

substituent constants which gave reliable correlations with eq 1, 17 have values of ϵ which are significantly different from the value for σ_p . Thus there is no special importance to be attached to those σ_o constants which do

happen to have the same composition as the σ_p constants.

We hope that we have now laid to rest the assumption of equality between the *ortho*- and *para*-electrical effects.

The Temperature Variation of the H_0 Acidity Function in Aqueous Sulfuric Acid Solution

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Abstract: The variation of the H_0 acidity function, as defined by primary nitroaniline indicators, with temperature, has been examined by measurement of the scale at 25, 40, 60, 80, and 90°. Empirical equations correlating H_0 with temperature are deduced. The variation of pK_a values with temperature and the application of the scale to other measurements on acidity scales and acid-catalyzed reactions, at elevated temperatures, are discussed.

Many acid-catalyzed reactions have been reported in concentrated solutions of aqueous sulfuric acid at elevated temperatures. The H_0 values of such solutions relevant to the interpretation of such reactions have usually been assumed to be those of the solutions at room temperature. In particular, this assumption has been very commonly employed in recent and extensive investigations into the mechanism of aromatic and heteroaromatic nitration and hydrogen exchange;¹⁻³ however, it has become increasingly apparent that this assumption is a gross one, and this prompted us to accumulate accurate information on the effect of temperature on the H_0 scale.

Similar previous investigations have concerned aqueous solutions of phosphoric and hydrochloric acid,⁴ and also sulfuric acid⁵ (the latter indicated diagrammatically in Figure 1). We believe that the values reported for the study of sulfuric acid may be in error for several reasons. The indicators used by these workers were 4-nitro-, 2-nitro-, 4-chloro-2-nitro-, 2,4-dichloro-6-nitro-, 2,4-dinitro-, 2-bromo-4,6-dinitro-, and 2,4,6-trinitroaniline. Overlap between the third and fourth of these indicators necessitated measuring $\log I$ ($\log [B]/[BH^+]$) values of up to -2.38 ; values of this magnitude are subject to large experimental uncertainty. Furthermore, there was no overlap at all between the fifth and sixth, and sixth and seventh of these indicators; the pK_a values of the latter two indicators were calculated by an extrapolation for which there is no theoretical justification.

The only other investigation of the temperature variation of an acidity function in aqueous sulfuric acid is that of H_R by Arnett and Bushick.⁶

(1) A. R. Katritzky, H. O. Tarhan, and S. Tarhan, *J. Chem. Soc., B*, in press, and references therein.

(2) S. R. Hartshorn and J. H. Ridd, *ibid.*, 1068 (1968), and references therein.

(3) R. G. Coombes, R. B. Moodie, and K. Schofield, *ibid.*, 52 (1969), and references therein.

(4) A. I. Gel'bshtein, G. G. Shcheglova, and M. I. Temkin, *Zh. Neorg. Khim.*, 1, 282 (1956).

(5) A. I. Gel'bshtein, G. G. Shcheglova, and M. I. Temkin, *ibid.*, 1, 506 (1956).

(6) E. M. Arnett and R. D. Bushick, *J. Amer. Chem. Soc.*, 86, 1564 (1964).

Experimental Section

Materials. Sulfuric and hydrochloric acids were AnalaR grade reagents. Fuming sulfuric acid was prepared by distillation of sulfur trioxide into AnalaR grade sulfuric acid, using a process similar to that for the preparation of deuteriosulfuric acid.⁷ Water was deionized and further purified by distillation from potassium permanganate in glass apparatus.

The nitroaniline indicators used, (1) 4-nitro-, (2) 2-nitro-, (3) 4-chloro-2-nitro-, (4) 2,5-dichloro-4-nitro-, (5) 2-chloro-6-nitro-, (6) 2,6-dichloro-4-nitro-, (7) 2,4-dinitro-, (8) 2,6-dinitro-, (9) 2-bromo-4,6-dinitro-, (10) 3-methyl-2,4,6-trinitro-, (11) 3-bromo-2,4,6-trinitro-, and (12) 2,4,6-trinitroaniline, were obtained commercially or made by standard procedures.⁸ All were recrystallized several times from appropriate solvents and had accurate analyses and melting points which agreed with accepted literature values.

Preparation of Solutions. A stock acid solution was made by dilution of concentrated sulfuric acid with water, and estimated by titration with standard sodium hydroxide using screened methyl orange as indicator, or by adding an excess of potassium iodide-potassium iodate and titrating the liberated iodine against standard sodium thiosulfate using sodium starch glycollate as indicator. This stock acid solution was then diluted with water to give acids of the requisite strength; the procedure was carried out by weighing, and frequently checked by titration as above, agreement between the two results being well within experimental error. For more concentrated solutions, dilution of concentrated or fuming acid was employed.

The indicator stock solutions were prepared by addition of a weighed amount of the indicator to a volumetric flask and dissolving this in aqueous acid of sufficient strength to protonate it completely (to aid dissolution). A suitable volume of the stock solution was withdrawn by a micrometer syringe and added to standard acid (20 ml). The same operation was carried out using acids of the same strength, but without indicator present to yield a reference solution. All the above operations were checked by weighing.

Spectrophotometric Measurements. Two matched "UV grade" 1-cm cells (Unicam Instruments, Ltd., Cambridge, England) were filled with the indicator and reference solution, respectively, and closed with polyethylene stoppers (for measurements up to 60°) and with polypropylene stoppers (for higher temperatures). Absorbances were measured on a Unicam SP 500 spectrophotometer fitted with an electrically thermostated cell holder and controller (A. Adkins and Sons Ltd., Leicester, England). This cell holder was designed to take the two 1-cm cells, and was wired with 15 yards of Eureka 32 S. W. G. enamel-covered wire, half of it wound clockwise on one side of the block and half of it anticlockwise on

(7) A. P. Best and C. L. Wilson, *J. Chem. Soc.*, 239 (1946).

(8) For full details, see S. A. Shapiro, Ph.D. Thesis, University of East Anglia, 1969.

Table I. Density of Sulfuric Acid Solutions between 0 and 2% (Weight for Weight) at 25°

| Wt % H ₂ SO ₄ | ρ |
|-------------------------------------|--------|
| 0.05 | 0.9975 |
| 0.10 | 0.9978 |
| 0.20 | 0.9986 |
| 0.30 | 0.9992 |
| 0.40 | 0.9999 |
| 0.50 | 1.0006 |
| 0.60 | 1.0012 |
| 0.80 | 1.0026 |
| 1.00 | 1.0039 |
| 1.20 | 1.0052 |
| 1.40 | 1.0065 |
| 1.60 | 1.0078 |
| 1.80 | 1.0091 |
| 2.00 | 1.0105 |

Table II. Measurement of the Absorbance and Volume Correction for 2,4-Dinitroaniline at 25°

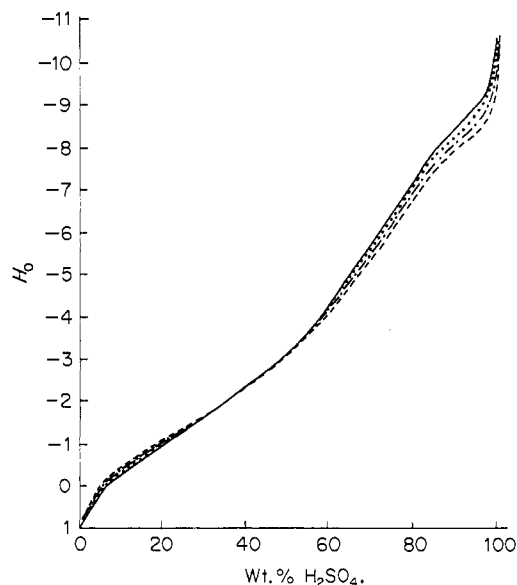
| $\epsilon_R = A \frac{\text{total weight of solution}}{\rho_{25}(\text{weight of stock indicator solution})}$ | | | | | | |
|---------------------------------------------------------------------------------------------------------------|-------------|-------------------------------|---------------------|---------|-------------------|------|
| Strength wt % | ρ_{25} | Wt of stock indicator soln, g | Total wt of soln, g | A | $10^3 \epsilon_R$ | |
| 1 | 32.69 | 1.2370 | 0.1592 | 24.9127 | 0.822 | 1040 |
| 2 | 39.30 | 1.2930 | 0.1710 | 26.0164 | 0.884 | 1040 |
| 3 | 44.55 | 1.3396 | 0.1605 | 26.9333 | 0.801 | 1003 |
| 4 | 49.01 | 1.3815 | 0.1637 | 27.7208 | 0.787 | 965 |
| 5 | 51.87 | 1.4095 | 0.1648 | 28.2176 | 0.739 | 898 |
| 6 | 54.69 | 1.4381 | 0.1645 | 28.8284 | 0.650 | 792 |
| 7 | 56.22 | 1.4539 | 0.1545 | 29.1150 | 0.554 | 718 |
| 8 | 58.44 | 1.4773 | 0.1639 | 29.6046 | 0.471 | 576 |
| 9 | 58.34 | 1.4762 | 0.1657 | 29.6618 | 0.480 | 582 |
| 10 | 64.16 | 1.5396 | 0.1648 | 30.9374 | 0.169 | 206 |
| 11 | 65.72 | 1.5570 | 0.1646 | 31.2183 | 0.116 | 141 |
| 12 | 68.22 | 1.5853 | 0.1707 | 31.8391 | 0.059 | 69 |
| 13 | 70.09 | 1.6069 | 0.1691 | 32.3019 | 0.029 | 35 |
| 14 | 73.37 | 1.6451 | 0.1709 | 32.8830 | 0.019 | 22 |
| 15 | 76.23 | 1.6788 | 0.1733 | 33.8915 | 0.017 | 20 |

the other side. This was capable of maintaining the cell contents at constant temperatures up to 100°. The current for the heating coil was supplied by the controller, which also incorporated an internal bridge used for balancing the resistance of the heating coil. In this way a temperature could be maintained to $\pm 0.1^\circ$. The temperature difference between the contents of the two cells was also within this limit.

Measurement of temperature was by means of a thermocouple built into the stopper of the reference cell and connected to a Sclamp thermocouple (W. G. Pye and Co. Ltd., Cambridge, England) galvanometer. The galvanometer was fitted with an automatic "cold" junction compensating device calibrated for direct reading when a copper-advance thermocouple of 30 ohms resistance was used. The accuracy of the instrument is quoted as being $\pm 0.5^\circ$ and the tolerance on the thermocouple resistance as 0.12% error for a 0.5-ohm deviation from the nominal value.

$$\log I = \log \left\{ \frac{A - A_{\text{BH}^+}}{A_{\text{B}} - A} \right\} \quad (1)$$

The $\log I$ ratios were determined by the standard eq 1, where A , A_{BH^+} , and A_{B} are the measured absorbances of the solution under investigation, the conjugate acid, and the free base, respectively. The accurate use of this equation requires that the stoichiometric concentration of the indicator is the same in all solutions, a circumstance very difficult to realize experimentally; the following correction was therefore made. We may deduce from Beer's law, for a 1-cm path length cell, that relation 2 connects ϵ_R (the relative extinction coefficient of the indicator solution) with A (its absorb-

**Figure 1.** Acidity function for the H₂SO₄-H₂O system, taken from ref 5: —, 20°; ···, 40°; - · - ·, 60°; and ---, 80°.

ance), W_1 and W_2 (the weights of the indicator and final solution,

$$\epsilon_R = AW_2/\rho W_1 \quad (2)$$

respectively), and ρ (the density of this solution) (all measurements at 25°). Densities were obtained from the International Critical Tables,⁹ and elsewhere¹⁰ for oleum solutions. In the region 0-2% sulfuric acid ρ changes rapidly with composition, but values of ρ are given only at 13 and 18°. The densities between 0 and 2% at 25° (Table I) were thus obtained by an extrapolation procedure as detailed.⁹ The accuracy of this procedure can be judged from the values of 1.0038 and 1.0104 quoted⁹ for 1 and 2% solutions, respectively. (The same procedure was carried out for the determination of the ionization constant of 4-nitroaniline in hydrochloric acid except that the density at 17° was used.⁹) As an example of the manner in which these corrections were applied, the details for the spectral measurement of 2,4-dinitroaniline at 25° are given in Table II.

The ratio $\rho_{25^\circ}/\rho_{100^\circ}$ is constant at 1.043 ± 0.002 over an acid composition range of 0-90% aqueous sulfuric acid. The assumption of a constant value for $\rho_{25^\circ}/\rho_{x^\circ}$ where x° stands for the temperatures at which measurements were made (25, 40, 60, 80, and 90°) implied (and we accepted the implication) that no net corrections need be made for the variation of the volume of the solutions with temperature.

Results

The pK_a Value of 4-Nitroaniline. The pK_a value for any base is given by eq 3 where $\text{pcH} = -\log [H^+]$ and f_{B} , f_{H^+} , and f_{BH^+} refer to the activity coefficients of the base, hydrogen ion, and conjugate acid, respectively.

$$pK_a = \text{pcH} - \log [B]/[BH^+] - \log \{ (f_{\text{B}}f_{\text{H}^+})/f_{\text{BH}^+} \} \quad (3)$$

$$pK_a = \text{pcH} - \log [B]/[BH^+] + \text{const}[H^+] \quad (4)$$

$$= pK_a(\text{apparent}) + \text{const}[H^+]$$

For solutions in which the (spectrophotometric) concentration of base is very much less than the acid concentration, eq 3 reduces to eq 4. A plot of $pK_a(\text{apparent})$ vs. $[H^+]$ should thus yield a straight line with intercept pK_a , correctly considered as an accurate thermodynamic quantity as it is defined for infinite dilution.¹¹

(9) "International Critical Tables," E. W. Washburn, Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1928, pp 51-56.

(10) R. Takeno, *Ryusan*, 17, 29 (1964); *Chem. Abstr.*, 63, 17 (1965).

(11) M. A. Paul and F. A. Long, *Chem. Rev.*, 57, 1 (1957).

Table III. pK_a Determinations for 4-Nitroaniline^a

| Molal concn, pcH m_{HCl} | | Log I | | | | | pK_{app} 60° | | | | |
|-------------------------------|--------|---------|--------|--------|--------|--------|-------------------|-------|-------|-------|-------|
| | | 25° | 40° | 60° | 80° | 90° | 25° | 40° | 60° | 80° | 90° |
| 0.098 | 1.008 | -0.014 | 0.097 | 0.235 | 0.345 | 0.392 | 1.022 | 0.911 | 0.773 | 0.663 | 0.616 |
| 0.147 | 0.831 | -0.200 | -0.087 | 0.049 | 0.167 | 0.213 | 1.031 | 0.918 | 0.782 | 0.664 | 0.618 |
| 0.246 | 0.609 | -0.435 | -0.324 | -0.185 | -0.067 | -0.026 | 1.044 | 0.933 | 0.794 | 0.676 | 0.635 |
| 0.393 | 0.406 | -0.669 | -0.557 | -0.405 | -0.293 | -0.241 | 1.075 | 0.963 | 0.811 | 0.699 | 0.645 |
| 0.591 | 0.228 | -0.880 | -0.758 | -0.609 | -0.491 | -0.450 | 1.108 | 0.986 | 0.837 | 0.719 | 0.678 |
| 0.784 | 0.105 | -1.032 | -0.916 | -0.759 | -0.630 | -0.596 | 1.137 | 1.021 | 0.864 | 0.735 | 0.701 |
| 0.999 | 0.001 | -1.180 | -1.047 | -0.896 | -0.754 | -0.718 | 1.181 | 1.048 | 0.897 | 0.755 | 0.719 |
| 1.227 | -0.089 | -1.305 | -1.170 | -1.012 | -0.880 | -0.842 | 1.216 | 1.081 | 0.923 | 0.791 | 0.753 |
| 1.572 | -0.197 | -1.475 | -1.322 | -1.163 | -1.020 | -1.000 | 1.278 | 1.125 | 0.966 | 0.823 | 0.803 |

| pK_a | Temp, °C | Correlation coeff |
|---------------|----------|-------------------|
| 1.004 ± 0.001 | 25 | 0.9997 |
| 0.897 ± 0.003 | 40 | 0.9981 |
| 0.761 ± 0.001 | 60 | 0.9995 |
| 0.651 ± 0.002 | 80 | 0.9978 |
| 0.601 ± 0.003 | 90 | 0.9979 |

^a Absorbance measured at 384 $m\mu$.

Table III gives the relevant data for application of eq 4 to 4-nitroaniline at temperatures of 25, 40, 60, 80, and 90° at the wavelengths quoted, and the resultant values of the thermodynamic pK_a values at these temperatures.

pK_a Values of the Indicator Series in Sulfuric Acid. The log I values at different temperatures for the indicators in sulfuric acid are given in Table IV. At the higher temperatures in acid of under 25% strength, slow volatilization of the indicator 2-chloro-6-nitroaniline was found to occur. To correct for this, the absorbance was measured at various time intervals and extrapolated back to zero time; in most cases the correction was small.

Slow decomposition of 3-methyl-2,4,6-trinitroaniline occurred at higher temperatures in acid above 92% as observed previously.¹² The effects of this decomposition were avoided completely by measuring the solutions immediately after making them up.

The measurements for all the indicators were made on the intense free base peak in the 350–450- $m\mu$ region. Medium effects were in general negligibly small as noted by previous workers. In the case of the 3-substituted 2,4,6-trinitroanilines measurement was made along a shoulder in the 370- $m\mu$ region rather than at the more intense maximum occurring near 340 $m\mu$, which previous workers have found to be unsuitable for ionization determinations.^{12–14} Since these measurements were on a peak shoulder, measurements were carried out at different wavelengths along it. In both cases agreement for the different wavelengths was excellent (see Table IV). 2,4,6-Trinitroaniline has absorption maxima at 340 and 420 $m\mu$; again measurements of the ionization ratios at these two wavelengths were in good agreement (Table IV).

Calculations of the H_0 Acidity Function. The values of log I for each indicator were plotted as a function of percentage H_2SO_4 and smooth curves drawn through the experimental points. The results for the upper (90°) and lower (25°) temperature limits studied are given in Figure 2. Parallelism between adjacent plots for the intermediate temperatures was equally good. The

overlap technique originally defined by Hammett and Deyrup¹⁵ is required for assessment of the pK_a values of the primary nitroaniline indicators from the pK_a of 4-nitroaniline and the subsequent evaluation of the H_0 scale at the different temperatures. Careful consideration was given to the most accurate method of application of this technique. Many workers have confirmed that the smaller the value of log I , the greater its accuracy,^{16,17} and this is convincingly illustrated for the results on 2,4-dinitroaniline at 25° (Table IV). This justifies the weighting of log I values according to their magnitude. From the log I vs. percentage H_2SO_4 graphs (Figure 2) values of log I were read off at integral values of per cent H_2SO_4 . Each of the log I values was then weighted according to eq 5,⁸ which gives $W_{\log I}$ as 100 when $I = 1.0$, setting p , q , and r in Moodie's equation¹⁷ equal to unity, and eq 6 then used to evaluate the pK_a values of the increasingly weaker indicators. In eq 6 the summations of bases i and j were carried out over the overlap region. H_0 values were then evaluated

$$W_{\log I} = \frac{1200I^2}{(I+1)^2(I^2+I+1)} \quad (5)$$

$$pK_j - pK_i = \frac{\sum W_i W_j (\log I_i - \log I_j)}{\sum W_i W_j} \quad (6)$$

$$H_0 = \frac{\sum [W_i (\log I_i + pK_i)]}{\sum W_i} \quad (7)$$

from eq 7 applied to a given acidity, where the range of the summation depends on whether log I_i can be measured at the particular acidity considered. The above calculations were performed by use of a computer program.⁸

Values for the ionization constants for the 12 indicators are given in Table V, and the H_0 acidity functions in Table VI and Figure 3.

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

(16) H. H. Jaffé and M. Orchin, "Theory and Application of Ultraviolet Spectroscopy," John Wiley & Sons, Inc., London, 1962, p 566; E. M. Arnett and G. W. Mach, *J. Amer. Chem. Soc.*, **86**, 2671 (1964); A. J. Kresge, G. W. Barry, K. R. Charles, and Y. Chiang, *ibid.*, **84**, 4343 (1962); R. W. Alder, G. R. Chalkley, and M. C. Whiting, *Chem. Commun.*, 405 (1966).

(17) V. C. Armstrong and R. B. Moodie, *J. Chem. Soc., B*, 275 (1968).

(12) M. J. Jorgenson and D. R. Hartter, *J. Amer. Chem. Soc.*, **85**, 878 (1963).

(13) K. Yates and H. Wal, *ibid.*, **86**, 5408 (1964).

(14) R. S. Ryabova, I. M. Medvet'skaya, and M. I. Vinnik, *Russ. J. Phys. Chem.*, **40**, 182 (1966).

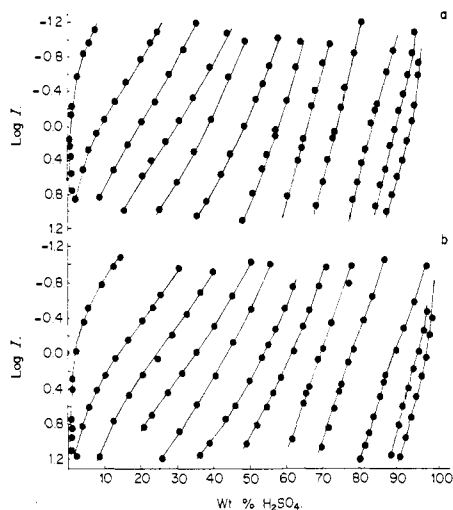


Figure 2. Logarithm of the ionization ratios *vs.* per cent sulfuric acid at (a) 25 and (b) 90°.

Discussion

Errors. The variation of pK_a values with temperature for the "anchoring" base, 4-nitroaniline, has been considered by several workers,^{5,18,19} and their results are compared with the present work in Table VII. For Biggs¹⁸ and Boyd's¹⁹ data, which only extended up to 60°, plots of pK_a *vs.* reciprocal absolute temperature were made and extrapolations were drawn to give values at 80 and 90°. The good agreement between the various values (Table VII), except for those of Gel'bshtein,⁵ at the higher temperatures, is encouraging, and suggests that the acidity function is anchored accurately to neutral water as the standard state for all temperatures, indicating comparisons between the scales at different temperatures may be made with confidence.

Equally reassuring is comparison of the estimated thermodynamic pK_a values of the whole range of indicators with those obtained by previous workers¹¹⁻¹⁴ (Table VIII), again with the exception of Gel'bshtein's work.⁵ The results for the first five indicators agree well, although at higher acidities accumulative errors become quite considerable reflecting in the larger differences in pK_a values (and H_0 values,^{11,12,14} given in Table IX) from one author to another. Further, Paul and Long's scale¹¹ incorporates aromatic carbonyl compounds, a class of compound whose ionization behavior has subsequently been shown to deviate frequently from that of primary nitroanilines,²⁰ while Jorgenson and Hartter¹² considered that the individual $\log I$ -% H_2SO_4 plots should be linear, which seems to be unjustified since the over-all H_0 -% H_2SO_4 plot is curved. This may well account in some measure for the poor parallelism of their indicator plots. The present pK_a and H_0 values fall within the range encompassed by the variation of previous values. The H_0 results of this work differ appreciably from those of other workers only for the 50-60% acid region. If the proton in dilute aqueous acid solution is tetrahydrated,²¹ then from approxi-

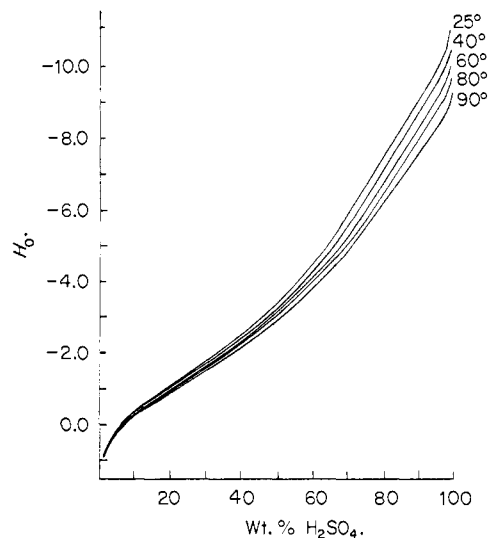


Figure 3. H_0 *vs.* per cent sulfuric acid.

mately 56% sulfuric acid onward, there are no longer sufficient water molecules present to ensure complete tetrahydration. In Figure 3 it can be seen that the rate of change of H_0 with per cent sulfuric acid decreases quite sharply in this region. Ryabova¹⁴ reasoned that indicator measurements made in this region would be susceptible to medium effects, and thus only made use of the concentration range below 56% sulfuric acid for the determination of the pK_a value of 2,4-dinitroaniline.

In this work, the overlap between 2,6-dichloro-4-nitroaniline and 2,4-dinitroaniline was averaged over the entire overlap region (45-60%), possibly accounting for the difference in the pK_a value of 2,4-dinitroaniline reported here and that reported by Ryabova,¹⁴ and subsequently also for the difference in H_0 values in this region of acidity.

A test of parallelism between the indicators comprising the scale was made in the following way. For the first indicator eq 8 holds; the $\log I_2$ values for the second indicator are then plotted against H_1 in the overlap region. This plot should be linear and of unit slope. However, it can be represented as eq 9 from which eq 10 follows. From eq 11 we have eq 12; similarly for the i th indicator, relationship 13 holds. In

$$H_1 = \log I_1 + pK_1 \quad (8)$$

$$\log I_2 = a_{2,1}H_1 - pK_2 \quad (9)$$

$$\log I_2 = a_{2,1} \log I_1 + a_{2,1}pK_1 - pK_2 \quad (10)$$

$$H_2 = \log I_2 + pK_2 \quad (11)$$

$$H_2 = a_{2,1}H_1 \quad (12)$$

$$H_i = a_{i,i-1}a_{i-1,i-2} \dots a_{2,1}H_1 \quad (13)$$

eq 8-13 suffixes 1, 2 . . . i refer to the individual indicators, with acidity functions $H_1, H_2 \dots H_i$. The product $a_{i,i-1}a_{i-1,i-2} \dots a_{2,1}$ should indicate how the acidity function generated by the i th indicator behaves relative to H_1 , defined for the first indicator. Individual values of $a_{i,i-1}$ were obtained from plots of $\log I_i$ *vs.* $\log I_{i-1}$ in the region where the i th and $(i-1)$ th indicators overlapped; the calculations were computerized⁸ and the results are given in Table X. The average slope product for all twelve indicators is 1.02. This, together

(18) A. I. Biggs, *J. Chem. Soc.*, 2572 (1961).

(19) R. H. Boyd and C.-H. Wang, *J. Amer. Chem. Soc.*, **87**, 430 (1965).

(20) C. C. Greig and C. D. Johnson, *ibid.*, **90**, 6453 (1968).

(21) R. P. Bell, "The Proton in Chemistry," Methuen and Co., Ltd., London, 1959, p 83.

Table IV (Continued)

| (x) 3-Methyl-3,4,6-trinitroaniline (370 and 380 m μ) | | | | | | | | | | | | | |
|-----------------------------------------------------------|-------|-------|-------|-------|-------|-------|----------------------------------------|-------|-------|-------|-------|-------|-------|
| Wt % H ₂ SO ₄ | Log I | | | | | | Wt % H ₂ SO ₄ | Log I | | | | | |
| | 25° | | | 40° | | | | 60° | | | 80° | | |
| | 370° | 380 | Av | 370 | 380 | Av | | 370 | 380 | Av | 370 | 380 | Av |
| 78.60 | 1.15 | 1.09 | 1.12 | 1.46 | 1.34 | 1.40 | 78.57 | 1.27 | 1.23 | 1.25 | 1.43 | 1.35 | 1.39 |
| 80.16 | 0.87 | 0.85 | 0.86 | 1.14 | 1.08 | 1.11 | 80.11 | 1.04 | 1.00 | 1.02 | 1.18 | 1.17 | 1.17 |
| 81.30 | 0.67 | 0.65 | 0.66 | 0.92 | 0.89 | 0.91 | 81.26 | 0.86 | 0.82 | 0.84 | 1.10 | 1.07 | 1.09 |
| 82.58 | 0.44 | 0.42 | 0.43 | 0.61 | 0.59 | 0.60 | 82.52 | 0.58 | 0.54 | 0.56 | | 0.81 | 0.81 |
| 83.56 | 0.29 | 0.27 | 0.28 | 0.45 | 0.43 | 0.44 | 83.52 | 0.52 | 0.49 | 0.51 | 0.74 | 0.69 | 0.72 |
| 85.27 | 0.00 | -0.01 | 0.00 | 0.15 | 0.14 | 0.15 | 85.22 | 0.22 | 0.02 | 0.21 | 0.42 | 0.39 | 0.41 |
| 86.45 | -0.16 | -0.18 | -0.17 | -0.02 | -0.03 | -0.03 | 86.40 | 0.07 | 0.04 | 0.06 | 0.20 | 0.18 | 0.19 |
| 86.86 | -0.22 | -0.23 | -0.23 | -0.11 | -0.12 | -0.12 | 86.81 | -0.05 | -0.05 | -0.05 | 0.17 | 0.14 | 0.16 |
| 89.60 | -0.60 | -0.62 | -0.61 | -0.47 | -0.48 | -0.48 | 89.55 | -0.30 | -0.34 | -0.32 | -0.18 | -0.20 | -0.19 |
| 91.48 | -0.85 | -0.87 | -0.86 | -0.73 | -0.73 | -0.73 | 91.43 | -0.53 | -0.55 | -0.54 | -0.43 | -0.44 | -0.44 |
| 94.09 | -1.31 | -1.34 | -1.33 | -1.17 | -1.17 | -1.17 | 94.05 | -0.97 | -0.99 | -0.98 | -0.81 | -0.82 | -0.82 |
| | | | | | | | 97.09 | | | | -1.32 | -1.34 | -1.33 |
| | 90° | | | | | | | 90° | | | | | |
| | 370° | 380 | Av | | | | | 370° | 380 | Av | | | |
| 78.67 | 1.39 | 1.35 | 1.37 | | | | 86.43 | 0.28 | 0.26 | 0.27 | | | |
| 80.20 | 1.16 | 1.14 | 1.15 | | | | 86.84 | 0.23 | 0.20 | 0.22 | | | |
| 81.34 | 1.01 | 1.00 | 1.00 | | | | 89.55 | -0.07 | -0.09 | -0.08 | | | |
| 82.59 | 0.87 | 0.85 | 0.86 | | | | 91.41 | -0.32 | -0.33 | -0.33 | | | |
| 83.57 | 0.68 | 0.66 | 0.67 | | | | 94.05 | -0.65 | -0.64 | -0.65 | | | |
| 85.26 | 0.46 | 0.44 | 0.45 | | | | 97.01 | -1.05 | -1.05 | -1.05 | | | |

| (xi) 3-Bromo-2,4,6-trinitroaniline | | | | | | | | | | | | |
|----------------------------------------|-------|-------|-------|-------|-------|-------|----------------------------------------|-------|-------|-----|-----|----|
| Wt % H ₂ SO ₄ | Log I | | | | | | Wt % H ₂ SO ₄ | Log I | | | | |
| | 25° | | | 40° | | | | 60° | | 80° | | |
| | 370° | 380 | Av | 370 | 380 | Av | 370 | 380 | Av | 370 | 380 | Av |
| 84.60 | | 1.44 | 1.44 | | | | | | | | | |
| 86.50 | 0.96 | 0.92 | 0.94 | 1.11 | 1.06 | 1.09 | 1.37 | 1.30 | 1.34 | | | |
| 87.67 | 0.70 | 0.68 | 0.69 | 0.87 | 0.84 | 0.86 | 1.04 | 1.02 | 1.03 | | | |
| 89.12 | 0.53 | 0.49 | 0.51 | 0.69 | 0.67 | 0.68 | 0.89 | 0.89 | 0.89 | | | |
| 90.50 | 0.25 | 0.23 | 0.24 | 0.38 | 0.37 | 0.38 | 0.56 | 0.56 | 0.56 | | | |
| 91.65 | 0.05 | 0.04 | 0.05 | 0.20 | 0.19 | 0.20 | 0.34 | 0.33 | 0.34 | | | |
| 93.05 | -0.16 | -0.18 | -0.17 | -0.01 | -0.03 | -0.02 | 0.14 | 0.13 | 0.14 | | | |
| 94.34 | -0.36 | -0.36 | -0.36 | -0.22 | -0.24 | -0.23 | -0.09 | -0.11 | -0.10 | | | |
| 95.44 | -0.58 | -0.59 | -0.59 | -0.39 | -0.41 | -0.40 | -0.27 | -0.27 | -0.27 | | | |
| 96.87 | -0.85 | -0.85 | -0.85 | -0.68 | -0.69 | -0.69 | -0.55 | -0.56 | -0.56 | | | |
| 97.50 | -1.09 | -1.08 | -1.09 | -0.87 | -0.89 | -0.88 | -0.73 | -0.74 | -0.74 | | | |

| Wt % H ₂ SO ₄ | Log I | | | | | | Wt % H ₂ SO ₄ | Log I | | | | | |
|----------------------------------------|-------|------|------|------|------|------|----------------------------------------|-------|-------|-------|-------|-------|-------|
| | 80° | | | 90° | | | | 80° | | | 90° | | |
| | 370° | 380 | Av | 370 | 380 | Av | | 370° | 380 | Av | 370 | 380 | Av |
| 84.60 | | | | | | | 93.05 | 0.27 | 0.26 | 0.27 | 0.35 | 0.33 | 0.34 |
| 86.50 | 1.44 | 1.37 | 1.41 | | | | 94.34 | 0.05 | 0.02 | 0.04 | 0.12 | 0.11 | 0.12 |
| 87.67 | 1.20 | 1.18 | 1.19 | 1.36 | 1.27 | 1.32 | 95.44 | -0.14 | -0.16 | -0.15 | -0.06 | -0.08 | -0.07 |
| 89.12 | 1.08 | 1.04 | 1.06 | 1.18 | 1.10 | 1.14 | 96.87 | -0.38 | -0.41 | -0.40 | -0.30 | -0.32 | -0.31 |
| 90.50 | 0.70 | 0.70 | 0.70 | 0.76 | 0.76 | 0.76 | 97.50 | -0.61 | -0.63 | -0.62 | -0.52 | -0.53 | -0.53 |
| 91.65 | 0.50 | 0.46 | 0.48 | 0.57 | 0.54 | 0.56 | 99.31 | -1.19 | -1.23 | -1.21 | -1.34 | -1.37 | -1.36 |

| (xii) 2,4,6-Trinitroaniline | | | | | | | | | | | | | |
|----------------------------------------|-------|-------|-------|-------|-------|-------|----------------------------------------|-------|-------|-----|-----|----|--|
| Wt % H ₂ SO ₄ | Log I | | | | | | Wt % H ₂ SO ₄ | Log I | | | | | |
| | 25° | | | 40° | | | | 60° | | | 80° | | |
| | 340° | 420 | Av | 340 | 420 | Av | 340 | 420 | Av | 340 | 420 | Av | |
| 87.82 | 1.34 | 1.26 | 1.30 | | | | 1.31 | 1.31 | 1.27 | | | | |
| 89.53 | 1.03 | 0.96 | 1.00 | 1.07 | 1.02 | 1.05 | 1.14 | 1.12 | 1.13 | | | | |
| 91.05 | 0.84 | 0.75 | 0.80 | 0.92 | 0.82 | 0.87 | 0.95 | 0.95 | 0.95 | | | | |
| 92.42 | 0.61 | 0.55 | 0.58 | 0.74 | 0.65 | 0.70 | 0.77 | 0.75 | 0.76 | | | | |
| 93.87 | 0.42 | 0.38 | 0.40 | 0.49 | 0.45 | 0.47 | 0.58 | 0.56 | 0.57 | | | | |
| 95.19 | 0.19 | 0.15 | 0.17 | 0.25 | 0.21 | 0.23 | 0.32 | 0.32 | 0.32 | | | | |
| 96.55 | -0.06 | -0.07 | -0.06 | -0.01 | -0.03 | -0.01 | 0.09 | 0.08 | 0.09 | | | | |
| 97.51 | -0.22 | -0.26 | -0.24 | -0.14 | -0.21 | -0.18 | -0.13 | -0.12 | -0.12 | | | | |
| 98.50 | -0.57 | -0.60 | -0.59 | -0.52 | -0.54 | -0.53 | -0.45 | -0.45 | -0.45 | | | | |
| 98.76 | -0.71 | -0.77 | -0.74 | -0.70 | -0.69 | -0.70 | -0.64 | -0.66 | -0.65 | | | | |
| 99.33 | -1.19 | -1.29 | -1.24 | -1.13 | -1.19 | -1.16 | -1.07 | -1.04 | -1.05 | | | | |

| Wt % H ₂ SO ₄ | Log I | | | | | | Wt % H ₂ SO ₄ | Log I | | | | | |
|----------------------------------------|-------|------|------|------|------|------|----------------------------------------|-------|-------|-------|-------|-------|-------|
| | 80° | | | 90° | | | | 80° | | | 90° | | |
| | 340° | 420 | Av | 340 | 420 | Av | | 340° | 420 | Av | 340 | 420 | Av |
| 87.82 | | | | | | | 96.55 | 0.17 | 0.15 | 0.16 | 0.21 | 0.19 | 0.20 |
| 89.53 | 1.33 | | 1.33 | 1.34 | 1.34 | 1.34 | 97.51 | -0.05 | -0.05 | -0.05 | -0.03 | -0.01 | -0.02 |
| 91.05 | 1.04 | 1.00 | 1.02 | 1.13 | 1.13 | 1.13 | 98.50 | -0.35 | -0.35 | -0.35 | -0.25 | -0.29 | -0.27 |
| 92.42 | 0.88 | 0.80 | 0.84 | 0.90 | 0.87 | 0.89 | 98.76 | -0.52 | -0.49 | -0.51 | -0.50 | -0.44 | -0.47 |
| 93.87 | 0.64 | 0.60 | 0.62 | 0.69 | 0.64 | 0.67 | 99.33 | -0.96 | -0.92 | -0.94 | -0.90 | -0.83 | -0.87 |
| 95.19 | 0.33 | 0.35 | 0.34 | 0.43 | 0.42 | 0.43 | 99.70 | -1.45 | -1.45 | -1.45 | -1.45 | -1.40 | -1.43 |

Table V. pK_a Values for the Ionization of Primary Nitroanilines in Aqueous Sulfuric Acid

| Indicator | Compd | 25° | 40° | 60° | 80° | 90° |
|-----------|--------------------------------|--------|-------|-------|-------|-------|
| 1 | 4-Nitroaniline | 1.00 | 0.90 | 0.76 | 0.65 | 0.60 |
| 2 | 2-Nitroaniline | -0.30 | -0.39 | -0.44 | -0.53 | -0.51 |
| 3 | 4-Chloro-2-nitroaniline | -1.06 | -1.11 | -1.13 | -1.20 | -1.15 |
| 4 | 2,5-Dichloro-4-nitroaniline | -1.75 | -1.80 | -1.77 | -1.83 | -1.76 |
| 5 | 2-Chloro-6-nitroaniline | -2.38 | -2.41 | -2.38 | -2.43 | -2.35 |
| 6 | 2,6-Dichloro-4-nitroaniline | -3.27 | -3.25 | -3.18 | -3.19 | -3.12 |
| 7 | 2,4-Dinitroaniline | -4.27 | -4.14 | -4.01 | -3.96 | -3.81 |
| 8 | 2,6-Dinitroaniline | -5.39 | -5.20 | -4.97 | -4.87 | -4.72 |
| 9 | 2-Bromo-4,6-dinitroaniline | -6.69 | -6.44 | -6.17 | -6.02 | -5.81 |
| 10 | 3-Methyl-2,4,6-trinitroaniline | -8.33 | -8.15 | -7.32 | -7.63 | -7.31 |
| 11 | 3-Bromo-2,4,6-trinitroaniline | -9.34 | -9.15 | -8.75 | -8.61 | -8.19 |
| 12 | 2,4,6-Trinitroaniline | -10.03 | -9.78 | -9.29 | -9.12 | -8.67 |

with the results discussed in this section, would imply that the over-all acidity function, even if it is regarded as being comprised of 12 individual acidity functions, would adequately represent the protonation behavior of any of the constituent indicators from neutral water to concentrated sulfuric acid.

The Variation of H_0 with Temperature. It was found that at particular acid strengths plots of $\log I$ against the reciprocal of the absolute temperature were straight lines.¹⁹ Thus the variation of H_0 with temperature is given by an expression of the type 14 and hence eq 15, where K is $(\alpha + A)$ and L is $(\beta + B)$.

$$H_0(T) = \log I(T) + pK_a(T) \quad (14)$$

$$= \alpha/T + \beta + A/T + B$$

$$H_0(T) = K/T + L \quad (15)$$

The values of H_0 in sulfuric acid at concentration intervals of 2% were plotted against $1/T$ and the method of least squares³ used to evaluate the constants K and L . These are recorded in Table XI.

The results were checked as follows: at 25°, eq 16 holds, while at temperature T , eq 15 applies, and combining eq 15 and 16 yields eq 17.

$$H_0(25) = K/298.15 + L \quad (16)$$

$$H_0(T) = H_0(25) + K(298.15 - T)/298.15T \quad (17)$$

Equation 17 was used to evaluate H_0 for different acid strengths at 5° intervals between 25 and 90° and the results were compared to the experimentally observed results at 40, 60, 80, and 90°. The maximum difference observed was $0.2H_0$ unit, *i.e.*, within experimental error.

Polynomials of varying degree were fitted by computer⁸ to the curve of K vs. H_0 and eq 18 was thus derived, with a correlation coefficient of 0.999.

$$K = -3.20255[H_0(25)]^3 - 56.6898[H_0(25)]^2 + 4.61041[H_0(25)] - 204.341 \quad (18)$$

$$H_0(T) = 298.15H_0(25)/T + L(T - 298.15)/T \quad (19)$$

Table VI. H_0 Values at Different Temperatures

| Wt % H_2SO_4 | 25° | 40° | 60° | 80° | 90° |
|----------------|--------|--------|--------|-------|-------|
| 2 | 0.53 | 0.54 | 0.62 | 0.65 | 0.66 |
| 4 | 0.20 | 0.18 | 0.26 | 0.27 | 0.30 |
| 6 | -0.02 | -0.03 | 0.03 | 0.04 | 0.07 |
| 8 | -0.20 | -0.21 | -0.15 | -0.13 | -0.10 |
| 10 | -0.35 | -0.34 | -0.29 | -0.29 | -0.25 |
| 12 | -0.50 | -0.48 | -0.44 | -0.43 | -0.38 |
| 14 | -0.65 | -0.62 | -0.58 | -0.57 | -0.51 |
| 16 | -0.78 | -0.76 | -0.71 | -0.69 | -0.63 |
| 18 | -0.92 | -0.90 | -0.84 | -0.82 | -0.76 |
| 20 | -1.06 | -1.03 | -0.96 | -0.95 | -0.87 |
| 22 | -1.20 | -1.16 | -1.09 | -1.08 | -0.99 |
| 24 | -1.34 | -1.29 | -1.22 | -1.20 | -1.11 |
| 26 | -1.47 | -1.42 | -1.34 | -1.33 | -1.23 |
| 28 | -1.60 | -1.56 | -1.46 | -1.45 | -1.35 |
| 30 | -1.73 | -1.69 | -1.58 | -1.56 | -1.47 |
| 32 | -1.85 | -1.83 | -1.71 | -1.69 | -1.59 |
| 34 | -1.99 | -1.96 | -1.83 | -1.80 | -1.72 |
| 36 | -2.12 | -2.10 | -1.96 | -1.92 | -1.84 |
| 38 | -2.27 | -2.25 | -2.10 | -2.06 | -1.97 |
| 40 | -2.42 | -2.40 | -2.25 | -2.21 | -2.10 |
| 42 | -2.60 | -2.55 | -2.40 | -2.36 | -2.25 |
| 44 | -2.77 | -2.71 | -2.56 | -2.51 | -2.39 |
| 46 | -2.95 | -2.86 | -2.72 | -2.67 | -2.55 |
| 48 | -3.12 | -3.01 | -2.88 | -2.83 | -2.70 |
| 50 | -3.30 | -3.18 | -3.04 | -2.98 | -2.86 |
| 52 | -3.48 | -3.34 | -3.20 | -3.14 | -3.02 |
| 54 | -3.68 | -3.53 | -3.37 | -3.32 | -3.19 |
| 56 | -3.90 | -3.74 | -3.57 | -3.49 | -3.36 |
| 58 | -4.13 | -3.95 | -3.77 | -3.68 | -3.55 |
| 60 | -4.37 | -4.18 | -3.99 | -3.88 | -3.73 |
| 62 | -4.62 | -4.40 | -4.21 | -4.08 | -3.92 |
| 64 | -4.91 | -4.66 | -4.45 | -4.30 | -4.12 |
| 66 | -5.20 | -4.94 | -4.70 | -4.54 | -4.35 |
| 68 | -5.52 | -5.24 | -4.98 | -4.78 | -4.59 |
| 70 | -5.82 | -5.54 | -5.25 | -5.05 | -4.84 |
| 72 | -6.13 | -5.86 | -5.52 | -5.33 | -5.10 |
| 74 | -6.47 | -6.18 | -5.82 | -5.61 | -5.36 |
| 76 | -6.81 | -6.49 | -6.11 | -5.88 | -5.63 |
| 78 | -7.13 | -6.79 | -6.39 | -6.16 | -5.90 |
| 80 | -7.46 | -7.08 | -6.68 | -6.44 | -6.16 |
| 82 | -7.80 | -7.39 | -7.00 | -6.73 | -6.42 |
| 84 | -8.13 | -7.78 | -7.32 | -7.04 | -6.70 |
| 86 | -8.42 | -8.11 | -7.63 | -7.33 | -6.98 |
| 88 | -8.71 | -8.40 | -7.87 | -7.59 | -7.21 |
| 90 | -9.01 | -8.69 | -8.14 | -7.86 | -7.44 |
| 92 | -9.34 | -9.00 | -8.44 | -8.16 | -7.71 |
| 94 | -9.66 | -9.32 | -8.77 | -8.49 | -8.01 |
| 96 | -9.98 | -9.66 | -9.12 | -8.84 | -8.34 |
| 98 | -10.43 | -10.11 | -9.58 | -9.27 | -8.82 |
| 99 | -10.94 | -10.64 | -10.09 | -9.74 | -9.26 |

Table VII. pK_a of 4-Nitroaniline

| 25° | 40° | 60° | 80° | 90° | Ref |
|------|------|------|-------------------|-------------------|--------------|
| 1.00 | 0.90 | 0.76 | 0.65 | 0.60 | ^a |
| 1.00 | 0.89 | | | | 18 |
| 1.00 | 0.90 | 0.77 | 0.66 ^b | 0.61 ^b | 19 |
| | 0.91 | 0.71 | 0.54 | | 5 |

^a This work. ^b Extrapolated value.

As a conclusion to these empirical correlations, plots of $H_0(T)$ vs. $H_0(25)$ were made. These gave excellent straight lines over the entire acidity range, each of the four lines passing through a common intersection point $H_0 = 0$. From eq 15 we may deduce eq 19 and calculations show that $298.15/T$ is 0.95, 0.89, 0.84, and 0.82 at 40, 60, 80, and 90°, respectively, values in agreement with the slopes of the appropriate plots, while all the factors $L(T - 298.15)/T$ are near zero.

Table VIII. Comparison of pK_a Values at 25°

| Indicator ^a | This work ^b | Ref 14 ^b | Ref 13 ^c | Ref 11 ^d | Ref 12 ^b | Ref 5 ^{b,e} |
|------------------------|------------------------|---------------------|---------------------|---------------------|---------------------|----------------------|
| 1 | 1.00 | 1.00 | | 0.99 | | 1.11 |
| 2 | -0.30 | -0.33 | | -0.29 | | -0.13 |
| 3 | -1.06 | | -1.07 | -1.03 | | -0.87 |
| 4 | -1.75 | -1.90 | -1.79 | | -1.78 | |
| 5 | -2.38 | -2.54 | -2.41 | | -2.43 | |
| 6 | -3.27 | -3.28 | -3.20 | | -3.27 | -2.94 |
| 7 | -4.27 | -4.45 | -4.26 | -4.53 | | -4.39 |
| 8 | -5.39 | -5.64 | -5.25 | | -5.54 | |
| 9 | -6.69 | -7.09 | -6.69 | -6.71 | -6.68 | |
| 10 | -8.33 | -8.34 | -8.56 | | -8.22 | |
| 11 | -9.34 | | -9.77 | | -9.46 | |
| 12 | -10.03 | -9.98 | | -9.41 | -10.10 | -9.28 |

^a Numbers refer to those given to the indicators in Table V. ^b Sulfuric acid medium. ^c Perchloric acid medium. ^d "Best value." ^e 20°. ^f This value is the pK_a of 2,4-dichloro-6-nitroaniline, which has the same ionization curve as 2,6-dichloro-4-nitroaniline.¹²

Table IX. Comparison of H_0 Values in Sulfuric Acid at 25°

| Wt % H ₂ SO ₄ | This work | Ref 11 | Ref 12 | Ref 14 | Ref 5 ^a |
|-------------------------------------|-----------|--------|--------|--------|--------------------|
| 5 | 0.09 | | | -0.02 | |
| 10 | -0.35 | -0.31 | | -0.43 | -0.27 |
| 15 | -0.70 | -0.66 | | -0.78 | -0.60 |
| 20 | -1.06 | -1.01 | | -1.10 | -0.92 |
| 25 | -1.40 | -1.37 | | -1.47 | -1.25 |
| 30 | -1.73 | -1.72 | | -1.82 | -1.60 |
| 35 | -2.05 | -2.06 | | -2.19 | -1.96 |
| 40 | -2.42 | -2.41 | | -2.54 | -2.33 |
| 45 | -2.86 | -2.85 | | -2.95 | -2.75 |
| 50 | -3.30 | -3.38 | | -3.41 | -3.16 |
| 55 | -3.80 | -3.91 | | -3.91 | -3.70 |
| 60 | -4.37 | -4.46 | -4.46 | -4.51 | -4.24 |
| 65 | -5.06 | | -5.07 | -5.18 | -4.97 |
| 70 | -5.82 | | -5.80 | -5.92 | -5.70 |
| 75 | -6.64 | | -6.56 | -6.71 | -6.39 |
| 80 | -7.46 | | -7.34 | -7.52 | -7.18 |
| 85 | -8.28 | | -8.14 | -8.29 | -7.90 |
| 90 | -9.01 | | -8.92 | -9.03 | -8.41 |
| 95 | -9.81 | | -9.85 | -9.74 | -8.98 |

^a 20°.

Table X. Value of the Slope Errors in the Regions of Indicator Overlap

| Indicator ^a | Value of slope | Value of product |
|------------------------|----------------|------------------|
| i | $a_{i,i-1}$ | $a_{i,i-1}$ |
| 1 | 1.00 | 1.00 |
| 2 | 1.04 | 1.04 |
| 3 | 1.07 | 1.12 |
| 4 | 0.88 | 0.98 |
| 5 | 1.10 | 1.07 |
| 6 | 0.85 | 0.92 |
| 7 | 1.01 | 0.93 |
| 8 | 1.05 | 0.98 |
| 9 | 0.97 | 0.95 |
| 10 | 1.05 | 1.00 |
| 11 | 1.15 | 1.15 |
| 12 | 0.91 | 1.04 |

^a Numbers refer to those given to the indicators in Table V. Note $i = 0$ refers to the first indicator.

Applications of the H_0 Scale at Elevated Temperatures to Previous Data. (i) Other Acidity Scales. The only pertinent study, apart from that of Gel'bshtein⁶ discussed above, is due to Arnett and Bushick,⁶ who measured the H_R acidity scale at 0, 15, 30, and 45°,

Table XI. Values of the Constants K and L in the Expression $H_0(T) = K/T + L$ and $H_R(T) = K/T + L$

| Wt % H ₂ SO ₄ | H_0 | | H_R | |
|-------------------------------------|--------------------|---------|--------------------|---------|
| | $K \times 10^{-3}$ | L | $K \times 10^{-3}$ | L |
| 2 | -0.2400 | 1.3259 | -0.1403 | 1.165 |
| 4 | -0.1745 | 0.7995 | -0.2947 | 1.341 |
| 6 | -0.1581 | 0.5055 | 0.0555 | -0.329 |
| 8 | -0.1770 | 0.3894 | -0.5431 | 1.673 |
| 10 | -0.1567 | 0.1744 | -0.5867 | 1.618 |
| 12 | -0.1799 | 0.1065 | -0.5815 | 1.384 |
| 14 | -0.2041 | 0.0398 | -0.5350 | 0.997 |
| 16 | -0.2297 | -0.0059 | -0.5669 | 0.853 |
| 18 | -0.2496 | -0.0808 | -0.5451 | 0.540 |
| 20 | -0.2858 | -0.0978 | -0.5691 | 0.329 |
| 22 | -0.3100 | -0.1546 | -0.5346 | -0.029 |
| 24 | -0.3420 | -0.1859 | -0.4857 | -0.474 |
| 26 | -0.3541 | -0.2762 | -0.5357 | -0.588 |
| 28 | -0.3807 | -0.3207 | -0.5527 | -0.814 |
| 30 | -0.4084 | -0.3602 | -0.5539 | -1.098 |
| 32 | -0.4130 | -0.4660 | -0.5927 | -1.257 |
| 34 | -0.4429 | -0.5094 | -0.5696 | -1.651 |
| 36 | -0.4685 | -0.5550 | -0.5766 | -1.925 |
| 38 | -0.4994 | -0.6014 | -0.6450 | -2.015 |
| 40 | -0.5127 | -0.6743 | -0.6027 | -2.493 |
| 42 | -0.5610 | -0.7201 | -0.6248 | -2.767 |
| 44 | -0.6041 | -0.7429 | -0.6610 | -2.977 |
| 46 | -0.6237 | -0.8539 | -0.6367 | -3.427 |
| 48 | -0.6412 | -0.9610 | -0.6099 | -3.889 |
| 50 | -0.6821 | -1.0058 | -0.5188 | -4.583 |
| 52 | -0.7085 | -1.0963 | -0.3862 | -5.471 |
| 54 | -0.7536 | -1.1468 | -0.0731 | -7.025 |
| 56 | -0.8433 | -1.0652 | 0.0890 | -8.027 |
| 58 | -0.9084 | -1.0767 | 0.2425 | -9.032 |
| 60 | -1.0013 | -1.0019 | 0.4444 | -10.236 |
| 62 | -1.0897 | -0.9513 | 0.6167 | -11.367 |
| 64 | -1.2288 | -0.7719 | 0.7878 | -12.536 |
| 66 | -1.3315 | -0.7194 | 0.9509 | -13.669 |
| 68 | -1.4732 | -0.5640 | 1.1348 | -14.913 |
| 70 | -1.5549 | -0.5916 | 1.2966 | -16.085 |
| 72 | -1.6444 | -0.6077 | 1.4686 | -17.356 |
| 74 | -1.7703 | -0.5231 | 1.7652 | -19.037 |
| 76 | -1.8874 | -0.4709 | 2.0938 | -20.805 |
| 78 | -1.9646 | -0.5327 | 2.4832 | -22.802 |
| 80 | -2.0582 | -0.5428 | 2.9103 | -24.955 |
| 82 | -2.1675 | -0.5062 | 3.5049 | -27.698 |
| 84 | -2.2796 | -0.4692 | 4.0300 | -30.170 |
| 86 | -2.3154 | -0.6415 | 4.2626 | -31.575 |
| 88 | -2.4102 | -0.6182 | 4.4820 | -32.869 |
| 90 | -2.5072 | -0.5891 | 3.7089 | -34.154 |
| 92 | -2.5865 | -0.6489 | 4.8807 | -35.239 |
| 94 | -2.5996 | -0.9184 | 4.9149 | -35.827 |
| 96 | -2.5754 | -1.3158 | 5.1288 | -36.986 |
| 98 | -2.5571 | -1.8318 | 5.2197 | -37.735 |
| 99 | -2.6790 | -1.9296 | | |

finding that H_R became more negative with an increase in temperature. These results were fitted by us to eq 15 and checked with eq 17 using the value of H_R at 0° as a basis for the other temperatures (see Table XI). The maximum difference between the experimental results and those calculated was $0.35H_R$ unit. It must be pointed out that the results calculated for 25° from these figures do not agree with the H_R values for 25° given by Deno,²² nor do the pK_a values of indicators common to both studies agree. The observation²³ that acidity functions H_X are linearly related to H_0 by eq 20 was then tested for the above results of H_0 and H_R at temperatures of 25, 30, 35, 40, and 45°. At each temperature, plots of H_R vs. H_0 gave good straight lines,

(22) N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, *J. Amer. Chem. Soc.*, **77**, 3044 (1955).

(23) K. Yates and R. A. McClelland, *ibid.*, **89**, 2686 (1967).

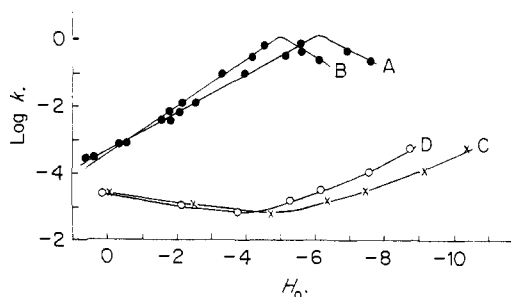


Figure 4. Change of rate profile due to a correction for the variation of H_0 with temperature: (A) 4-aminopyridine using $H_0(25)$, (B) 4-aminopyridine using $H_0(107)$ (calculated using eq 17 and 18), (C) 4-quinolone using $H_0(25)$, and (D) 4-quinolone using $H_0(90)$.

but the slope parameter varied with the temperature as follows: m , 2.11 (25°), 2.18 (30°), 2.27 (35°), 2.32 (40°), and 2.40 (45°). This result complicates attempts to reassess kinetic data obtained at high temperatures, as it implies that the relationship which exists between acidity functions at 25° is not necessarily the same at higher temperatures.

$$H_x = mH_0 + \text{constant} \quad (20)$$

$$\log A_{fb} = \log A_{ms} + \Delta S^\circ/2.303R + H_A - \frac{ldH_A}{Td(1/T)} \quad (21)$$

(ii) **Nitration of Heteroaromatics.** Moodie and Schofield²⁴ have carried out a critical appraisal of the possible free base mechanism of nitration of heteroaromatic N-oxides. These authors showed, for example, that in the case of 2,6-dimethylpyridine 1-oxide the most probable mechanism of nitration was *via* the free base species. However, on this basis the Arrhenius preexponential factor, $\log A_{fb}$, obtained for the nitration was anomalously high. The authors derived eq 21 relating $\log A_{fb}$ to $\log A_{ms}$, the Arrhenius preexponential factor for a normal majority species (in this case the conjugate acid).

The H_A scale is used because this is considered to be the scale appropriate for ionization of N-oxides.²⁵ The calculated value of $\log A_{fb}$ was 4.0 at 81.3%, assuming that $dH_A/d(1/T)$ was the same as $dH_0/d(1/T)$, and obtaining a value for this quantity from the work of Gel'bshtein.⁵ The discrepancy between this value and the experimental one, 10.7, led Schofield and his co-workers to question the normal free base mechanism in this case, although the assumption of a similar temperature dependence between H_A and H_0 was, as pointed out by the authors, unjustified. From the present work,

(24) J. T. Gleghorn, R. B. Moodie, E. A. Qureshi, and K. Schofield, *J. Chem. Soc., B*, 316 (1968).

(25) C. D. Johnson, A. R. Katritzky, and N. Shakir, *ibid.*, 1235 (1967).

however, the value of $(1/T)\{dH_0/d(1/T)\}$ for 81.3% sulfuric acid is -7.2 , which yields a calculated $\log A_{fb}$ value of 9.3, much closer to the observed value. There is hence no longer any reason to doubt the free base mechanism.

(iii) **Nitration of Nitroanilines.** A case where $dH_0/d(1/T)$ can be used directly stems from the work of Hartshorn and Ridd on the nitration of 4-nitroaniline and 2-chloro-4-nitroaniline² where rate profile and kinetic evidence suggested free base reaction at encounter rate. The activation energies, 18.2 and 19.1 kcal/mole, respectively, in 98% sulfuric acid were, however, high for an encounter reaction, the calculated value, from eq 22, being 13 kcal/mole, where the old data of Gel'bshtein were used. In 98% sulfuric acid, we now find $dH_0/(1/T)$ is -2557 and the revised contribution from the final term is thus 11.7 kcal. ΔH° is obtained from the plot of pK_a vs. $1/T$ and the value for 4-nitroaniline can be calculated from the data in Table V to be 3.08. Thus the recalculated value of E is 19.1 kcal/mole, in good agreement with the observed value of 18.2.

$$E = -2.303R d \log k_2/d(1/T) + \Delta H_0 - 2.303 dH_0/d(1/T) \quad (22)$$

The value of ΔH° for 2-chloro-4-nitroaniline is not known, but since the pK_a value of this compound (0.85) is close to that of 4-nitroaniline (1.00), it is likely that the value of ΔH° will be similar, and thus again the calculated value of E should be in agreement with the observed value.

(iv) **Acid-Catalyzed Hydrogen Exchange.** The influence of the variation of H_0 with temperature in changing the shape of rate profiles for acid-catalyzed hydrogen exchange can be seen in Figure 4, for the exchange of the 3 and 5 position protons in 4-aminopyridine²⁶ at 107° and for the exchange of the 3 position in 4-quinolone²⁷ at 90° .

Although Figure 4 illustrates that plotting $\log k$ vs. H_0 at 25° , when k has been determined at a higher temperature, does not affect the general shape of the $\log k$ vs. H_0 rate profile and thus the validity of conclusions drawn from it, it does show that values of dH_x/dH_0 and dH_y/dH_0 , where H_x is the acidity function for kinetic C protonation and H_y for equilibrium protonation of the free base, are affected by change in temperature. Unfortunately no correction can be applied until the variations of other acidity functions with temperature have been investigated, and possible relationships between the acidity functions at different temperatures have been proposed.

Acknowledgment. We thank Mr. S. Joyce for help in computer programming.

(26) G. P. Bean, C. D. Johnson, A. R. Katritzky, B. J. Ridgewell, and A. M. White, *ibid.*, 1219 (1967).

(27) P. Bellingham, C. D. Johnson, and A. R. Katritzky, *ibid.*, 1226 (1967).