6 H), 1.30 (s, 6 H), 3.16 (sept, 1 H), 3.62 (br s, 1 H); mass spectrum *m/e* 130.0982, calcd for $C_7H_{14}O_2$ 130.0993.

4-Deuterio-2-deuterioxy-2,4-dimethyl-3-pentanone (7-D): nmr $\delta_{TMS}^{CCl_4}$ 1.07 (br s, 6 H), 1.30 (s, 6 H); mass spectrum *m/e* 132.1101, calcd for $C_7H_{12}D_2O_2$ 132.1103.

2-Acetoxy-2,4-dimethyl-3-pentanone (9): nmr $\delta_{TMS}^{CCl_4}$ 1.03 (d, 6 H, J = 7 Hz), 1.45 (s, 6 H), 2.00 (s, 3 H), 2.93 (sept, 1 H); mass spectrum *m/e* 172.1098, calcd for $C_9H_{16}O_3$ 172.1099.

2-Acetoxy-4-deuterio-2,4-dimethyl-3-pentanone (9-D): nmr $\delta_{TMS}^{CCl_4}$ 1.02 (br s, 6 H), 1.46 (s, 6 H), 2.03 (s, 3 H); mass spectrum *m/e* 173.1154, calcd for $C_9H_{15}DO_3$ 173.1162.

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Solvent Effects in Organic Chemistry. XV. Thermodynamics of Solution for Nonelectrolytes in Aqueous Acid and Salt Solutions[1,2]

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Abstract: Partial molar heats of solution ($\Delta\bar{H}_s$) at 25° are reported for a variety of organic compounds of widely differing basicity in aqueous sulfuric acid solutions ranging from dilute to highly concentrated. Comparisons are made of the heats of transfer from weak to strongly acid solutions for a variety of quaternary ammonium salts, strongly basic amines, weak oxygen bases, and several nonelectrolytes which are not protonated by even the most acidic media. There is very little difference between the behavior of salts and nonbasic nonelectrolytes, both of which show only minor changes in $\Delta\bar{H}_s$ across the range of acid solutions. In contrast, basic molecules undergo large changes in $\Delta\bar{H}_s$ as the strength of acid increases from dilute to concentrated, the size of the change being proportional to the pK_a of the base. This is consistent with the correlations between pK_a and heats of ionization in strong acids, which we have reported previously. The large enthalpy changes (*e.g.*, 20 kcal/mol) for the transfer of strongly basic solutes from dilute to concentrated acids are directly attributable to the heat of transfer of sulfuric acid used for protonation from the weakest to the strongest solution. The use of enthalpimetric titration for the determination of pK_a of weak bases appears to fail in aqueous sulfuric acid and to be of dubious value in sulfuric–acetic acid. The enthalpy data in sulfuric acid are compared in a few cases with some obtained in aqueous phosphoric acid. The effect of varying acid concentration on the heat of solution is combined with comparable changes in free energy of solution (from distribution experiments) to generate $\delta\Delta\bar{G}_s$, $\delta\Delta\bar{H}_s$, and $T\delta\Delta\bar{S}_s$ for transfer from water across the whole spectrum of aqueous sulfuric acid solutions for anilinium ion, *N,N*-dimethylanilinium ion (both relative to tetraethylammonium ion), benzonitrile, nitrobenzene, tetrahydrofuran, acetone, and acetophenone. These data provide the first complete thermodynamic analysis for the behavior of solutes in this system. In highly aqueous solutions the normal compensation of $\delta\Delta\bar{H}_s$ and $T\delta\Delta\bar{S}_s$ which we have found in other aqueous binaries is seen. In solutions stronger than *ca.* 30% H_2SO_4, entropies of transfer for all of the above solutes remain nearly constant so that increasingly negative trends in free energy and enthalpy parallel each other. For comparison, heats of solution of several solutes are measured in a number of aqueous salt solutions and complete thermodynamic analyses of $\delta\Delta\bar{G}_s$, $\delta\Delta\bar{H}_s$, and $T\delta\Delta\bar{S}_s$ are given (again these analyses appear to be novel). No general pattern is found, but in the majority of cases free-energy changes are enthalpy controlled. Some discussion is presented of extrathermodynamic relationships between free energies and enthalpies of solution and also of linear enthalpy correlations. This leads to estimates of the acid strengths of HSO_3F (H_0 = −14) and "magic acid," HSO_3F-SbF_5 (H_0 = −18, H_R = −36).

The study of the kinetics and equilibria of acid–base interactions in aqueous acid is of fundamental importance since acid-catalyzed reactions are probably the largest mechanistic class in organic chemistry and aqueous media are the most thoroughly explored systems of solution chemistry. A great deal is known about such processes in dilute aqueous acid (*i.e.*, within the pH range). There are, however, a large number of weak Brønsted bases whose proton transfer equilibria must be studied in much more acidic media. By far the majority of these latter cases have been investigated using aqueous sulfuric acid solutions. Sulfuric acid is a natural choice for such studies since it offers a wide range of acidities, is an excellent ionizing solvent, and is relatively cheap and easy to handle.

An understanding of the kinetics of acid-catalyzed reactions in these solutions is directly dependent upon a knowledge of the acid–base equilibria between the Brønsted base substrates and their conjugate acids in the reactant media. Therefore, any information regarding the thermodynamic behavior of such solutes in aqueous sulfuric acid solutions is relevant to the general problems of equilibrium and kinetic processes in these systems.

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(2) The majority of the results presented here are taken from the doctoral theses of C. F. D. (1965) and J. J. B. (1966).

The first quantitative treatment of acid–base equilibria in strongly acidic solutions was made possible by the development of the H_0 acidity function by Hammett and Deyrup.[3] Over the past 40 years this has been used extensively in the correlation and interpretation of acid-catalyzed reactions.[4–9]

It was hoped originally that H_0 was a singular function of the acidity of the medium itself and that it would be applicable to the protonation of all neutral weak bases. However, as time passed it has become clear that although the acidity function concept is basically sound and broadly useful, no single acidity function can be applied to all types of Brønsted bases. In fact, if high precision is required, each type of basic group and ultimately each basic compound follow their own acidity function.

The application of acidity functions and the relations between them depend ultimately on the extrathermodynamic assumption that linear relationships will hold between the changes of partial molar free energy (*i.e.*, log activity coefficient) for one Brønsted base across a given range of acidity and that of another base across the same range; a similar assumption is made for their protonated (onium) ions. It is now generally recognized that failure of this assumption is the factor which limits the usefulness of acidity functions.

To our knowledge, there are at this writing no reported data on the enthalpies or entropies of transfer in the aqueous sulfuric acid system for neutral basic solutes of any kind except water.[10] The main goal of the work reported here has been to gather enthalpies of transfer for various kinds of solutes across the range of aqueous sulfuric acid solutions in order to determine whether any general patterns of behavior exist which might provide new insight into the problem of solute–solvent interactions in this system.

In this article we will report partial molar heats of solution ($\Delta\bar{H}_s$) for a variety of molecules and ions in aqueous sulfuric acid. In a number of cases we will combine them with activity coefficient data to give a complete thermodynamic account in terms of free energies ($\delta\Delta\bar{G}_s$), enthalpies ($\delta\Delta\bar{H}_s$), and entropies ($T\delta\Delta\bar{S}_s$) of transfer for the solute, or its protonated form, from dilute to concentrated acid. These will be compared with a few similar data for the same solutes in aqueous phosphoric acid and aqueous salt solutions.

Various extrathermodynamic relations between the results will be examined and applied to current problems of acidity functions and the protonation of weak bases in strong acids. The detailed measurements are presented in tables which are chiefly in the Results section. However, the qualitative trends of all important derived data are presented graphically in the Discussion for more cursory reading. A glossary of symbols is presented at the end.

Experimental Section

Sources and Purification of Compounds. Most of the compounds used in this study were available commercially. Liquids were usually dried, using an appropriate agent, and then distilled through a 20 in., vacuum-jacketed column packed with glass helices and rated at six theoretical plates. Solids were usually dried at room temperature in a vacuum oven or dessicator. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Refractive indices were measured using an Abbé refractometer thermostated at 25°. Melting points were obtained with a Thomas-Hoover melting point apparatus.

Acetonitrile, which had been highly purified for use as a solvent in polarography,[11] was obtained from Professor J. Coetzee. Sulfolane (tetramethylene sulfone) was highly purified as for use in the establishment of an acidity function scale.[12] Nitrobenzene was used as received from J. T. Baker Chemical Co. 2,6-Di-*tert*-butylpyridine was a generous gift from Professor H. C. Brown of Purdue University and was used as received.[13,14] Tetraalkylammonium salts were purchased or prepared[15] and were carefully recrystallized and dried. Their purity was established by elemental analysis.[6]

Sulfuric and Phosphoric Acid Solutions. Sulfuric and phosphoric acid solutions were made by diluting either Baker and Adamson CP grade concentrated sulfuric acid or NF grade concentrated phosphoric acid with distilled water. The weight per cent acid in a given solution was usually determined by density measurements at 25°.[10,16]

Sodium chloride, lithium chloride, and potassium iodide of the highest purity available were purchased from Fisher Scientific Co. These were used, without further purification, to make up solutions ranging from approximately 0.5 to 4.0 *N* in 0.5 *N* increments. Distilled water was passed through an ILLCO-WAY ion exchange column (from the Illinois Water Treatment Co., Rockford, Ill.) before it was used to prepare the salt solutions.[17]

The potassium iodide solutions were prepared with distilled water which was freed of oxygen by simultaneous boiling and flushing with argon. These solutions were not stored for any length of time but were prepared immediately prior to use. Early experiments showed that significant amounts of iodine were formed in the iodide solutions when untreated water was used.

At the time when the salts were weighed out to prepare the solutions, three representative samples of each salt were oven-dried to constant weight. The amount of water initially present in each salt was thus determined and the apparent weights of the salts used to make the solutions were then corrected for moisture content. The per cent moisture by weight in NaCl, LiCl, and KI was found to be 0.00, 5.54, and 0.01 respectively.

Enthalpy Measurements. Heats of solution were determined at high dilution in a solution calorimeter such as we have described elsewhere.[18] At least three, and often eight, increments of solute were introduced sequentially into a calorimeter full of the acid or salt solution used as solvent. In all cases the molar heats of solution calculated for these increments were in close agreement and did not change systematically as the solute concentration increased. This demonstrated that partial molar heats were actually being measured without interference from solute–solute interactions.

Precision and Accuracy of the Measurements. Normally the precision was dependent upon the size of the recorder pen deflection.[18] This in turn depends on several factors such as sample

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[3] L. P. Hammett and A. J. Deyrup, *J. Amer. Chem. Soc.*, **54**, 2721 (1932).

[4] I. Zucker and L. P. Hammett, *ibid.*, 61, 2791 (1939).

[5] L. P. Hammett, "Physical Organic Chemistry," 1st ed, McGraw-Hill, New York, N. Y., 1940; 2nd ed, 1970.

[6] F. A. Long and M. A. Paul, *Chem. Rev.*, **57**, 935 (1957).

[7] J. F. Bunnett, *J. Amer. Chem. Soc.*, **83**, 4956, 4968, 4973, 4978 (1971).

[8] C. H. Rochester, "Acidity Functions," Academic Press, New York, N. Y., 1970.

[9] R. K. Boyd in "Solute–Solvent Interactions," J. F. Coetzee and C. D. Ritchie, Ed., Marcel Dekker, New York, N. Y., 1969.

[10] W. F. Giauque, E. W. Hornung, J. E. Kunzler, and T. R. Rubin, *J. Amer. Chem. Soc.*, **82**, 62 (1960).

[11] J. F. Coetzee, G. P. Cunningham, D. K. McGuire, and G. R. Padmanabhan, *Anal. Chem.*, **34**, 1139 (1962).

[12] E. M. Arnett and C. F. Douty, *J. Amer. Chem. Soc.*, **86**, 409 (1964).

[13] The refractive index of this compound, $n^{25}\text{D} = 1.4712$, did not agree with the literature value, $n^{20}\text{D} = 1.5733$.[14] (Corrected $n^{25}\text{D} = 1.5713$ using $\delta n/\delta T = 0.0004$.) However, the nmr spectrum showed no detectable proton-containing impurities and an elemental analysis gave the following results. *Anal.* Calcd for $C_{13}H_{21}N$: C, 81.61; H, 11.06. Found: C, 81.83; H, 11.16. We, therefore, conclude that there was an error in transcribing the literature value for the refractive index.

[14] H. C. Brown and B. Kanner, *J. Amer. Chem. Soc.*, **75**, 3865 (1953).

[15] J. Le Grande Hedrick, M.S. Thesis, University of Pittsburgh, 1962.

[16] G. N. Lewis and M. Randall, "Thermodynamics," McGraw-Hill, New York, N. Y., 1961, p 232.

[17] E. M. Arnett, W. B. Kover, and J. V. Carter, *J. Amer. Chem. Soc.*, **91**, 4028 (1969).

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

Table I. Comparison of $\Delta\bar{H}_s$ Observed with Literature Values for Various Solutes and Solvents

Solute	Solvent	$-\Delta\bar{H}_s$, kcal/mol (obsd at 25°)	$-\Delta\bar{H}_s$, kcal/mol (lit. at 25°)
H_2O	39.94% H_2SO_4	0.336 ± 0.012	0.348[a]
H_2O	50.09% H_2SO_4	0.672 ± 0.009	0.666[a]
H_2O	59.54% H_2SO_4	1.113 ± 0.021	1.098[a]
H_2O	69.63% H_2SO_4	1.870 ± 0.029	1.866[a]
H_2O	80.53% H_2SO_4	3.591 ± 0.045	3.574[a]
H_2O	89.73% H_2SO_4	6.307 ± 0.043	6.360[a]
KCl	H_2O	−4.15 ± 0.03	−4.185 ± 0.001[b]
$(CH_3)_4NCl$	H_2O	−0.94 ± 0.01	−0.975 ± 0.075[c]
Pyridine	H_2O	2.28 ± 0.08	2.320 ± 0.010[d]
CH_3CH_2OH	H_2O	2.43 ± 0.04	2.39 ± 0.02[e]

[a] Reference 10. [b] R. J. Irving and I. Wadsö, *Acta Chem. Scand.*, **18**, 195 (1964). [c] V. B. Parker, "Thermal Properties of Aqueous Uni-Univalent Electrolytes," National Standard Reference Data Series, National Bureau of Standards, No. 2, 1965. [d] L. Sacconi, P. Paoletti, and M. Ciampolini, *J. Amer. Chem. Soc.*, **82**, 3828 (1960). [e] R. Aveyard and A. S. C. Lawrence, *Trans. Faraday Soc.*, **60**, 2265 (1964).

size, heat of solution, and the heat capacity of the system. Where small deflections were measured (10–40 mm) standard deviations as high as ±10% of the $\Delta\bar{H}_s$ values were found, whereas for medium to large deflections (100–200 mm) deviations as low as ±1% were estimated.

Accuracy was maintained by frequent check runs against well-established systems for which high precision data may be found in the literature. The results of some of these comparisons are shown in Table I.

Results

The principal aim in our study has been to obtain a general picture of medium effects on the partial molal thermodynamic properties of solution of various kinds of solutes in aqueous sulfuric acid. We have measured heats of solution for various solutes in aqueous sulfuric acid and have examined these data for general behavior patterns. Heats of solution were measured for amine bases (which give ammonium salts in all of the acid solutions studied), quaternary ammonium salts, neutral molecules, and several compounds which undergo a transition from neutral species to ions at concentrations somewhere between water and concentrated sulfuric acid. This was done in order to allow comparison between enthalpies of solution for ions and neutral molecules as well as compounds which can be either ions or neutral species depending on the acidity of the medium. These are presented in Tables II and III.

Relative Partial Molar Heats of Solution in Aqueous Phosphoric Acid Solutions. Relative partial molar heats of solution ($\Delta\bar{H}_s$) were measured for water and tetraethylammonium bisulfate in aqueous phosphoric acid solutions (up to 85% H_3PO_4). The results of these measurements are tabulated in Table IV. Table V contains $\Delta\bar{H}_s$ values for several organic compounds in this same solvent system.

Relative Partial Molar Heats of Solution in Aqueous Salt Solutions. Relative partial molar heats of solution were measured for the following solutes in aqueous NaCl, LiCl, and KI solutions which ranged from 0.0 to 4.0 *N* in added salt: acetone, butanone, diacetone alcohol, ethanol, *tert*-butyl alcohol, ethyl acetate, and piperidine. These are presented in Table VI.

In all cases, we were able to derive analytical expressions for the behavior of $-\Delta\bar{H}_s$ as a function of salt normality (*N*) by the least-squares method.[19] These equations are listed in Table VII. Also listed in this table are the equations obtained by fitting the data for acetone, diacetone alcohol, butanone, and ethyl acetate in potassium iodide solutions to a straight line.

In all cases where we were able to use a linear equation to describe the experimental results, we also calculated the standard deviation of the slope and intercept of each line according to the method described by Youden.[20] These values can be found in Table VIII.

Calculation of Free Energies of Transfer. Partial molar free energies of transfer were obtained from published solubility or distribution data. It was assumed that at high dilution the solutes obeyed Henry's law (note previous comment regarding lack of solute–solute interactions[18]).

Standard free-energy and entropy values are dependent on the standard state chosen including not only the reference state but also the concentration units. Since molarity is the concentration scale commonly used for handling solutions of aqueous acids and salts, we have used it for our free energies. Sample calculations (see Table IX) showed that except in the most concentrated acid solutions, the free energies of transfer were not strongly dependent on the concentration units.

Comparison of Enthalpy and Free Energy of Transfer for Some Ammonium Ions in Aqueous Sulfuric Acid. Boyd[21] has reported measurements of the dependence of activity coefficients on acid concentration for some ammonium 1,1,2,3,3-pentacyanopropenide (PCP^-) salts in aqueous sulfuric acid up to 70% H_2SO_4. These ingenious experiments take advantage of the very low basicity of this unusual anion as a result of its great resonance stabilization and also of the low solubility and easily observed color of its salts.

He measured activity coefficients by determining the solubility of these solutes in acid solutions where equilibrium was established between the salt in solution and the solid salt. Free energies of transfer can be calculated from his ionic activity coefficients by the expression

$$\delta\Delta\bar{G}_s^{\text{salt}}(\text{a,b}) = 2RT \ln \gamma_2(\pm\text{b})$$

Among the salts studied by Boyd were the following: anilinium$^+$PCP$^-$, *N*,*N*-dimethylanilinium$^+$PCP$^-$, and tetraethylammonium$^+$PCP$^-$. Since we had enthalpies

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(19) I. Klotz, "Chemical Thermodynamics," Prentice-Hall, Englewood Cliffs, N. J., 1957, p 21.

(20) W. J. Youden, "Statistical Methods for Chemists," Wiley, New York, N. Y., 1951.

(21) R. H. Boyd, *J. Amer. Chem. Soc.*, **85**, 1555 (1963); R. H. Boyd and C. Wang, *ibid.*, **87**, 430 (1965).

Table II. $-\Delta \bar{H}_s$ (kcal/mol) of Several Solutes in Aqueous Sulfuric Acid Solutions

% H_2SO_4	Aniline	*N*-Methylaniline	*N*,*N*-Dimethylaniline	2,6,*N*,*N*-Tetramethylaniline	Pyridine	2,6-Dimethylpyridine	2,6-Di-*tert*-butylpyridine	Tri-*n*-butylamine	Acetonitrile
0.00	−0.33 ± 0.07				2.28 ± 0.08	3.68 ± 0.03			0.38 ± 0.04
2.60	7.81 ± 0.16	6.72 ± 0.09	6.33 ± 0.01	6.76 ± 0.40	7.75 ± 0.07	11.14 ± 0.02			
8.01									
8.99									
9.93	7.17 ± 0.09	6.24 ± 0.05	6.16 ± 0.02	6.76 ± 0.04	7.85 ± 0.06	10.91 ± 0.05	5.66 ± 0.28	16.09 ± 0.24	−0.11 ± 0.01
10.19									
19.12		6.08 ± 0.13	6.18 ± 0.04						
20.79	7.35 ± 0.09								−0.44 ± 0.01
21.08				6.83 ± 0.07	8.46 ± 0.08	10.92 ± 0.08	5.07 ± 0.17	15.43 ± 0.22	
21.51									
23.15									
30.09	7.64 ± 0.06	6.96 ± 0.08	7.06 ± 0.11	7.98 ± 0.17	9.50 ± 0.13	11.93 ± 0.06	6.14 ± 0.29	16.07 ± 0.33	−0.45 ± 0.04
30.11									
34.24									
34.98									
38.71							8.38 ± 0.25	17.50 ± 0.15	
39.94	9.10 ± 0.11	8.39 ± 0.10	9.18 ± 0.11		11.37 ± 0.08	13.69 ± 0.10			−0.15 ± 0.01
45.15									
46.20									
49.76				12.74 ± 0.16	13.62 ± 0.26	15.63 ± 0.37	11.25 ± 0.14	20.23 ± 0.27	
50.09									0.41 ± 0.02
52.07	11.24 ± 0.10								
52.09		10.74 ± 0.20	11.78 ± 0.20						
56.04									
57.25									
58.08					15.56 ± 0.10	17.11 ± 0.36			
58.99									
59.25				14.86 ± 0.16			13.52 ± 0.59	22.28 ± 0.59	
59.54									0.82 ± 0.03
61.92	13.85 ± 0.38	13.18 ± 0.10	13.91 ± 0.47						
65.66									
68.31					18.33 ± 0.17	20.28 ± 0.07			
69.63									1.52 ± 0.06
70.09				17.77 ± 0.63			16.23 ± 0.35	25.38 ± 0.05	
71.34	16.99 ± 0.37	16.09 ± 0.20	17.93 ± 0.58						
72.09									
72.86									
73.08									
79.44				21.62 ± 0.50	23.73 ± 0.81	25.02 ± 0.77	21.82 ± 0.14	30.98 ± 1.02	
80.53									2.64 ± 0.04
82.42	19.82 ± 0.24	20.46 ± 0.38	23.18 ± 0.33						
82.48									
87.75									
88.00									
91.87	25.20 ± 0.34	26.83 ± 0.50	29.10 ± 0.56		30.36 ± 0.62	30.99 ± 0.16			
92.15	24.49 ± 0.18			29.55 ± 0.19			25.92 ± 0.33	36.27 ± 0.19	4.99 ± 0.06
96.00									
96.48					31.70 ± 0.27	32.89 ± 0.37			

% H_2SO_4	Sulfolane[a]	Sulfolane[b]	Acetone	Ethanol	Tetrahydrofuran	*N*,*N*-Dimethylformamide	Ethyl acetate	Benzaldehyde	Ethyl ether	Dioxane
0.00	−0.45 ± 0.05	−0.73 ± 0.11	2.44 ± 0.05	2.49 ± 0.09	3.68 ± 0.07	3.8	2.5		4.6	2.1
2.60	−0.72 ± 0.06		2.34 ± 0.06		3.56 ± 0.04					
8.01									3.5	
8.99						3.2	1.7			
9.93	−0.96 ± 0.05	−1.11 ± 0.07		1.63 ± 0.02						
10.19			1.81 ± 0.04		2.71 ± 0.02					
19.12									2.6	
20.79		−1.13 ± 0.20		0.95 ± 0.02		2.8	0.7			
21.08	−1.35 ± 0.03		1.32 ± 0.01		1.93 ± 0.02					
21.51										1.2
23.15								−0.8		
30.09	−1.18 ± 0.02	−1.22 ± 0.08		0.70 ± 0.01						1.3
30.11			1.36 ± 0.11		1.71 ± 0.06					
34.24								−0.5	1.7	
34.98						3.8	0.3			
38.71	−0.66 ± 0.04	−0.54 ± 0.02	1.71 ± 0.01		2.01 ± 0.04					
39.94				0.78 ± 0.03						1.8
45.15						5.6	1.1			
46.20								−0.5	2.3	
49.76	0.44 ± 0.04		2.35 ± 0.12		2.83 ± 0.04					
50.09				1.16 ± 0.02						2.8
52.07		0.58 ± 0.03								
52.09										
56.04								−0.3	2.8	
57.25						7.6	1.9			
58.08										
58.99										3.9
59.25	1.05 ± 0.12		3.07 ± 0.14		3.80 ± 0.05					
59.54				1.68 ± 0.01						
61.92		1.14 ± 0.06							3.4	
65.66						9.3	2.2	0.2		
68.31										
69.63				2.50 ± 0.05						5.2
70.09	1.85 ± 0.06		4.06 ± 0.06		5.08 ± 0.05					
71.34		1.77 ± 0.11								
72.09								1.0		
72.86									4.3	
73.08						10.7	3.1			
79.44	2.74 ± 0.09		4.94 ± 0.08		7.07 ± 0.11					
80.53				4.80 ± 0.07				2.6	5.2	
82.42		3.08 ± 0.07								
82.48						13.9	5.4			
87.75								6.4	8.9	
88.00						16.2	8.0			
91.87						17.8	9.7			
92.15	5.82 ± 0.09	5.40 ± 0.09	10.05 ± 0.48	9.79 ± 0.22	12.98 ± 0.25					
96.00						19.1	10.5	9.2	12.1	
96.48										

[a] 1.4×10^{-1} *m* in H_2O. [b] 2.2×10^{-1} *m* in diphenyl sulfone.

Table III. $-\Delta\bar{H}_s$ (kcal/mol) of Some Tetraalkylammonium Salts in Aqueous Sulfuric Acid Solutions

% H_2SO_4	$(CH_3)_4NCl$	$(CH_3CH_2)_4NCl$	$(CH_3CH_2)_4NHSO_4$	$(CH_3CH_2)_4NClO_4$
0.00	−0.94 ± 0.01	3.09 ± 0.07	6.04 ± 0.63	−7.21 ± 0.14
10.19	−1.29 ± 0.06	1.93 ± 0.02	1.32 ± 0.06	−7.88 ± 0.07
21.08	−1.50 ± 0.03	1.41 ± 0.06	0.82 ± 0.10	−7.84 ± 0.15
30.11	−1.36 ± 0.05	1.58 ± 0.02	0.87 ± 0.04	−7.60 ± 0.01
40.34	−0.64 ± 0.02	2.54 ± 0.07	1.24 ± 0.05	−6.29 ± 0.08
51.89	0.46 ± 0.03	3.65 ± 0.02		
52.39			1.93 ± 0.05	−4.68 ± 0.09
60.38	1.25 ± 0.04	4.44 ± 0.23	2.36 ± 0.01	−4.04 ± 0.05
70.09	2.07 ± 0.11	5.17 ± 0.07	3.17 ± 0.07	−3.75 ± 0.13
82.48			4.89 ± 0.22	−3.55 ± 0.15

Table IV. $-\Delta\bar{H}_s$ (kcal/mol) of H_2O and $(CH_3CH_2)_4NHSO_4$ in Some Aqueous Phosphoric Acid Solutions

% H_3PO_4	H_2O	$(CH_3CH_2)_4NHSO_4$
10.14		3.16 ± 0.04
21.41		3.07 ± 0.05
30.46	0.05 ± 0.01	3.18 ± 0.03
43.24	0.12 ± 0.01	3.62 ± 0.06
53.38	0.24 ± 0.01	3.90 ± 0.01
61.90	0.36 ± 0.01	4.26 ± 0.12
75.96	0.83 ± 0.01	5.32 ± 0.09
84.97	1.30 ± 0.01	6.74 ± 0.18

of transfer for the corresponding bisulfate salts, we were able to make enthalpy–free energy comparisons in this system.

Sample Calculation of the Enthalpy–Free-Energy Relationship for Anilinium and Tetraethylammonium Salts in Aqueous Sulfuric Acid. The free energy terms $\delta\Delta\bar{G}_s^{\text{salt}}$(a,b) for anilinium$^+PCP^-$ and tetraethylammonium$^+$-PCP$^-$ were calculated from eq 1 using Boyd's ($\gamma\pm$) activity coefficients. In order to eliminate the anion from the calculations, the results for tetraethylammonium$^+$-PCP$^-$ were subtracted from those for anilinium$^+$PCP$^-$.

Table V. $-\Delta\bar{H}_s$ (kcal/mol) of Organic Compounds in Aqueous Phosphoric Acid Solutions

% H_3PO_4	$-H_0$	Acetone	Dimethylformamide	Methyl alcohol	Pyridine	Tetrahydrofuran	Water
0		2.5	3.9	1.8	2.4	3.9	
26.50	0.10	2.3	3.8	1.1	9.5	2.9	0.07
33.75	0.40	3.8	3.8	1.1	10.2	2.7	0.1
39.90	0.69	2.2	4.4	1.4	11.0	2.7	0.1
46.70	1.07	2.2	4.7	1.2	11.8	2.7	0.1
50.80	1.36	2.4	4.7	1.1	11.7	2.6	0.3
56.50	1.78	2.4	5.7	1.1	13.0	2.8	0.4
61.90	2.09	2.8	6.6	1.4	14.1	2.8	0.4
64.25	2.34	2.7	6.7	1.3	14.4	3.0	0.5
67.75	2.58	2.7	6.9	1.4	14.2	2.9	0.8

Table VI. $-\Delta\bar{H}_s$ (kcal/mol) of Several Organic Compounds in Aqueous NaCl, LiCl, and KI Solutions

Normality	Acetone	*tert*-Butyl alcohol	Butanone	Ethyl acetate	Diacetone alcohol	Piperidine	Ethanol
				NaCl			
0.512	2.35 ± 0.05	4.00 ± 0.06	2.46 ± 0.03	2.21 ± 0.03	4.16 ± 0.04	5.87 ± 0.05	2.30 ± 0.03
0.980	2.32 ± 0.01	3.66 ± 0.02	2.42 ± 0.02	2.12 ± 0.05	4.10 ± 0.02	5.84 ± 0.06	2.16 ± 0.01
1.495	2.30 ± 0.01	3.40 ± 0.03	2.35 ± 0.02	2.01 ± 0.03	3.96 ± 0.01	5.83 ± 0.04	2.00 ± 0.01
1.973	2.20 ± 0.04	3.22 ± 0.01	2.27 ± 0.01	1.97 ± 0.03	3.94 ± 0.02	5.72 ± 0.04	1.86 ± 0.02
2.533	2.23 ± 0.02	2.94 ± 0.06	2.24 ± 0.03	1.84 ± 0.03	3.82 ± 0.05	5.61 ± 0.05	1.71 ± 0.03
3.005	2.18 ± 0.03	2.69 ± 0.02	2.09 ± 0.05	1.81 ± 0.01	3.70 ± 0.02	5.52 ± 0.04	1.57 ± 0.01
3.532	2.14 ± 0.04	2.51 ± 0.04	2.00 ± 0.04	1.69 ± 0.02	3.53 ± 0.04	5.44 ± 0.05	1.44 ± 0.02
4.019	2.14 ± 0.03	2.26 ± 0.04	1.94 ± 0.00	1.58 ± 0.02	3.40 ± 0.04	5.37 ± 0.03	1.26 ± 0.02
				LiCl			
0.476	2.39 ± 0.03	3.99 ± 0.02	2.54 ± 0.01	2.23 ± 0.04	4.16 ± 0.04	5.97 ± 0.08	2.33 ± 0.03
0.950	2.35 ± 0.01	3.84 ± 0.08	2.50 ± 0.04	2.17 ± 0.03	4.17 ± 0.11	5.96 ± 0.05	2.28 ± 0.01
1.468	2.36 ± 0.05	3.65 ± 0.07	2.48 ± 0.02	2.07 ± 0.02	4.11 ± 0.04	5.89 ± 0.08	2.17 ± 0.03
1.929	2.32 ± 0.03	3.51 ± 0.05	2.49 ± 0.03	2.09 ± 0.03	4.09 ± 0.06	5.79 ± 0.08	2.03 ± 0.02
2.385	2.37 ± 0.06	3.36 ± 0.07	2.43 ± 0.01	2.02 ± 0.02	4.05 ± 0.06	5.84 ± 0.06	2.02 ± 0.02
2.830	2.38 ± 0.02	3.20 ± 0.05	2.45 ± 0.03	1.99 ± 0.02	3.94 ± 0.02	5.83 ± 0.08	1.92 ± 0.03
3.290	2.37 ± 0.01	3.09 ± 0.02	2.38 ± 0.04	1.98 ± 0.01	3.94 ± 0.07	5.86 ± 0.05	1.89 ± 0.03
3.785	2.39 ± 0.04	2.96 ± 0.03	2.43 ± 0.02	1.89 ± 0.03	3.95 ± 0.04	5.97 ± 0.09	1.78 ± 0.03
				KI			
1.001	2.39 ± 0.01	3.43 ± 0.03	2.53 ± 0.03	2.22 ± 0.02	4.08 ± 0.02	5.78 ± 0.08	2.05 ± 0.02
2.000	2.28 ± 0.02	2.76 ± 0.03	2.32 ± 0.03	2.04 ± 0.02	3.87 ± 0.06	5.55 ± 0.01	1.70 ± 0.02
3.000	2.20 ± 0.02	2.10 ± 0.03	2.09 ± 0.02	1.80 ± 0.03	3.43 ± 0.05	5.30 ± 0.04	1.28 ± 0.03
4.000	2.00 ± 0.03	1.45 ± 0.01	1.84 ± 0.04	1.52 ± 0.02	3.10 ± 0.05	4.96 ± 0.11	0.96 ± 0.03

Table VII. Equations Describing the Behavior of $-\Delta\bar{H}_s$ (kcal/mol) of Various Solutes as a Function of the Normality (N) of Aqueous NaCl, LiCl, and KI Solutions

	$-\Delta\bar{H}_s$, kcal/mol		
Solute	LiCl	NaCl	KI
Acetone	$2.37 + 0.002\,N$	$2.37 - 0.063\,N$	$2.43 - 0.093\,N$ $2.38 + 0.024\,N - 0.029\,N^2$
Butanone	$2.54 - 0.037\,N$	$2.56 - 0.152\,N$	$2.64 - 0.0186$ $2.57 - 0.049\,N - 0.034\,N^2$
Piperidine	$6.00 - 0.043\,N$	$6.04 - 0.169\,N$	$6.09 - 0.278\,N$
Ethyl acetate	$2.26 - 0.094\,N$	$2.28 - 0.168\,N$	$2.34 - 0.186\,N$ $2.27 - 0.036\,N - 0.039\,N^2$
Diacetone alcohol	$4.22 - 0.082\,N$	$4.28 - 0.204\,N$	$4.32 - 0.291\,N$ $4.24 - 0.120\,N - 0.043\,N^2$
Ethanol	$2.41 - 0.169\,N$	$2.44 - 0.289\,N$	$2.42 - 0.370\,N$
tert-Butyl alcohol	$4.13 - 0.315\,N$	$4.15 - 0.473\,N$	$4.10 - 0.664\,N$

Table VIII. Standard Deviations of Intercepts and Slopes for Equations Listed in Table VII

	LiCl		NaCl		KI	
Solute	Intercept	Slope	Intercept	Slope	Intercept	Slope
Acetone	±0.01	±0.006	±0.01	±0.005		
Butanone	±0.01	±0.005	±0.01	±0.006		
Piperidine	±0.04	±0.016	±0.02	±0.008	±0.03	±0.012
Ethyl acetate	±0.01	±0.005	±0.01	±0.005		
Diacetone alcohol	±0.02	±0.009	±0.02	±0.008		
Ethanol	±0.01	±0.005	±0.01	±0.003	±0.01	±0.005
tert-Butyl alcohol	±0.02	±0.008	±0.09	±0.041	±0.02	±0.007

Table IX. Free Energies of Transfer for Tetrahydrofuran in Aqueous Sulfuric Acid Solutions, Calculated Using Molar (c), Molal (m), and Mole Fraction (N) Units for Solute Concentration

% H_2SO_4[a]	$[\delta\Delta\bar{G}_s^{\text{solute}}(\text{a,b})]_c$, kcal/mol	$[\delta\Delta\bar{G}_s^{\text{solute}}(\text{a,b})]_m$, kcal/mol	$[\delta\Delta\bar{G}_s^{\text{solute}}(\text{a,b})]_N$, kcal/mol
0.0	0.000	0.000	0.000
20.0	0.150	0.228	0.123
30.0	0.071	0.188	0.022
40.0	−0.27	−0.11	−0.35
50.0	−0.89	−0.69	−1.00
60.0	−1.8	−1.6	−2.0
70.0	−2.8	−2.5	−3.0

[a] (a) taken as 0.0% H_2SO_4.

The $\delta\Delta G$ data were then plotted *vs.* per cent H_2SO_4 and values of $\delta\Delta G$ were interpolated from this graph starting at 10.00% and going up to 60.00% H_2SO_4 in 10.00% intervals, taking 10.00% H_2SO_4 as the reference point. The standard state is the hypothetical 1 *M* solute in water.

The enthalpy data for anilinium bisulfate and tetraethylammonium bisulfate were handled in much the same way; however, we first plotted the original $\Delta\bar{H}_s$ data, then interpolations were made, and differences $[\delta\Delta\bar{H}_{(\text{a,b})}]$ were taken. Finally, entropies of transfer were calculated from free-energy and enthalpy data as follows.

$$T\delta\Delta\bar{S}_{(\text{a,b})} = \delta\Delta\bar{H}_{(\text{a,b})} - \delta\Delta\bar{G}_{(\text{a,b})}$$

Discussion

Amines. Behavior of Ammonium Ions. Relative partial molar heats of solution were measured for the following amines in aqueous sulfuric acid solutions (from ~3 to 93% H_2SO_4): tri-*n*-butylamine, pyridine, 2,6-dimethylpyridine, 2,6-di-*tert*-butylpyridine, aniline, *N*-methylaniline, *N*,*N*-dimethylaniline, and 2,6,*N*,*N*-tetramethylaniline. These measurements are presented in Table II.

All of the above-mentioned amines are completely protonated across the entire acid region studied. Therefore, one might naively expect that changes in the heat of solution for a given amine as a function of acid concentration would be quite small. In fact, very large changes are observed for all amines. For instance, the heat of solution of pyridine in 97% H_2SO_4 is approximately 24 kcal/mol more exothermic than the heat of solution of pyridine in 10% H_2SO_4.

In order to understand the reason for this increase in exothermicity with increasing acid concentration, it is instructive to examine the equations which describe the reaction of 1 mol of base (such as an amine) in its pure liquid state (L) with 1 mol of sulfuric acid at two different acid concentrations (a and b).

The first step is the heat of solution of the pure base (B) from its liquid state (L) into solution a or b. The heat change associated with this will be (for example) into solution a

$$\Delta\bar{H}_s{}^{\text{B}} = \bar{H}^{\text{B}}(\text{a}) - \bar{H}^{\text{B}}(\text{L}) \qquad (1)$$

The heat of transfer for 1 mol of pure unprotonated base from infinite dilution in acid solution a to solution b is therefore

$$\delta\bar{H}^{\text{B}}(\text{a,b}) = \bar{H}^{\text{B}}(\text{b}) - \bar{H}^{\text{B}}(\text{a}) \qquad (2)$$

using the symbol δ as an operator to represent medium change.

For strongly basic solutes, such as the amines, which are protonated completely in both solutions, this term obviously cannot be determined experimentally. However, by analogy to the behavior of weakly basic solutes (such as acetonitrile which is described in a later section), we would expect this term to amount to only 1 or 2 kcal/mol across the whole range of acidity. We will see in the following analysis that it can probably be ignored safely in its contribution to the change in observed heat of reaction for the base from solution a to b.

The protonation reaction in solution a occurs as follows

$$\mathrm{B\,(a) + H_2SO_4\,(a) = BH^+\,(a) + HSO_4^-\,(a)} \quad (3)$$

for which the heat change is

$$\Delta\bar{H}^{\mathrm{reaction}}(\mathrm{a}) = \bar{H}^{\mathrm{BH^+}}(\mathrm{a}) + \bar{H}^{\mathrm{HSO_4^-}}(\mathrm{a}) - \bar{H}^{\mathrm{H_2SO_4}}(\mathrm{a}) - \bar{H}^{\mathrm{B}}(\mathrm{a}) \quad (4)$$

If eq 4 is subtracted from the corresponding equation for the protonation reaction in solution b we have

$$\delta\Delta\bar{H}^{\mathrm{reaction}}(\mathrm{a,b}) = (\bar{H}_{\mathrm{b}}^{\mathrm{BH^+}} - \bar{H}_{\mathrm{a}}^{\mathrm{BH^+}}) + (\bar{H}_{\mathrm{b}}^{\mathrm{HSO_4^-}} - \bar{H}_{\mathrm{a}}^{\mathrm{HSO_4^-}}) - (\bar{H}_{\mathrm{b}}^{\mathrm{H_2SO_4}} - \bar{H}_{\mathrm{a}}^{\mathrm{H_2SO_4}}) - (\bar{H}_{\mathrm{b}}^{\mathrm{B}} - \bar{H}_{\mathrm{a}}^{\mathrm{B}}) \quad (5)$$

which we can rewrite for the terms in parentheses

$$\delta\Delta\bar{H}^{\mathrm{reaction}}(\mathrm{a,b}) = \delta\bar{H}^{\mathrm{salt}}(\mathrm{a,b}) - \delta\bar{H}^{\mathrm{acid}}(\mathrm{a,b}) - \delta\bar{H}^{\mathrm{base}}(\mathrm{a,b}) \quad (6)$$

where the first two terms on the right side of eq 6 represent the heat of transfer for 1 mol of salt ($\mathrm{BH^+\ HSO_4^-}$) or 1 mol of acid from infinite dilution in solution a or b. These two terms can be evaluated directly in several cases and if we assume, as suggested above, that the last term in eq 6 is negligible, we can test the overall consistency of our analysis as follows.

The term $\delta\bar{H}_{\mathrm{s}}^{\mathrm{acid}}(\mathrm{a,b})$ can be evaluated for the reaction of piperidine in (a) 34.67% H_2SO_4 and (b) 96.48% H_2SO_4 using the data in Table X. For this salt $\delta\bar{H}_{\mathrm{s}}^{\mathrm{salt}}(\mathrm{a,b}) = -5.8$ kcal/mol while the value for $\delta\Delta\bar{H}^{\mathrm{reaction}}(\mathrm{a,b}) = -19.2$ kcal/mol. Therefore $\delta\bar{H}_{\mathrm{s}}^{\mathrm{acid}}(\mathrm{a,b})$ (eq 5) is equal to 13.6 kcal/mol. In other words, *most (14 kcal/mol) of the large difference (19.2 kcal/mol) between the heat of solution for piperidine in 34.67% H_2SO_4 and in 96.48% H_2SO_4 is due to the transfer of the H_2SO_4 from one acid solution to the other.*

Table X. $-\Delta\bar{H}_{\mathrm{s}}$ (kcal/mol) for Piperidine, Piperidine Hydrochloride, Tetraethylammonium Chloride, and Tetraethylammonium Bisulfate in 34.67 and 96.48% H_2SO_4

Compound	34.67% H_2SO_4	96.48% H_2SO_4
Piperidine	20.7 ± 0.2	39.9 ± 0.3
Piperidine hydrochloride	−3.2 ± 0.2	2.6 ± 0.1
Tetraethylammonium chloride	1.5 ± 0.1	10.6 ± 0.4
Tetraethylammonium bisulfate	0.81 ± 0.01	9.3 ± 0.3

Table XI. Variation of $-\Delta\bar{H}^{\mathrm{reaction}}(\mathrm{b})$, $-\delta\Delta\bar{H}^{\mathrm{reaction}}(\mathrm{a,b})$, $\delta\Delta\bar{H}^{\mathrm{acid}}(\mathrm{a,b})$, and $-\delta\Delta\bar{H}^{\mathrm{salt}}(\mathrm{a,b})$ for Tri-*n*-butylamine as a Function of Acid Concentration

% H_2SO_4 (b)	$-\Delta H^{\mathrm{reaction}}(\mathrm{b})$, kcal/mol	$-\delta\Delta H^{\mathrm{reaction}}(\mathrm{a,b})$, kcal/mol	$\delta\Delta\bar{H}^{\mathrm{acid}}(\mathrm{a,b})$, kcal/mol	$-\delta\Delta\bar{H}^{\mathrm{salt}}(\mathrm{a,b})$, kcal/mol
9.93	16.09	0.09	−0.003	0.09
21.08	15.43	−0.57	0.937	−1.51
30.09	16.07	0.07	2.438	−2.37
38.71	17.50	1.50	4.271	−2.77
49.76	20.23	4.23	6.587	−2.36
59.25	22.28	6.28	8.517	−2.24
70.09	25.38	9.38	10.943	−1.56
79.44	30.98	14.98	13.504	1.48
92.15	36.27	20.27	16.781	3.49

This heat term associated with $\delta\Delta\bar{H}_{\mathrm{s}}^{\mathrm{reaction}}(\mathrm{a,b})$ can also be evaluated independently by using results reported by Giauque, *et al.*[10] From their data $\delta\bar{H}_{\mathrm{s}}^{\mathrm{acid}}(\mathrm{a,b}) = 13.61$ kcal/mol may be estimated, which is in excellent agreement with that derived from our data.

The data of Giauque, *et al.*,[10] cover the concentration range from approximately 10 to 100% H_2SO_4. We can therefore correct our heat measurements for the amines to take into account the heat of transfer of the acid increment from one solution to another. This enables us to calculate the heat changes for transfer of the bisulfate salt of a given amine from one solution to another across the entire range of sulfuric acid concentrations. The heats of solution for all of the amines studied were corrected using this method.

A detailed example of the use of this procedure for the case of tri-*n*-butylamine is given here as a sample calculation. In this treatment for convenience (a) will always be taken to be 10.00% H_2SO_4 while (b) will vary across the entire range of acid concentrations studied. The heats of transfer for the bisulfate salt of the amine are calculated using eq 6.

The value of $\delta\Delta\bar{H}_{\mathrm{s}}^{\mathrm{reaction}}(\mathrm{a})$, where (a) is 10.00% H_2SO_4, is interpolated from a plot of our experimental data. Similarly, the values of $\delta\bar{H}^{\mathrm{acid}}(\mathrm{a,b})$ are obtained by interpolation (where necessary) from Giauque's data.[10] The results for tri-*n*-butylamine are shown in Table XI.

The results are plotted in Figure 1 from which it is clear that the major portion of the exothermic change in the heat of solution of the base $[-\delta\Delta\bar{H}_{\mathrm{s}}^{\mathrm{reaction}}(\mathrm{a,b})]$, on going from 10 to 93% H_2SO_4, is due to the acid transfer process, since the difference term $[-\delta\Delta\bar{H}_{\mathrm{s}}^{\mathrm{salt}}(\mathrm{a,b})]$ associated with the transfer of the bisulfate salt shows either an endothermic or small exothermic contribution across this same region. The acid term $[\delta\Delta\bar{H}_{\mathrm{s}}^{\mathrm{acid}}(\mathrm{a,b})]$ is independent of the base, provided that the latter is completely protonated in all of the acid solutions considered.

The derived values of $[\delta\bar{H}_{\mathrm{s}}^{\mathrm{salt}}(\mathrm{a,b})]$ for pyridine, 2,6-dimethylpyridine, and 2,6-di-*tert*-butylpyridine are shown in Figure 2 and for aniline, *N*-methylaniline, *N*,*N*-dimethylaniline, and 2,6,*N*,*N*-tetramethylaniline in Figure 3.

The behavior of $[-\delta\bar{H}_{\mathrm{s}}^{\mathrm{salt}}(\mathrm{a,b})]$ as a function of acid concentration is quite similar for all of the amines studied. This heat quantity first displays a slight endothermic trend in the region 10–40% H_2SO_4 with a minimum in the region 40–60% acid and finally increasing exothermic behavior between 60 and 93% H_2SO_4.

However, there are clear differences in the specific behavior of $[-\delta\bar{H}_{\mathrm{s}}^{\mathrm{salt}}(\mathrm{a,b})]$ for different aniline bases

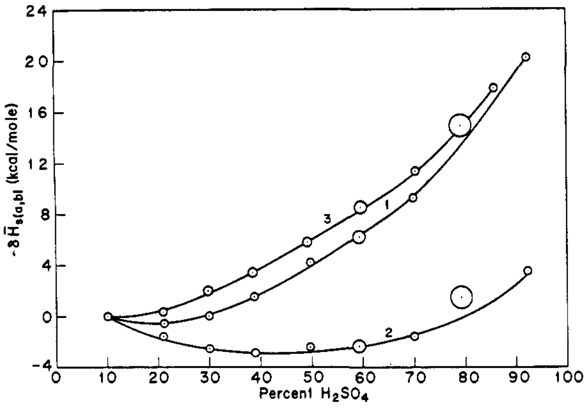

Figure 1. Variation of $[-\delta\Delta H_s^{\text{reaction}}(\text{a,b})]$ (curve 1), $[\delta\bar{H}_s^{\text{salt}}(\text{a,b})]$ (curve 2), and $[\delta\bar{H}_s^{\text{acid}}(\text{a,b})]$ (curve 3) for tri-*n*-butylamine as a function of acidity in aqueous sulfuric acid.

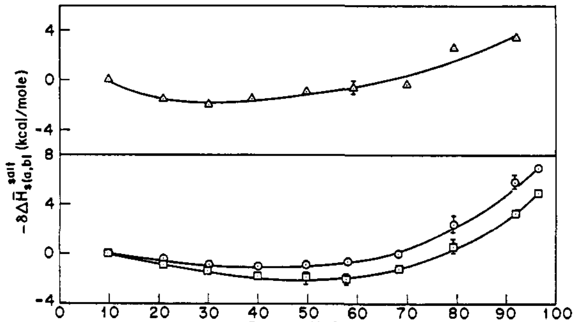

Figure 2. Variation of $[-\delta\bar{H}_s^{\text{salt}}(\text{a,b})]$ for several pyridines as a function of acidity in aqueous sulfuric acid: pyridine (—○—), 2,6-dimethylpyridine (—□—), 2,6-di-*tert*-butylpyridine (—△—).

(Figure 3). There appears to be a rough correlation between the degree of substitution and the rate of change of $[-\delta\bar{H}_s^{\text{salt}}(\text{a,b})]$ in these cases, but this correlation does not accommodate the curves for the pyridine bases (Figure 2).

Probably the most important fact that emerges from these data is that *the overall behavior of* $[-\delta\bar{H}_s^{\text{salt}}(a,b)]$ *is primarily a function of acid strength and not of the molecular structure of the salt.* It is not known if this effect is general for different kinds of salts. We examined a number of alkali metal salts such as $NaHSO_4$, $KHSO_4$, etc., to test this question, but none was found to be soluble and stable over the entire range of H_2SO_4 concentrations.

A check on the consistency of these results is provided by the relative partial molar heats of solution for tetramethylammonium chloride, tetraethylammonium bisulfate, and tetraethylammonium perchlorate in these same solutions. These measurements are tabulated in Table III. The chloride salts could not be studied reliably in acid concentrations beyond about 70% H_2SO_4 because the chloride anion was protonated.

A comparison of the directly measured $[-\delta\bar{H}_s^{\text{salt}}(\text{a,b})]$ for tetraethylammonium bisulfate with the derived value for 2,6,*N*,*N*-tetramethylaniline, which should be a good model, is displayed in Figure 4. The trends for these salts as a function of acid concentration are virtually identical thus supporting the treatment for the liquid amines. The generality of the behavior is shown by comparison with Figure 5.

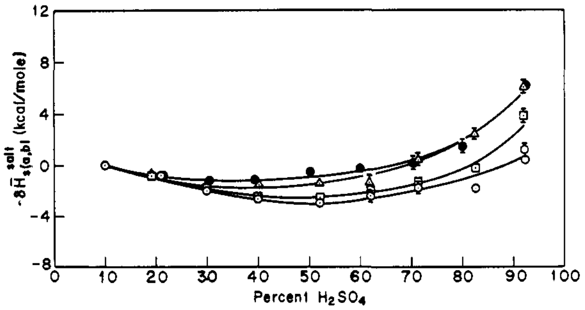

Figure 3. Variation of $[-\delta\bar{H}_s^{\text{salt}}(\text{a,b})]$ for several anilines as a function of acidity in aqueous sulfuric acid: aniline (—○—), *N*-methylaniline (—□—), *N*,*N*-dimethylaniline (—△—), 2,6,*N*,*N*-tetramethylaniline (—●—).

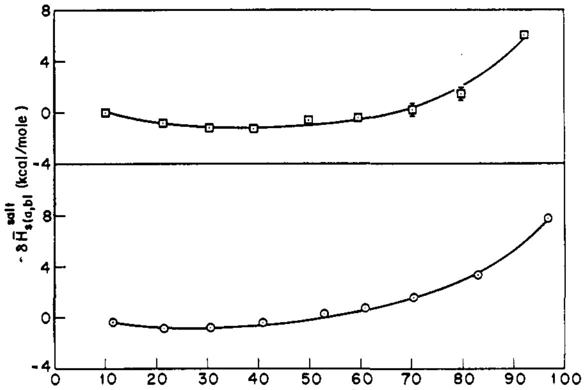

Figure 4. Variation of $[-\delta\bar{H}_s^{\text{salt}}(\text{a,b})]$ for tetraethylammonium bisulfate and 2,6,*N*,*N*-tetramethylaniline as a function of aqueous sulfuric acid concentration: tetraethylammonium bisulfate (—○—), derived value for 2,6,*N*,*N*-tetramethylaniline (—□—).

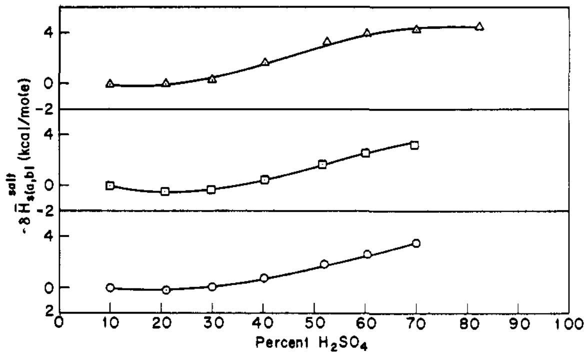

Figure 5. Variation of $[-\delta\bar{H}_s^{\text{salt}}(\text{a,b})]$ for several quaternary ammonium salts as a function of aqueous sulfuric acid concentration: tetramethylammonium chloride (—○—), tetraethylammonium chloride (—□—), tetraethylammonium perchlorate (—△—).

These results give a qualitative picture of the general behavior of the heats of solution and heats of transfer of ammonium salts in aqueous sulfuric acid solutions. It would be natural to expect a completely different kind of enthalpy behavior for solutes which are present as neutral molecules in all of these same acid media. Data for such solutes can be used to estimate the pattern of the heats of solution of strongly basic amines if they were not protonated. In addition, data for neutral solutes and organic ions should allow us to understand the behavior of solutes which become

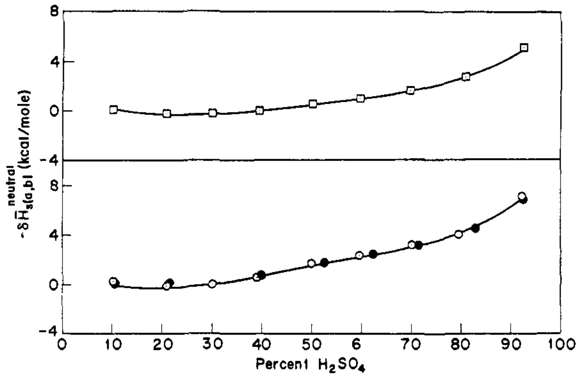

Figure 6. Variation of $[-\delta\bar{H}_s^{\text{neutral}}(a,b)]$ for acetonitrile and sulfolane as a function of aqueous sulfuric acid concentration: acetonitrile (—□—), sulfolane with water (—○—), sulfolane with phenyl sulfone (—●—).

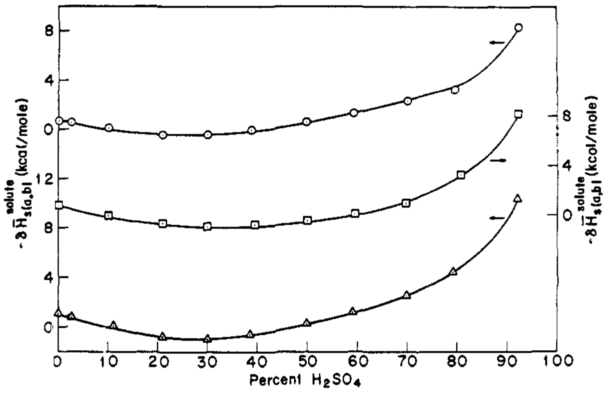

Figure 7. Variation of $[-\delta\bar{H}_s^{\text{solute}}(a,b)]$ for some oxygen bases as a function of concentration of aqueous sulfuric acid: acetone (—○—), ethyl alcohol (—□—), tetrahydrofuran (—△—).

protonated in the region between 10 and 90% H_2SO_4 (*e.g.*, oxygen bases).

With these aims in mind let us now examine the experimental results which were obtained for some compounds which are probably not protonated at all in concentrated sulfuric acid.

Neutral Nonbases. The relative partial molar heats of solution for sulfolane and acetonitrile in various sulfuric acid solutions (from ~3 to 93% H_2SO_4) have been measured and are displayed in Figure 6, both of which are essentially unprotonated[12,22,23] in all of these media.

Sulfolane is a solid at room temperature and its melting point (28.37°) was lowered in order to make it liquid at 25° by the addition of a small amount (about 1 mol %) of either water (0.14 *m*) or diphenyl sulfone (0.22 *m*). The heats of solution for sulfolane were found to be independent, within our experimental error, of the impurity added.

The formal description for the processes involving neutral molecules is similar to the treatment for amines except that we need not be concerned in these cases with the complication introduced by protonation. We may, therefore, describe the processes by the following equation in which subscripts and operators have the same meaning as in eq 1-6

$$\Delta\bar{H}_s^{\text{neutral}}(\text{b}) - \Delta\bar{H}_s^{\text{neutral}}(\text{a}) = \delta\Delta\bar{H}_s^{\text{neutral}}(\text{a,b}) \quad (7)$$

which represents the difference between the heat of solution of the neutral, nonbasic solute in solution a and solution b with no protonation in either medium. Referred to a standard medium, say 10% H_2SO_4, this corresponds to $\delta\bar{H}_s^{\text{neutral}}(\text{a,b})$, the heat of transfer for the solute from high dilution in the standard to high dilution in medium b.

The changes in $[\delta\bar{H}_s^{\text{neutral}}(\text{a,b})]$ for acetonitrile and for sulfolane as a function of acid concentration are shown in Figure 6. An examination of these curves leads us to the unanticipated conclusion that *there are no striking differences between the enthalpies of transfer for ammonium salts and nonbasic nonelectrolytes* throughout the range of sulfuric acid solutions studied. Acetonitrile (Figure 6) and tetraethylammonium bisulfate (Figure 4) display virturally identical changes as a function of acid concentration.

We now have a general picture of how the enthalpy of solution varies for a number of ammonium ions and nonbasic neutral molecules as a function of sulfuric acid concentration. With this in mind, we wish to turn our attention to the behavior of weak oxygen bases which undergo the transition from nonbasic neutral molecules to oxonium ions somewhere between 10% and concentrated sulfuric acid.

Weak Oxygen Bases. Behavior of Solutes Which Undergo a Transition from Neutral Molecules to Oxonium Ions in H_2SO_4 of Intermediate Strength. We have obtained the relative partial molar heats of solution for the following three oxygen bases in aqueous H_2SO_4: acetone, ethyl alcohol, and tetrahydrofuran. The results are given in Table II and presented in Figure 7. The heats of solution are represented by the symbol $[\delta\bar{H}_s^{\text{solute}}(\text{a,b})]$ where (a) is taken as 10.00% H_2SO_4 and (b) varies over the entire concentration range studied.

The overall behavior of these solutes is quite similar to that seen for other ions and molecules. The curves do not display any sudden inflections which might be indicative of protonation.[23] However, one noticeable difference we observe for these oxygen bases is that the overall enthalpy changes are somewhat larger than those seen for ammonium ions or neutral molecules. Furthermore, the rate of change of $[\delta\bar{H}_s^{\text{solute}}(\text{a,b})]$, especially for the higher acid concentrations, is greater for these solutes than for either ammonium salts or nonelectrolytes.

Although it is possible to derive formal expressions for curves such as these,[27] their application requires knowledge of the behavior of a model ammonium ion and also the pK_{BH^+} of the base in question as well as

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(22) M. Liler and D. Kosanovic, *J. Chem. Soc.*, 1084 (1958).

(23) The "pK_{BH^+}" value, which is a measure of the H_0 acid strength required to cause the base to be half-protonated, and the weight per cent sulfuric acid concentrations corresponding to this "pK_{BH^+}" value are given below for each of the compounds studied: acetone, "pK_{BH^+}" = −7.2,[24] 81.50% H_2SO_4; ethyl alcohol, "pK_{BH^+}" = −1.94 (see ref 41), 45.40% H_2SO_4, see also ref 25; tetrahydrofuran, "pK_{BH^+}" = −2.08,[26] 34.50% H_2SO_4.

(24) N. C. Deno and M. J. Wisotsky, *J. Amer. Chem. Soc.*, **85**, 1735 (1963); H. J. Campbell and J. T. Edward, *Can. J. Chem.*, **38**, 1518 (1960).

(25) J. T. Edward, J. B. Leane, and I. C. Wang, *ibid.*, **40**, 1521 (1962).

(26) E. M. Arnett and C. Y. Wu, *J. Amer. Chem. Soc.*, **84**, 1684 (1962).

(27) J. J. Burke, Ph.D. Thesis, University of Pittsburgh, 1966, pp 62–66.

Table XII. Summary of Results for Enthalpimetric Titration of Various Bases in Sulfuric–Acetic Acid Solutions

Acid system and compd	Estd by enthalpimetric titration "pK_{BH^+}"	 ΔH_i, kcal/mol	Lit. values in aqueous acid pK_a	 $\Delta H_i°$, kcal/mol
Aqueous sulfuric acid	4.66 ± 0.09	7.0	4.64[a]	7.28[j]
Aniline				
Pyridine	5.3	4.9	5.29[b]	4.72[j]
Sulfuric–acetic acid				
Water	−2.13	3.74	−2.35[c] (in perchloric–acetic acid)	
Methyl alcohol	−2.61	2.8	−4.7[d]	
Ethyl alcohol	−2.60	2.8	−4.6[d] est. −1.94[k]	
sec-Butyl alcohol	−2.35	2.56	−2.16[e]	
Allyl alcohol	−2.67	1.96	−3.28[e]	
2-Chloroethyl alcohol	−3	1.44	−3.82[e]	
4-Chloro-2-nitroaniline	−1.1	6.2	−1.03[f]	
2,5-Dichloro-4-nitroaniline	−1.6	6.3	−1.78[g]	
2,6-Dichloro-4-nitroaniline	−4.0	2.6	−2.4[g]	
Benzanilide	−2.4	3.1	−3.2[h]	
1,5,5-Trimethyl-3-methylenecyclohexene	−2.64	1.4	−3.27[i]	

[a] Reference 28. [b] H. H. Jaffe and G. O. Doak, *J. Amer. Chem. Soc.*, **77**, 4441 (1955). [c] H. Lemaire and H. J. Lucas, *ibid.*, **73**, 5198 (1951). [d] These values were estimated using the $pK_a - \Delta\bar{H}_{HSO_3F}{}^{prot}$ relationship outlined by Arnett, Quirk, and Burke, ref 33. [e] J. N. Anderson, Thesis, University of Pittsburgh, 1964. [f] M. A. Paul and F. A. Long, *Chem. Rev.*, **57**, 1 (1957). [g] M. J. Jorgenson and D. R. Hartter, *J. Amer. Chem. Soc.*, **85**, 878 (1963). [h] Reference 31. [i] N. C. Deno, *et al.*, *J. Amer. Chem. Soc.*, **85**, 2998 (1963). [j] Reference 29. [k] D. J. Lee and R. Cameron, *J. Amer. Chem. Soc.*, **93**, 4724 (1971).

the correct acidity function for protonation of the solute, none of which are available.

Enthalpimetric Titrations. We had hoped originally that a titration curve could be resolved for weak bases such as those shown in Figure 7. If the heat of ionization were large compared to solvent effects on the heats of solution of the free base and its onium ion, we reasoned that a sharp inflection might be found whose height would correspond to the strength of acid in which the base was half-ionized. A successful "enthalpimetric titration" for aniline was obtained in a series of aqueous potassium biphthalate buffered solutions. From it a pK_{BH^+} of 4.66 ± 0.9 and ΔH_i = 7.0 can be estimated in agreement with literature values of 4.63[28] and 7.28[29] obtained by conventional means. In view of our previous discussion, it is apparent that a major cause of the failure of enthalpimetric titrations for weak bases in strong acid must be the relatively large contribution from $\delta\Delta\bar{H}_s{}^{acid}$, the changing heat of transfer of sulfuric acid across the region of protonation. The titration curve for neutralization of the base is simply swamped by the other large heat terms. In dilute aqueous acid within the pH range the heats of transfer of the acid, base, and salt are negligible compared to the heat of neutralization of the base and a good enthalpimetric titration curve can be obtained.

An important part of the heat of transfer of sulfuric acid, $\delta\Delta\bar{H}_s{}^{acid}$, is probably attributable to the changing hydration of the proton across the range of aqueous sulfuric acid solutions.[30, 31]

Accordingly we used a series of acetic acid–sulfuric acid solutions[32] for enthalpimetric titration of a number of compounds shown in Table XII and obtained titration curves whose midpoints appeared at the H_0 values labeled "pK_{BH^+}." The agreement for a number of these compounds with values obtained in aqueous media by other methods is indeed encouraging. However, we believe that these results are to be regarded with suspicion for at least two reasons. First, there is considerable disagreement at this time regarding the pK_{BH^+} for simple alcohols[33] and we do not wish to give undue weight to our own values, obtained in aqueous acid by the distribution method,[34] just because they agree with those reported here which were obtained independently by enthalpimetric titration. The use of nmr to obtain titration curves for these alcohols in sulfuric–acetic acid might clarify this problem. Secondly, we were unable to obtain enthalpimetric titration curves for simple ethers in sulfuric–acetic acid solutions even though they should be strong enough bases to fall in the proper range of 0 to −5 pK_a units. The only reason we can propose at this time is that their heats of ionization may be too small to detect. In conclusion, we have found that the enthalpimetric titration method for weak bases in aqueous sulfuric acid is a total failure and in acetic acid–sulfuric acid it is of dubious value.

Phosphoric Acid. Having considered heats of solution of organic solutes in aqueous sulfuric acid one is naturally curious about what would happen in aqueous solutions of other acids or electrolytes. We might expect to see quite different behavior for the enthalpy of transfer for solutes in phosphoric acid as compared to sulfuric acid because of the lower acidity[35] and lower dielectric constant[36] of phosphoric acid. However, results shown in Table V and Figure 8 indicate that over the limited range of acidity obtainable with this medium, the general enthalpy behavior for an ammonium salt

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(28) B. Gutbezahl and E. Grunwald, *J. Amer. Chem. Soc.*, **75**, 559 (1953).

(29) D. L. Levi, W. S. McEwan, and J. H. Wolfenden, *J. Chem. Soc.*, 760 (1949).

(30) E. Grunwald, A. Loewenstein, and S. Meiboom, *J. Chem. Phys.*, **27**, 641 (1957).

(31) E. M. Arnett, *Progr. Phys. Org. Chem.*, **1**, 223 (1963).

(32) R. W. Taft and P. L. Levins, *Anal. Chem.*, **34**, 436 (1962).

(33) E. M. Arnett, R. P. Quirk, and J. J. Burke, *J. Amer. Chem. Soc.*, **92**, 1260 (1970). See Table I of this paper for a list of several literature pK_a values for methanol, ethanol, and 2-propanol.

(34) E. M. Arnett and J. N. Anderson, *ibid.*, **85**, 1542 (1963).

(35) E. M. Arnett and G. W. Mach, *ibid.*, **88**, 1177 (1966).

(36) J. H. Christensen, A. J. Smith, R. S. Reed, and K. L. Elinore, *Chem. Eng. Data*, **11**, 60 (1966).

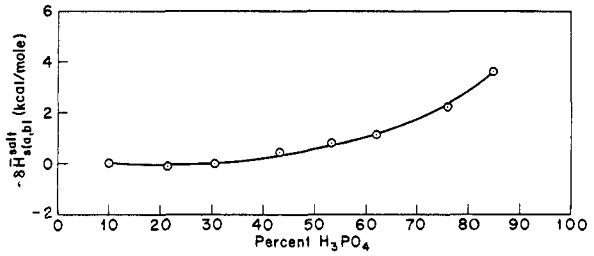

Figure 8. Variation of $[-\delta\bar{H}_s^{salt}(a,b)]$ for tetraethylammonium bisulfate as a function of aqueous phosphoric acid concentration. (a) is taken to be 10.00% H_3PO_4.

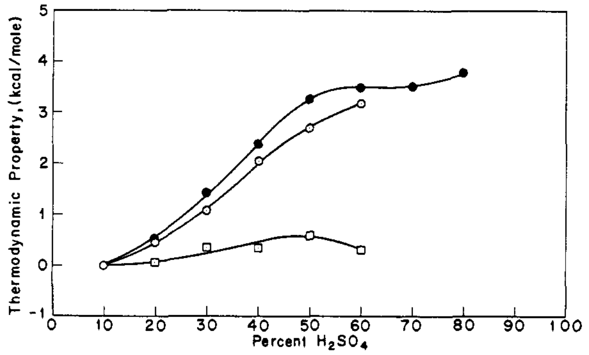

Figure 9. Variation of $\delta\Delta G°_{(1,2)}$, $\delta\Delta H°_{(1,2)}$, and $T\delta\Delta S°_{(1,2)}$ for anilinium ion relative to tetraethylammonium ion as a function of aqueous sulfuric acid concentration: $\delta\Delta G°_{(1,2)}$ (—⊙—), $\delta\Delta H°_{(1,2)}$ (—●—), $T\delta\Delta S°_{(1,2)}$ (—⊡—).

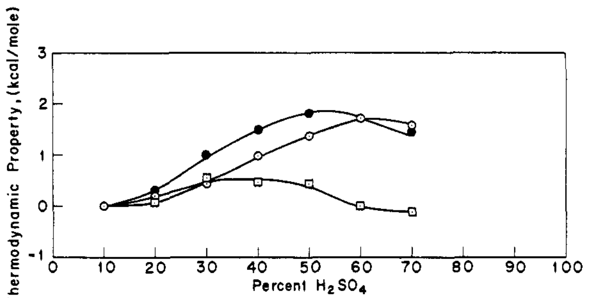

Figure 10. Variation of $\delta\Delta G°_{(1,2)}$, $\delta\Delta H°_{(1,2)}$, and $T\delta\Delta S°_{(1,2)}$ for N,N-dimethylanilinium ion relative to tetraethylammonium ion as a function of aqueous sulfuric acid concentration: $\delta\Delta G°_{(1,2)}$ (—⊙—), $\delta\Delta H°_{(1,2)}$ (—●—), $T\delta\Delta S°_{(1,2)}$ (—⊡—).

and several neutral molecules in phosphoric acid is quite similar to that observed in sulfuric acid.

Partial Molar Thermodynamic Properties for Various Solutes in Aqueous Sulfuric Acid. The relative partial molar heats of solution which we have reported above can be combined in a few cases with free energies of transfer to find entropies of transfer from one sulfuric acid solution to another. In this section we will present such complete analyses for two ammonium salts, two "nonbasic" neutral solutes (benzonitrile and nitrobenzene), and two weak oxygen bases (tetrahydrofuran and acetone).

Boyd's solubility data[9] were treated as described in the Results section to give free energies of transfer for anilinium and N,N-dimethylanilinium ion relative to tetraethylammonium ion, the contribution of the anion being cancelled out. Figures 9 and 10 show clearly that entropy changes are small and that the free-energy changes are mostly controlled by enthalpy changes.

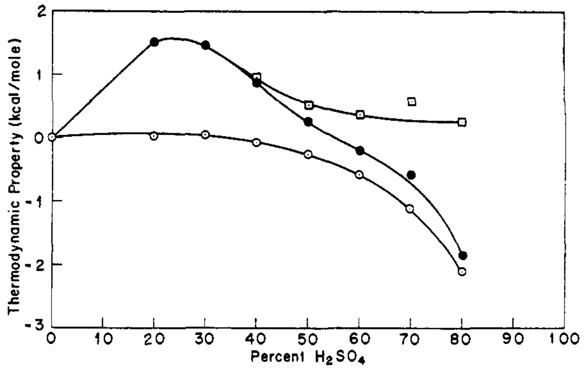

Figure 11. Variation of the thermodynamic properties of transfer for benzonitrile as a function of aqueous sulfuric acid concentration: $\delta\Delta G_s{}^{\circ solute}(a,b)$ (—⊙—), $\delta\Delta H_s{}^{\circ solute}(a,b)$ (—●—), $T\delta\Delta S_s{}^{\circ solute}(a,b)$ (—⊡—).

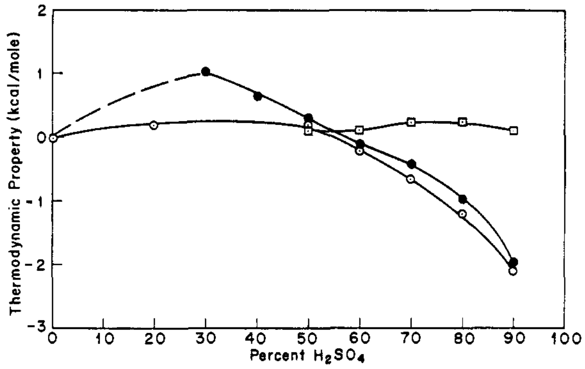

Figure 12. Variation of the thermodynamic properties of transfer for nitrobenzene as a function of aqueous sulfuric acid concentration: $\delta\Delta G_s{}^{\circ solute}(a,b)$ (—⊙—), $\delta\Delta H_s{}^{\circ solute}(a,b)$ (—●—), $T\delta\Delta S_s{}^{\circ solute}(a,b)$ (—⊡—).

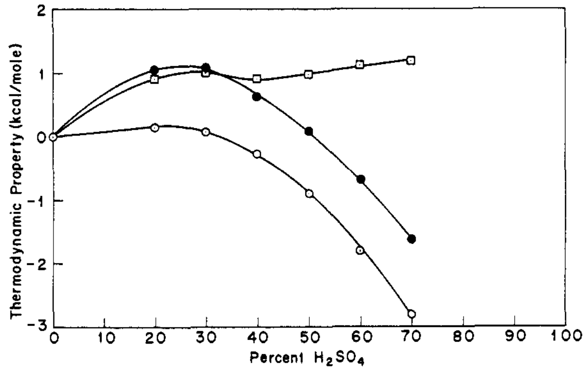

Figure 13. Variation of the thermodynamic properties of transfer for tetrahydrofuran as a function of aqueous sulfuric acid concentration: $\delta\Delta G_s{}^{\circ solute}(a,b)$ (—○—), $\delta\Delta H_s{}^{\circ solute}(a,b)$ (—●—), $T\delta\Delta S_s{}^{\circ solute}(a,b)$ (—□—).

The slight reduction in $\delta\Delta G°$ and $\delta\Delta H°$ for N,N-dimethylaniline compared to aniline is not surprising in view of the reference ion being a tetrasubstituted ammonium ion.

Anderson[34] has determined distribution constants for a number of nonelectrolytes between isooctane and aqueous sulfuric acid solutions. When converted into free energies and combined with heat data, the results shown in Figures 11–15 are generated. Again entropy changes are small compared

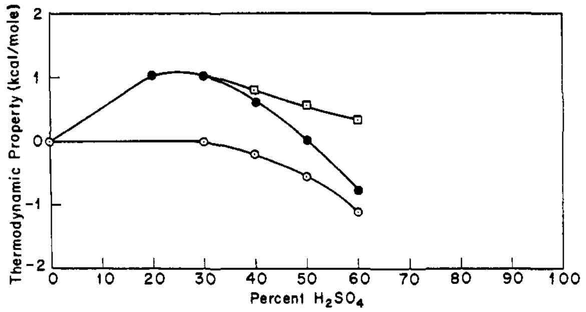

Figure 14. Variation of the thermodynamic properties of transfer for acetone as a function of aqueous sulfuric acid concentration: $\delta\Delta G_s{}^{\circ\text{solute}}(a,b)$ (—○—), $\delta\Delta H_s{}^{\circ\text{solute}}(a,b)$ (—●—), $T\delta\Delta S_s{}^{\circ\text{solute}}(a,b)$ (—□—).

to those for free energies and enthalpies, while enthalpy and free-energy changes are nearly equivalent at concentrations above 25% H_2SO_4. It is interesting to note that heats and entropies of solutions tend to show compensating behavior in dilute sulfuric acid with relatively large endothermic maxima while free energies remain nearly constant. This is exactly like the behavior we have reported[18] for nonelectrolytes in highly aqueous binary solutions and contrasts with that reported for aqueous salt solutions described in the section immediately following.

Comparison of Relative Partial Molar Heats of Solution for Solutes in Aqueous Salt Solutions with the Corresponding Free Energies. Electrolytes can either increase or decrease the solubility of nonelectrolytes in water, these processes being called "salting-in" or "salting-out," respectively. This subject has been reviewed by Sergeeva[37] and was discussed extensively in an earlier paper by Long and McDevit.[38] In general, in the absence of solute–solute interactions, the solute solubility is related to the salt concentration by the equation

$$\log S_0/S = k_{\text{salt}}C_{\text{salt}} \tag{8}$$

where S_0 is the solubility in moles per liter of the solute in water, which is taken as the reference state, S is the solubility of the solute in the solution whose salt concentration is C_{salt} (normality), and k_{salt} is a proportionality constant called the Setschenow parameter.[38]

The activity coefficient of the solute in the salt solution is related to the solubility[39] so that we may write

$$\log \gamma_2(b) = k_{\text{salt}}C_{\text{salt}} \tag{9}$$

The free-energy change accompanying the transfer of the solute from water to any given salt solution is thus given by

$$\Delta G^\circ = (2.303)(RT)k_{\text{salt}}C_{\text{salt}} \tag{10}$$

or using our symbolism

$$[\delta\Delta G_s{}^{\circ\text{solute}}(a,b)]_c = 1.364k_{\text{salt}}C_{\text{salt}} \tag{11}$$

where (a) is water and solubilities are expressed in molarity concentration units. This equation gives free energies of transfer in units of kilocalories per mole at 25°.

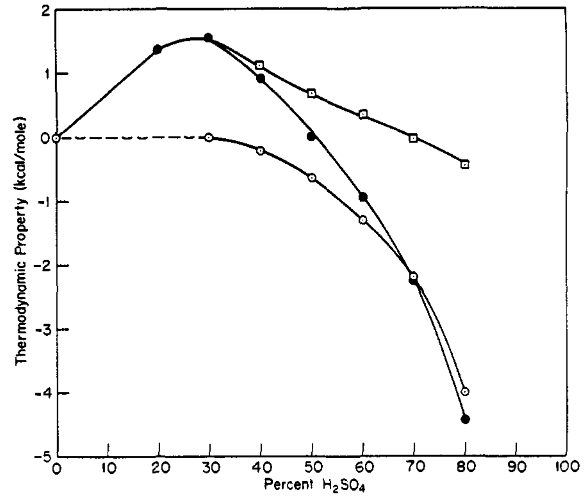

Figure 15. Variation of the thermodynamic properties of transfer for acetophenone as a function of aqueous sulfuric acid concentration: $\delta\Delta G_s{}^{\circ\text{solute}}(a,b)$ (—○—), $\delta\Delta H_s{}^{\circ\text{solute}}(a,b)$ (—●—), $T\delta\Delta S_s{}^{\circ\text{solute}}(a,b)$ (—□—).

Equations 9–11 show that there is a linear relationship between free energies of transfer and salt concentration. We also know from our enthalpy studies that this transfer term is a linear function of salt concentration in the majority of cases. We wish therefore to compare our data with free energies for some of the solutes we have studied. To the best of our knowledge these data are the first complete thermodynamic treatment of salt effects using calorimetrically determined heats of solution.

Free-energy terms for salt effects are scarcely changed by using molal or mole fraction concentration units. Accordingly, we will use only molar concentration activity coefficients in the following treatment.

Comparison of Enthalpy and Free Energy of Transfer for Some Nonelectrolytes in Aqueous Salt Solutions. Values of k_{salt} for several solutes in various salt solutions are given in Table XIII. Using these values and eq 11, we calculated $[\delta\Delta G_s{}^{\circ\text{solute}}(a,b)]_c$ terms for these solutes in the appropriate salt solution where the salt ranged from 0.0 to 4.0 N. We then combined the free-energy and enthalpy results to calculate the entropy terms. The results of these calculations are shown in Tables XIV–XXII.

Table XIII. Values of k_{salt} for Several Solutes in Various Salt Solutions at 25°

Solute	LiCl	NaCl	KI
Acetone[a]	0.076	0.117	0.03
Diacetone alcohol[b]	0.077	0.139	0.034
Butanone[c]		0.135[f]	
Piperidine[d]	0.056[e]	0.156[e]	

[a] W. Herz and E. Stanner, *Z. Phys. Chem.*, **128**, 399 (1927). [b] G. Akerlöf, *J. Amer. Chem. Soc.*, **51**, 984 (1929). [c] A. B. Lindenberg, *C. R. Acad. Sci.*, **226**, 721 (1948). [d] F. A. Long and R. L. Bergen, Jr., *J. Phys. Chem.*, **58**, 166 (1954). [e] Standard state was 0.12 N piperidinium chloride. [f] Temperature not reported.

Inspection of the preceding tables leads to the following conclusions. In five cases, the free energy of transfer is almost completely enthalpy controlled. There are two instances where the free-energy change is small

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(37) V. F. Sergeeva, *Russ. Chem. Rev.*, 34, 309 (1965).

(38) F. A. Long and W. F. McDevit, *Chem. Rev.*, 51, 119 (1952).

(39) For solutes which are very soluble in these solutions, the activity coefficients must be determined by distribution experiments.

Table XIV. Thermodynamic Properties of Transfer for Acetone in Aqueous Sodium Chloride Solutions

N_{NaCl}	$[\delta\Delta G_s^{\circ\,\text{solute-}}(\text{a,b})]_c$, kcal/mol	$\delta\Delta H_s^{\circ\,\text{solute-}}(\text{a,b})$, kcal/mol	$T\delta\Delta S_s^{\circ\,\text{solute-}}(\text{a,b})$, kcal/mol
0.0	0.000	0.000	0.000
1.0	0.160	0.063	−0.097
2.0	0.320	0.126	−0.194
3.0	0.480	0.189	−0.291
4.0	0.640	0.252	−0.388

Table XV. Thermodynamic Properties of Transfer for Acetone in Aqueous Lithium Chloride Solutions

N_{LiCl}	$[\delta\Delta G_s^{\circ\,\text{solute}}(\text{a,b})]_c$, kcal/mol	$\delta\Delta H_s^{\circ\,\text{solute}}(\text{a,b})$, kcal/mol	$T\delta\Delta S_s^{\circ\,\text{solute}}(\text{a,b})$, kcal/mol
0.0	0.000	0.000	0.000
1.0	0.103	−0.002	−0.105
2.0	0.206	−0.004	−0.210
3.0	0.309	−0.006	−0.315
4.0	0.412	−0.008	−0.420

Table XVI. Thermodynamic Properties of Transfer for Acetone in Aqueous Potassium Iodide Solutions

N_{KI}	$[\delta\Delta G_s^{\circ\,\text{solute-}}(\text{a,b})]_c$, kcal/mol	$\delta\Delta H_s^{\circ\,\text{solute-}}(\text{a,b})$,[a] kcal/mol	$T\delta\Delta S_s^{\circ\,\text{solute-}}(\text{a,b})$, kcal/mol
0.0	0.000	0.000	0.000
1.0	0.041	0.093	0.052
2.0	0.082	0.186	0.104
3.0	0.123	0.279	0.156
4.0	0.164	0.372	0.208

[a] Calculated from approximate linear equation Table VII.

Table XVII. Thermodynamic Properties of Transfer for Diacetone Alcohol in Aqueous Sodium Chloride Solutions

N_{NaCl}	$[\delta\Delta G_s^{\circ\,\text{solute-}}(\text{a,b})]_c$, kcal/mol	$\delta\Delta H_s^{\circ\,\text{solute-}}(\text{a,b})$, kcal/mol	$T\delta\Delta S_s^{\circ\,\text{solute-}}(\text{a,b})$, kcal/mol
0.0	0.000	0.000	0.000
1.0	0.190	0.204	0.014
2.0	0.380	0.408	0.028
3.0	0.570	0.612	0.042
4.0	0.760	0.816	0.056

Table XVIII. Thermodynamic Properties of Transfer for Diacetone Alcohol in Aqueous Lithium Chloride Solutions

N_{LiCl}	$[\delta\Delta G_s^{\circ\,\text{solute-}}(\text{a,b})]_c$, kcal/mol	$\delta\Delta H_s^{\circ\,\text{solute-}}(\text{a,b})$, kcal/mol	$T\delta\Delta S_s^{\circ\,\text{solute-}}(\text{a,b})$, kcal/mol
0.0	0.000	0.000	0.000
1.0	0.105	0.082	−0.023
2.0	0.210	0.164	−0.046
3.0	0.315	0.246	−0.069
4.0	0.420	0.328	−0.092

Table XIX. Thermodynamic Properties of Transfer for Diacetone Alcohol in Aqueous Potassium Iodide Solutions

N_{KI}	$[\delta\Delta G_s^{\circ\,\text{solute-}}(\text{a,b})]_c$, kcal/mol	$\delta\Delta H_s^{\circ\,\text{solute-}}(\text{a,b})$, kcal/mol	$T\delta\Delta S_s^{\circ\,\text{solute-}}(\text{a,b})$, kcal/mol
0.0	0.000	0.000	0.000
1.0	0.046	0.291	0.245
2.0	0.092	0.582	0.490
3.0	0.132	0.873	0.735
4.0	0.184	1.164	0.980

Table XX. Thermodynamic Properties of Transfer for Butanone in Aqueous Sodium Chloride Solutions

N_{NaCl}	$[\delta\Delta G_s^{\circ\,\text{solute-}}(\text{a,b})]_c$, kcal/mol	$\delta\Delta H_s^{\circ\,\text{solute-}}(\text{a,b})$, kcal/mol	$T\delta\Delta S_s^{\circ\,\text{solute-}}(\text{a,b})$, kcal/mol
0.0	0.000	0.000	0.000
1.0	0.184	0.152	−0.032
2.0	0.368	0.304	−0.064
3.0	0.552	0.456	−0.096
4.0	0.736	0.608	−0.128

Table XXI. Thermodynamic Properties of Transfer for Piperidine in Aqueous Sodium Chloride Solutions[a]

N_{NaCl}	$[\delta\Delta G_s^{\circ\,\text{solute-}}(\text{a,b})]_c$, kcal/mol	$\delta\Delta H_s^{\circ\,\text{solute-}}(\text{a,b})$, kcal/mol	$T\delta\Delta S_s^{\circ\,\text{solute-}}(\text{a,b})$, kcal/mol
0.0	0.000	0.000	0.000
1.0	0.213	0.282	0.069
2.0	0.426	0.546	0.138
3.0	0.639	0.846	0.207
4.0	0.852	1.128	0.276

[a] A 0.12 N solution of piperidinium chloride is the reference state.

Table XXII. Thermodynamic Properties of Transfer for Piperidine in Aqueous Lithium Chloride Solutions[a]

N_{LiCl}	$[\delta\Delta G_s^{\circ\,\text{solute-}}(\text{a,b})]_c$, kcal/mol	$\delta\Delta H_s^{\circ\,\text{solute-}}(\text{a,b})$, kcal/mol	$T\delta\Delta S_s^{\circ\,\text{solute-}}(\text{a,b})$, kcal/mol
0.0	0.000	0.000	0.000
1.0	0.076	0.093	0.017
2.0	0.152	0.186	0.034
3.0	0.228	0.279	0.051
4.0	0.304	0.372	0.068

[a] A 0.12 N solution of piperidinium chloride is the reference state.

while the enthalpy and entropy changes mirror one another. The latter situation is similar to the behavior we have seen for very weak bases in low concentrations of sulfuric acid. There is one case in which the free-energy change is entropy controlled, and in one instance the enthalpy and entropy contribute equally to the free-energy changes observed.

Therefore, assuming that the free-energy data are reliable (*i.e.*, free of solute–solute contributions), there is no general pattern observed for the behavior of various solutes in any given salt solution. However, in the systems examined here, the majority of free-energy changes are enthalpy controlled.

Extrathermodynamic Relationships. The acidity function concept assumes a linear free energy relationship between the effect of changing acid concentration on one basic molecule (or its onium ion) and that on another related base. This is often expressed as the requirement that the activity coefficient ratio for two bases, B_1 and B_2, and their ions should be unity

$$f_{B_1}f_{B_2H^+}/f_{B_1H^+}f_{B_2} = 1$$

$$\log\,(f_{B_1}/f_{B_1H^+}) = \log\,(f_{B_2}/f_{B_2H^+})$$

$$(\bar{G}_{B_1} - \bar{G}_{B_1H^+}) = (\bar{G}_{B_2} - \bar{G}_{B_2H^+})$$

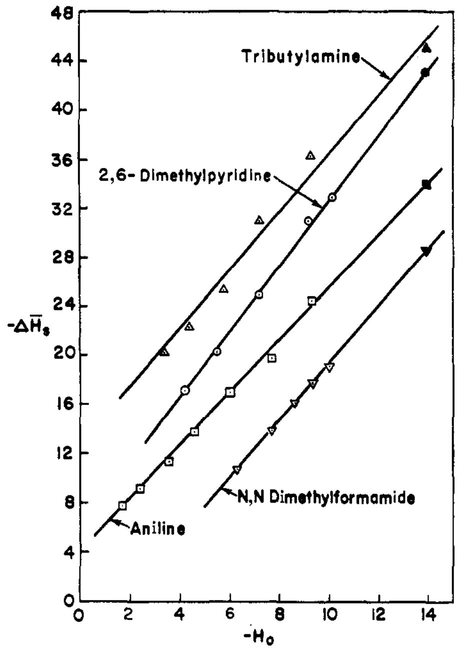

Figure 16. Plot of $\Delta\bar{H}_s$ *vs.* H_0 for various nitrogen bases in aqueous sulfuric acid (open points) and HSO_3F (black points) to estimate H_0 value for the latter.

Although this assumption is not supported by experiment insofar as unit slopes are not generally found, it can be seen from Figure 16 that the various acidity functions in aqueous sulfuric acid are related rather well by linear correlation over large ranges of acidity, the most important variations being in their slopes.

As we have seen above, there is a general tendency for the free energy of solution for a variety of organic molecules and ions to change in response to increasing acidity in a way that closely parallels the changing enthalpy of solution. This goes a long way to explain the success of correlations previously reported between pK_a's (free energies of ionization) for many kinds of bases in aqueous acid and their heats of ionization in concentrated sulfuric acid or fluorosulfuric acid.[33,40] If there is a large difference in free energy of ionization between two compounds in water and this difference is maintained across the range of acid strengths by a proportional free-energy difference which corresponds to an equivalent enthalpy difference, the pK_a in water is easily converted into an enthalpy change in concentrated acid. It is interesting to note that except in highly aqueous acid where "water structure" compensation effects might occur, changes in entropy of solvation are almost negligible for the compounds we have studied in water-sulfuric acid mixtures.

In our previous papers[33,40] we have used correlations between heats of solution in strong acid and their pK_a's in water for many compounds.[41] In view of the close correlation between free energies of transfer (*i.e.*, activity coefficients) and heats of transfer which we have found, it is not surprising that the heats of solution, $\Delta\bar{H}_s$, for completely ionized bases should vary linearly with H_0. We have used this fact to advantage in Figure 16, where heats of solution for several nitrogen bases extrapolated through the normal H_0 acidity range to give estimates of the H_0 of fluorosulfuric acid and the "magic acid" systems composed of antimony pentafluoride in fluorosulfuric acid. The value of −13.8 to which all four lines extrapolate is fairly close to the estimate of −15.1 obtained recently using aromatic nitro compounds as indicators.[42] A single value (43.2 ± 0.4 kcal/mol) for the heat of protona-

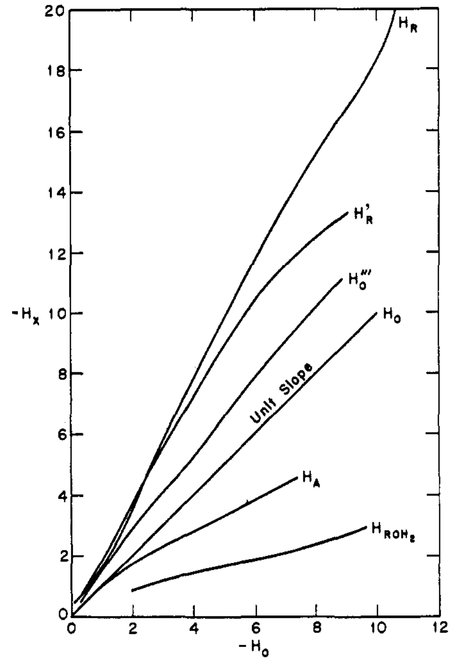

Figure 17. Relation between acidity functions for various classes of compounds (H_x) and H_0 for primary amines in aqueous sulfuric acid. See ref 8 for types of compounds associated with H_R, H_R', H_0''', and H_A. See ref 41 for meaning of $H_{ROH_2^+}$.

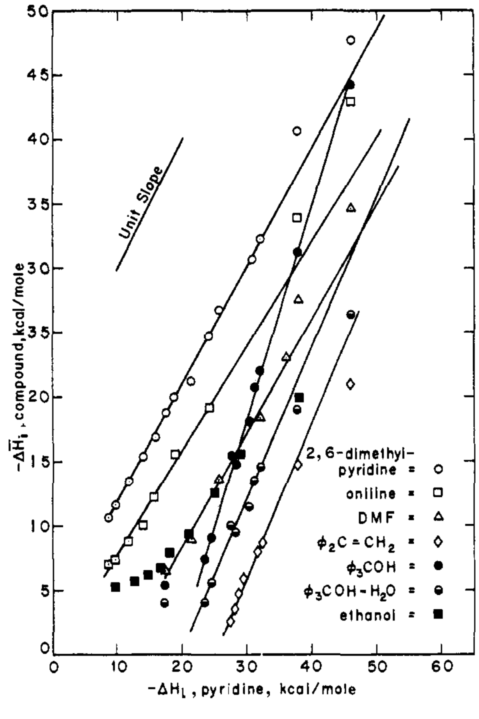

Figure 18. Plot of $\Delta\bar{H}_i$ for pyridine *vs.* $\Delta\bar{H}_i$ for various compounds.

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(40) E. M. Arnett, R. P. Quirk, and J. W. Larsen, *J. Amer. Chem. Soc.*, **92**, 2977 (1970).

(41) D. J. Lee and R. Cameron, *ibid.*, **93**, 4724 (1971).

(42) R. J. Gillespie, T. E. Peel, and E. A. Robinson, *ibid.*, **93**, 5083 (1971).

tion of aniline in 11.4 mol % SbF_5 in HSO_3F (*i.e.*, magic acid) leads to an estimate of $H_0 = -18$ for this superacid at 25°. If the linear correlation with slope 2.0 for H_R *vs.* H_0 seen in Figure 16 were to hold all the way to magic acid (doubtless a very crude assumption), it would lead to an H_R value of -36. for that medium. This would mean that magic acid is 10^{36} stronger than 1.0 molar H_2SO_4 for converting triarylcarbinols into their carbonium ions and water!

Linear Enthalpy Relationships. The linear correlations of $\delta\Delta\bar{G}_s$ (acidity function) for different bases, shown in Figure 17, and the corresponding correlations of the $\delta\Delta\bar{G}_s$ with $\delta\Delta\bar{H}_s$ imply at once that linear correlations of $\delta\Delta\bar{H}_s$ for different compounds should be found across the same range of acidity. Support for this is shown in Figure 18.

We have shown previously[33,40] that linear correlations between free energies and enthalpies may be as commonplace as linear free energy relationships and "isokinetic" or "isothermodynamic" correlations of entropy and enthalpy and *must* be found in any situation where both such correlations truly exist. It is clear that linear enthalpy correlations (ΔH *vs.* ΔH) must also be found when the same conditions hold.

One may expect to find linear enthalpy relations widely distributed in nature under many (but not all) of the same circumstances where linear free energy relationships exist. They should then have some of the predictive value that has made linear free energy correlations so valuable. The realization of this fact, originally proposed by Polanyi and Evans[43] in 1936, has been retarded for many reasons of which the lack of reliable enthalpy data is probably the most important. As solution calorimetry is applied more widely to physical organic chemistry problems, this shortcoming should be rectified.

Glossary of Symbols

The following list gives the definitions of the various symbols used in this article.

(a) and (b)	used to designate solvent composition
$\gamma \pm$ (b)	activity coefficient of an ionic solute in solution b
δ	medium effect operator representing change in a thermodynamic property as a result of indicated medium change
f	activity coefficient of a nonelectrolyte in a given acid solution referred to water as a standard state
$\Delta\bar{G}_s$	partial molar free energy of solution
$\delta\Delta\bar{G}_s^{\text{solute}}$(a,b)	change in partial molar free energy for solute from solvent a to solvent b
H_0	Hammett's acidity function for primary aniline bases in aqueous sulfuric acid
$\bar{H}_s$	partial molar enthalpy
$\Delta\bar{H}_s$	partial molar heat of solution from pure solute to high dilution in indicated solvent
$\delta\Delta\bar{H}^\circ$(a,b)	change in partial molar heat of solution from solvent a to solvent b; *i.e.*, the heat of transfer from (a) to (b)
ΔH_i	heat of ionization
k_{salt}	salting-out parameter
K_D	distribution constant
(L)	refers to pure liquid solute
m	molality
n	number of moles
N_2	mole fraction of a solute (2)
N or C_{salt}	normality of salt solution
pK_{BH^+}	negative logarithm of acid ionization constant
"pK_{BH^+}"	strength of acids on H_0 scale required to half protonate a base

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(43) M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, 32, 1333 (1936).