molecules should be reflected in the entropy term and the free energy variation through the series from ammonia to trimethylamine is largely entropy controlled.

This interpretation has since gained considerable acceptance[5] and has led to some elaborate equations relating free energy terms such as pK_a's and activity coefficients to hydration numbers.[6] The hydration concept was soon extended, through the leadership of Bell,[7] Wyatt,[8] and Taft,[9] to explain the differing response of weakly basic amines to increasingly strong aqueous acid in which water for hydration of the ammonium ions becomes decreasingly available.[10] However, no data on variation of entropy or heat capacity of the relevant ions have been available for the strong acid–weak base systems to support or refute these extensions from the strong base–weak acid reference point. It is the chief purpose of the present communication to show that the entropy criterion for hydration cannot be used for the aqueous sulfuric acid system over the 10–70% range.

In Tables I and II are presented the thermodynamic data for transfer of anilinium and dimethylanilinium ions from dilute aqueous sulfuric acid to a series of more concentrated acids up to 70%. In each case, the comparison is made relative to the tetraethylammonium ion as an unhydrated standard. The free energy data are calculated from the elegant solubility study of Boyd,[13] and the heats of transfer were measured in a calorimeter described by us recently.[14] Our enthalpy measurements were usually done at amine salt concentrations near 10^{-3} *M*, but $\Delta\bar{H}_s$ was independent of concentration up to 1.5×10^{-2} *M*, showing that solute–solute interactions are negligible at these levels.[15] The partial molar heats of solution of anilinium bisulfate and N,N-dimethylanilinium bisulfate were calculated from the heats obtained by direct injection of the amine from its pure liquid state (l) into the series of sulfuric acid solutions. The reaction in

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[1] Supported by NIH Grant G.M. 10872.

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[11] E. M. Arnett and G. W. Mach, *ibid.*, **86**, 2671 (1964).

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[13] R. H. Boyd, *ibid.*, **85**, 1555 (1963). The equation used to calculate $\Delta\Delta F$ was $\Delta\Delta F = 2RT \ln (f_{\pm\,\text{anilinium}^+\,\text{PCP}^-}/f_{\pm\,\text{TEA}^+\,\text{PCP}^-})$, the factor 2 being required to convert $f_\pm$ to f^+f^-. In this system with the solute at high dilution, the relative free energies and entropies do not depend on the concentration units used.

[14] E. M. Arnett, W. G. Bentrude, J. J. Burke, and P. M. Duggleby, *ibid.*, **87**, 1541 (1965).

[15] The thermodynamic properties described here are not to be confused with those derived in this laboratory through extrapolation for a series of ionic equilibria involving weak bases in dilute aqueous solution.[10]

solution 1 is

$$\text{amine(l)} + H_2SO_4(1) \longrightarrow \text{amine}\cdot H^+(1) + HSO_4^-(1)$$

and in solution 2

$$\text{amine(l)} + H_2SO_4(2) \longrightarrow \text{amine}\cdot H^+(2) + HSO_4^-(2)$$

Subtracting, we have for transferring the reaction from solution 1 to 2

$$\text{amine}\cdot H^+(1)HSO_4^-(1) + H_2SO_4(2) \longrightarrow \text{amine}\cdot H^+(2)HSO_4^-(2) + H_2SO_4(1)$$

Allowance must now be made for transferring from solution 1 to solution 2 the increment of H_2SO_4 needed to protonate the amine. This correction is made using data from the work of Giauque.[16]

When these enthalpies of transfer are combined with the corresponding free energies, the partial molar entropies of transfer (relative to the value in 10% H_2SO_4, *i.e.*, 1.085 *M*) result.[17] Tables I and II show that across all of the observable range of moderately concentrated sulfuric acid, the medium effect on the free energies of solution for the three kinds of ammonium ions relative to each other are almost completely controlled by the enthalpy term. *There is a nearly negligible difference in the way the entropies of solvation for the primary, tertiary, and quaternary anilinium ions respond to variation of acidity.* If these results may be generalized, it follows that the type of entropy argument which was a strong buttress of the original hydration interpretation for strong base ions in water is not applicable to similar ions in strong acid.

Table I. Thermodynamic Properties for Transfer of Anilinium Ion Relative to Tetraethylammonium[a]

Wt % H_2SO_4	$\Delta\Delta F$,[b] kcal/mole	$\Delta\Delta H$,[b,c] kcal/mole	$T\Delta\Delta S$, kcal/mole
10.00	0.00	0.00	0.00
20.00	0.46	0.53	0.07
30.00	1.08	1.43	0.35
40.00	2.05	2.40	0.35
50.00	2.70	3.29	0.59
60.00	3.19	3.50	0.31
70.00	...	3.53	...
80.00	...	3.79	...

[a] *E.g.*, $\Delta\Delta H$ (anilinium) − $\Delta\Delta H$ (tetraethylammonium). [b] $\Delta\Delta F$ and $\Delta\Delta H$ interpolated. To get original numbers (as read from graph), add 0.19 kcal/mole to $\Delta\Delta F$ and −5.77 to $\Delta\Delta H$. [c] Maximum error in ΔH measurements is estimated to be ±0.200 kcal/mole.

Table II. Thermodynamic Properties for Transfer of N,N-Dimethylanilinium Ion Relative to Tetraethylammonium[a]

Wt % H_2SO_4	$\Delta\Delta F$,[b] kcal/mole	$\Delta\Delta H$,[b,c] kcal/mole	$T\Delta\Delta S$, kcal/mole
10.00	0.00	0.00	0.00
20.00	0.22	0.30	0.08
30.00	0.45	1.01	0.56
40.00	1.00	1.49	0.49
50.00	1.37	1.82	0.45
60.00	1.72	1.73	0.01
70.00	1.58	1.46	−0.12
80.00	...	1.07	...

[a] *E.g.*, $\Delta\Delta H$ (N,N-dimethylanilinium) − $\Delta\Delta H$ (tetraethylammonium). [b] $\Delta\Delta F$ and $\Delta\Delta H$ interpolated. To get original numbers (as read from graph), add 0.105 kcal/mole to $\Delta\Delta F$ and −4.77 to $\Delta\Delta H$. [c] Maximum error in ΔH measurements is estimated to be ±0.200 kcal/mole.

A simple calculation shows that this is in accordance with expectation.

Between 10 and 70% sulfuric acid, the change in partial molal entropy of water[16] ($\Delta\bar{S}_{H_2O}$) is only −0.3 cal/deg mole. Employing the usual hydration formalism[9,11] and assuming no hydration of the tetraethylammonium ion through specific hydrogen bonds, we have for the entropy of transfer for a hydrated ion that loses Δn molecules of hydrating water over this acidity range

$$(\bar{S}_{\mathrm{BH^+}}\cdot n_{70}\mathrm{H_2O}) - (\bar{S}_{\mathrm{BH^+}}\cdot n_{10}\mathrm{H_2O}) = (n_{70} - n_{10})\Delta\bar{S}_{\mathrm{H_2O}} = 0.3\Delta n$$

Therefore, even if the anilinium ion lost all of the three water molecules that make up the formal hydration difference between it and the tetraethylammonium ion, it would only result in an entropy of transfer difference of about 1 entropy unit or 0.3 kcal/mole in $T\Delta\Delta S$ across this range. The corresponding change in $\Delta\bar{F}_{H_2O}$ is a decrease of about 1.8 kcal/mole. This is of the right magnitude to account for the $\Delta\Delta F$ values of our ammonium ions, but seems very small for the removal of hydrating water molecules if they are in fact held by strong (say 5–15 kcal/mole) hydrogen bonds such as are implied by the $B—H^+\cdots OH_2$ model.

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[17] In our work, the common anion for the various amines salts is formally the bisulfate anion, while in Boyd's work[13] it is the pentacyanopropenide anion. In each case, the anion contribution cancels out from comparisons of one salt with another.

The Ability of Anionic Detergents to Fold Disordered Polypeptide Chains of Histones in the α-Helical Form[1]

Sir:

According to previous optical rotatory dispersion studies,[2–4] anionic detergents increase the α-helix content of nonhelical proteins. This was concluded on the basis of the observed changes of the Drude constants (λ_c) and the Moffitt constants (b_0). Troitskii recently published a paper[5] in which an extended Moffitt equation[6] of Wada, *et al.*,[7] was applied to proteins, and Troitskii concluded that most of the ordinary globular proteins contain large amounts of the β conformation in addition to the α-helix and disorder. The possible existence of the β form in globular pro-

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