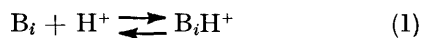


The M_C Activity Coefficient Function for Acid-Base Equilibria. Part 5.† The M_C Activity Coefficient for a Reliable Estimate of Thermodynamic Values

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The general validity of the relationship $\log (f_{Z_i}f_{A_i}/f_{D_i}) = n_{ij} (\log f_{Z_j}f_{A_j}/f_{D_j})$ (Z = base, A = acid, D = conjugated acid) has been tested using different weak bases involved in protonation, ionization, and rate processes. Experimental data in aqueous sulphuric and perchloric acid have been treated simultaneously by a mathematical procedure which allows the transference of data from one acid to another. The analysis of the thermodynamic values of equilibria and rate processes shows the advantages both of the new treatment and of the latter estimated $M_C f(x)$ functions.

In concentrated aqueous acid systems, the accurate thermodynamic pK value of a weak base B_i which is protonated according to equilibrium (1), can be obtained by relation (2), provided a reliable 'activity coefficient function'¹⁻⁴ or ' M_C function' [equation (3)] is known.



$$pK_{B_iH^+} = \log \frac{[B_iH^+]}{[B_i]} - \log [H^+] - \log \frac{f_{B_i}f_{H^+}}{f_{B_iH^+}} \quad (2)$$

$$M_{C_i} = -\log \frac{f_{B_i}f_{H^+}}{f_{B_iH^+}} = -n_{ij} \log \frac{f_{B_j}f_{H^+}}{f_{B_jH^+}} \quad (3)$$

Some M_C functions have been calculated by graphical¹ or numerical procedures,^{4,5} which demonstrated the validity of the linear dependence (3) for a very large number of indicators¹⁻⁵ protonated according to equilibrium (1). It guarantees confidence in the treatment of equilibria by equation (3), and allows further developments to take place.

In these studies, however, it is essential to examine whether the accuracy required to assign numerical values to the M_C functions is experimentally attainable. The M_C functions so far available, sometimes appear inadequate for determining accurate thermodynamic results. For example, very different pK values (referred to water as standard solvent) can be estimated for the same indicators, using M_C functions calculated through different regression analyses^{4,5} (Figure 1). What is more, very large discrepancies are often observed upon comparing the pK values of analogous compounds in sulphuric and perchloric acid, calculated by the same regression analysis (see e.g. Figure 6 of ref. 5).

Hence, there is a necessity of a better evaluation of M_C functions when reliable information or estimations are required.

Some attempts are reported here which make use of different compounds involved in protonation, ionization, and rate processes. For each of them, the validity of the linear relation (3), rewritten as (3') has been tested. In equation (3') Z = base, A = acid, and D = conjugated acid.

† Part 4; P. G. Traverso, N. C. Marziano, and R. C. Passerini, *J. Chem. Soc., Perkin Trans. 2*, 1977, 845.

$$\log \frac{f_{Z_i}f_{A_i}}{f_{D_i}} = n_{ij} \log \frac{f_{Z_j}f_{A_j}}{f_{D_j}} \quad (3')$$

The ' $M_{C_{ROH}}$ ' Function for Complex Ionizations.—The ionization equilibria (4) have been investigated for aqueous sulphuric acid solutions with the computational procedure previously adopted,⁴ using triphenyl- and

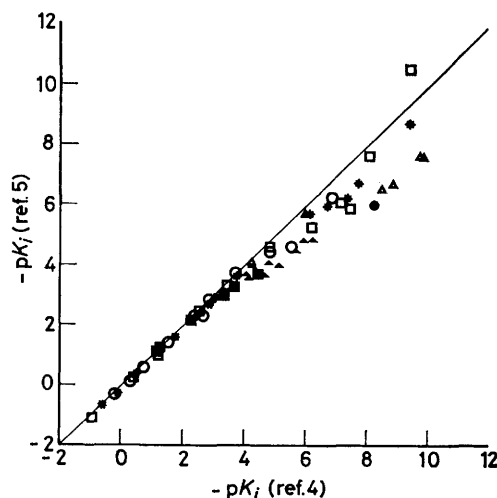
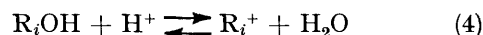


FIGURE 1 A comparison between thermodynamic pK_i values of some indicators, using two differently calculated M_C functions (refs. 4 and 5) in aqueous sulphuric acid. Indicators: \square , nitroanilines; \triangle , hydroxy-alkoxy-benzenes; *, tertiary amines; \blacksquare , amides; \blacktriangle , benzophenones; \circ , indoles

diphenyl-methanols as indicators.⁶ The linear relation-



ship (3') where $Z = ROH$, $A = H^+$, and $D = R^+$ for a number of solutes ROH has been tested by relation (5) where $G_i = \log([R_i^+]/[R_iOH] - \log[H^+] + \log a_w)$, n_{ij} and r_{ij} are constants, and suffixes i and j identify the indicators. (x) is the molar acid concentration. The

$$G_i(x) = n_{ij}G_j(x) + r_{ij} \quad (5)$$

reliability of the results has been tested by means of the σ^2 values obtained by the comparison between experimental and theoretical G_i values.

The general pattern supports the validity of (3') and allows the calculation of the corresponding $M_{C_{ROH}}$ function.⁷ The mean square roots of the deviations (σ^2 values) range from 0.003 to 0.049, as expected on the basis of the spread of the experimental data.

The General M_{C_i} Function.—New aspects concerning the validity of (3') have also been investigated by using, simultaneously, indicators which follow protonation equilibria (1) and (4). Thus, B_i and R_iOH solutes have been tested in sulphuric acid by relation (5') where $F_j = G_i$ or $(\log[B_iH^+]/[B_i] - \log[H^+])$. In all cases,

$$F_j(x) = n_{ij}F_j(x) + r_{ij} \quad (5')$$

the linear relationships (3') (where $Z = B$ or ROH , $A = H^+$, and $D_i = BH^+$ or R^+) have been verified by the σ^2 values which are consistent with those observed for indicators having the same basic site or protonation equilibrium.⁴ By a similar procedure additional tests which support previous evidence have been made, both in sulphuric and perchloric acid, using the same key compounds, whether for equilibria or for rate processes.

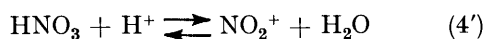
Thus, nitric acid was chosen since equilibrium (1), rewritten as (1'), has been studied⁸ in a wide acidity range of sulphuric (0–80%) and perchloric acid (0–



72%). The nitrations of benzene and halogenobenzenes^{10–12} in the range 50–82% sulphuric and 50–72% perchloric acids have been chosen as examples of chemical reactions and tested by equation (5'') [where $Y_i = F_i$ or $(\log k_{2obs} - \log[H^+] + \log a_w)$].

$$Y_i(x) = n_{ij}Y_j(x) + r_{ij} \quad (5'')$$

Moreover, as a sample of inorganic compounds protonated according to equilibrium (4), equilibrium (4') has been studied in 80–96% sulphuric acid.^{8,9}



The results of these investigations are of importance in the study of equilibria and reaction mechanisms. The reason for this lies in the observed validity of the linear relationship (3') tested through (5''), where widely different compounds and chemical systems are involved.

A Better M_C Function.—The results allow the utilization of a large number of compounds studied with the aim of determining unambiguous activity coefficient functions, both in sulphuric and perchloric acid. Since none of the factors limiting* the accuracy of M_C values is small enough to be neglected, further studies are reported, which are able to overcome many sources of uncertainty.

The first improvement on the accuracy of the functions can be achieved by using indicators for which a large number of experimental data over wide acidity ranges, or experimentally accurate data over high acidity ranges,

* The differences among the estimated M_C functions arise from various sources: the errors in experimental data, the limited number of indicators studied in some acids, the discrete set of points available in narrow acidity ranges for most of the indicators, and finally the regression procedure which is adopted.

are available. Thus, new pK values and M_C functions can be obtained. As can be seen (C in Figure 2), the latter give pK values for analogous compounds in different acids, with better agreement between them.

While more and significant new experimental data are awaited, the probability of obtaining further improvements in the M_C functions remains low, as long as only the above procedures are followed.

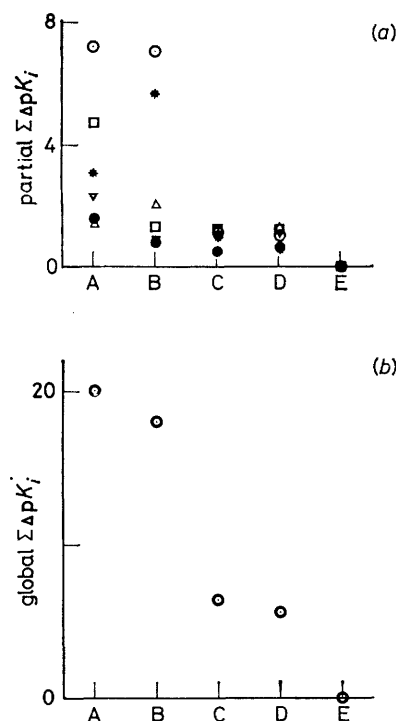


FIGURE 2 Partial (a) and global (b) $\Sigma\Delta pK_i$ values [$\Delta pK_i = pK_{i(H_2SO_4)} - pK_{i(HClO_4)}$] of key compounds, obtained by differently calculated M_C functions: A (ref. 5); B (ref. 4); C (using the indicators in Table 1 without any constraint between the key compounds); D (using plots of Y_i versus M_C in Table 1); E (values of Table 2). Key compounds: *, benzene, halogenobenzenes; ∇ , nitroanilines; \square , tertiary amines; Δ , amides; \circ , hydroxy-alkoxy-benzenes; \bullet , anions

Thus, a new procedure is proposed (see later for the details) which is able to account, simultaneously, for all the data available in two (or more) different acid solutions. For key compounds the identity between (or among) their thermodynamic values, referred to water as standard solvent, is imposed as an additional constraint. Thus, new values of σ^2 , n_{ij} , r_{ij} , and M_C are obtained as a consequence of the mutual interaction of the experimental data in two (or more) different acids. In Table 1 the M_C functions obtained by the new procedure are set out using, simultaneously, the whole set of experimental data available, both in sulphuric and perchloric acid.† In Table 2 slopes and pK values of some indicators used as key compounds are given.

† In every particular acid chosen, a correct comparison between any two estimated M_C functions requires plots of one against the other. Deviations from linearity [due to relationship (3)] show significant differences. Comparisons of their numerical values or by plots of M_C against acid concentrations,⁵ appear to be misleading.

TABLE 1

The M_G activity coefficient functions and estimated errors in aqueous sulphuric and perchloric acid at 25 °C *

[Acid]/M	$-M_G$ in H_2SO_4	$-M_G$ in $HClO_4$
0.2	0.044 ± 0.004	0.082 ± 0.005
0.4	0.094 ± 0.007	0.167 ± 0.009
0.6	0.150 ± 0.010	0.255 ± 0.013
0.8	0.211 ± 0.012	0.345 ± 0.017
1.0	0.276 ± 0.014	0.436 ± 0.019
1.2	0.347 ± 0.015	0.529 ± 0.021
1.4	0.421 ± 0.016	0.623 ± 0.023
1.6	0.500 ± 0.017	0.719 ± 0.025
1.8	0.583 ± 0.018	0.815 ± 0.026
2.0	0.670 ± 0.019	0.914 ± 0.027
2.2	0.760 ± 0.020	1.014 ± 0.027
2.4	0.853 ± 0.021	1.116 ± 0.028
2.6	0.950 ± 0.021	1.220 ± 0.028
2.8	1.049 ± 0.022	1.326 ± 0.028
3.0	1.152 ± 0.022	1.436 ± 0.029
3.2	1.257 ± 0.023	1.548 ± 0.029
3.4	1.365 ± 0.023	1.664 ± 0.029
3.6	1.475 ± 0.023	1.783 ± 0.029
3.8	1.588 ± 0.023	1.906 ± 0.029
4.0	1.703 ± 0.022	2.033 ± 0.029
4.2	1.820 ± 0.022	2.165 ± 0.029
4.4	1.940 ± 0.021	2.301 ± 0.030
4.6	2.062 ± 0.021	2.442 ± 0.030
4.8	2.185 ± 0.020	2.587 ± 0.030
5.0	2.312 ± 0.019	2.738 ± 0.030
5.2	2.440 ± 0.019	2.893 ± 0.030
5.4	2.570 ± 0.018	3.053 ± 0.031
5.6	2.702 ± 0.018	3.218 ± 0.031
5.8	2.837 ± 0.017	3.388 ± 0.031
6.0	2.973 ± 0.017	3.563 ± 0.031
6.2	3.112 ± 0.017	3.741 ± 0.031
6.4	3.253 ± 0.017	3.925 ± 0.031
6.6	3.396 ± 0.017	4.112 ± 0.030
6.8	3.541 ± 0.017	4.303 ± 0.029
7.0	3.688 ± 0.017	4.498 ± 0.028
7.2	3.838 ± 0.017	4.697 ± 0.027
7.4	3.989 ± 0.017	4.899 ± 0.026
7.6	4.143 ± 0.017	5.104 ± 0.024
7.8	4.299 ± 0.017	5.312 ± 0.022
8.0	4.457 ± 0.017	5.523 ± 0.020
8.2	4.618 ± 0.017	5.737 ± 0.019
8.4	4.780 ± 0.016	5.953 ± 0.017
8.6	4.945 ± 0.016	6.172 ± 0.015
8.8	5.112 ± 0.015	6.393 ± 0.014
9.0	5.281 ± 0.015	6.617 ± 0.013
9.2	5.452 ± 0.014	6.844 ± 0.013
9.4	5.626 ± 0.014	7.074 ± 0.013
9.6	5.801 ± 0.013	7.307 ± 0.014
9.8	5.978 ± 0.013	7.544 ± 0.014
10.0	6.157 ± 0.012	7.784 ± 0.014
10.2	6.337 ± 0.012	8.028 ± 0.014
10.4	6.519 ± 0.011	8.277 ± 0.014
10.6	6.703 ± 0.011	8.530 ± 0.014
10.8	6.888 ± 0.011	8.788 ± 0.015
11.0	7.074 ± 0.011	9.052 ± 0.016
11.2	7.261 ± 0.011	9.322 ± 0.018
11.4	7.450 ± 0.010	9.598 ± 0.022
11.6	7.639 ± 0.010	9.880 ± 0.027
11.8	7.829 ± 0.010	10.168 ± 0.033
12.0	8.019 ± 0.010	10.462 ± 0.039
12.2	8.210 ± 0.010	10.761 ± 0.046
12.4	8.401 ± 0.010	11.066 ± 0.053
12.6	8.592 ± 0.010	11.375 ± 0.062
12.8	8.784 ± 0.011	11.686 ± 0.072
13.0	8.975 ± 0.012	
13.2	9.166 ± 0.013	
13.4	9.356 ± 0.014	
13.6	9.547 ± 0.016	
13.8	9.737 ± 0.017	
14.0	9.927 ± 0.019	
14.2	10.116 ± 0.020	
14.4	10.306 ± 0.021	
14.6	10.495 ± 0.022	
14.8	10.685 ± 0.023	
15.0	10.876 ± 0.023	

TABLE 1 (continued)

[Acid]/M	$-M_G$ in H_2SO_4
15.2	11.067 ± 0.023
15.4	11.260 ± 0.022
15.6	11.455 ± 0.021
15.8	11.653 ± 0.019
16.0	11.854 ± 0.017
16.2	12.060 ± 0.016
16.4	12.272 ± 0.015
16.6	12.491 ± 0.016
16.8	12.717 ± 0.019
17.0	12.954 ± 0.023
17.2	13.203 ± 0.029
17.4	13.465 ± 0.035
17.6	13.744 ± 0.041
17.8	14.041 ± 0.048
18.0	14.360 ± 0.056
18.2	14.704 ± 0.065
18.4	15.075 ± 0.078

* Calculated by equation (6) (see Experimental section), using, simultaneously, sets of experimental data available for sulphuric and perchloric acid: Y_i values of primary nitroanilines, tertiary amines, benzophenones, amides, indoles, triphenyl- and diphenyl-methanols, anions, hydroxy- and methoxy-benzenes, nitric acid, benzene and monohalogenobenzenes (references in Table 2 and in ref. 4).

The evidence which warrants confidence in the new results is the σ^2 values. For all indicators, including the key compounds, they range between 0.007 and 0.05 (90% \leq 0.01), thus being consistent with those obtained in every acid, taken singly, notwithstanding the imposed constraint.

The gains achieved by the new M_G functions, compared with the previous ones, can be seen in Figure 2. It can be observed, for instance, that the pK values of key compounds calculated in sulphuric and perchloric acid by plotting experimental Y_i data against the new M_G functions (D in Figure 2), are able to give ΔpK_i values ($\Delta pK_i = pK_{i(H_2SO_4)} - pK_{i(HClO_4)}$) lower than those obtained by using any other function.

On the other hand, the best pK value of any indicator can be obtained when it is used as a key compound in general regression analysis (Table 2, E in Figure 2). The new method itself allows the transference of the experimental data available in two or more acids to any one of them. Thus, it works out as an increase in the amount of experimental data for either of the two acids. It also involves an advantage in the evaluation of M_G functions in acid solutions where few indicators are available.

Any comparison with ΔpK_i values obtained by the acidity functions (H_0, H_A, H_I) is irrelevant because of the breakdown of the basic Hammett assumption (see for instance n_{ij} values in Table 2) and the limitations of the stepwise procedure used in the calculation of acidity scales.

Mathematical Procedure.—This mathematical procedure used enables an analysis of the whole set of experimental data involved in equations (5), (5'), and (5'') to be performed. Since any indicator can be expressed by a single function or a 'generatrix function',† the previous equations can be rewritten as (6) or (6') and

† The term ' $M_G f(x)$ generatrix function' is used for its mathematically correct terminology.

TABLE 2

Slope (n_{ij}) and intercept * (r_{ij}) values † of some key compounds calculated by equation (6) using the experimental data in both aqueous sulphuric and perchloric acid at 25 °C

Nitration rates of ^a	H ₂ SO ₄	HClO ₄	H ₂ SO ₄ and HOCl ₄	No. of points
	n_{ij}	n_{ij}	r_{ij}	
Benzene	1.308 ± 0.009	1.387 ± 0.011	-12.962 ± 0.064	67
Fluorobenzene	1.292 ± 0.014	1.393 ± 0.013	-13.750 ± 0.101	34
Chlorobenzene	1.335 ± 0.020	1.426 ± 0.024	-14.376 ± 0.162	32
Bromobenzene	1.333 ± 0.023	1.428 ± 0.022	-14.398 ± 0.168	28
Iodobenzene	1.192 ± 0.022	1.265 ± 0.023	-12.733 ± 0.178	19
Equilibria of nitric acid ^b				
HNO ₃ ⇌ H ⁺ + NO ₃ ⁻	0.338 ± 0.003	0.343 ± 0.005	-2.242 ± 0.013	59
HNO ₃ + H ⁺ ⇌ H ₂ O + NO ₂ ⁺	0.899 ± 0.015		-15.049 ± 0.183	69
Equilibria of primary nitroanilines ^{c,d}				
2-Nitro	0.682 ± 0.009	0.628 ± 0.022	-0.306 ± 0.011	18
4-Chloro-2-nitro	0.671 ± 0.021	0.576 ± 0.014	-1.041 ± 0.026	21
2,5-Dichloro-4-nitro	0.603 ± 0.009	0.555 ± 0.009	-1.709 ± 0.020	31
2-Chloro-6-nitro	0.624 ± 0.009	0.586 ± 0.008	-2.392 ± 0.013	23
2,4-Dichloro-6-nitro	0.616 ± 0.007	0.598 ± 0.010	-3.043 ± 0.028	23
2,6-Dichloro-4-nitro	0.595 ± 0.008	0.571 ± 0.009	-3.125 ± 0.035	29
2-Bromo-4,6-dinitro	0.644 ± 0.006	0.681 ± 0.006	-6.807 ± 0.063	31
Equilibria of tertiary amines ^{e,f}				
NN-Dimethyl-4-nitroaniline	1.221 ± 0.035	1.138 ± 0.054	+0.668 ± 0.006	15
N-(2,4-Dinitrophenyl)piperidine	1.246 ± 0.044	1.131 ± 0.056	-0.427 ± 0.022	15
NN-Dimethyl-1-naphthyl-2,4-dinitroaniline	0.844 ± 0.012	0.873 ± 0.021	-2.171 ± 0.033	19
N-Methyl-4-nitrodiphenylamine	0.872 ± 0.020	0.788 ± 0.020	-2.996 ± 0.053	18
NN-Diethyl-2,4,6-trinitroaniline	0.839 ± 0.009	0.904 ± 0.007	-5.369 ± 0.054	13
NN-Dimethyl-2,4,6-trinitroaniline	0.866 ± 0.018	0.933 ± 0.018	-6.409 ± 0.112	13
N-Methyl-2,2',4,4'-tetranitrodiphenylamine	0.754 ± 0.011	0.820 ± 0.015	-9.807 ± 0.129	19
Equilibria of amides ^{g,h}				
Pyrrole-2-carboxamide	0.447 ± 0.005	0.398 ± 0.007	-1.117 ± 0.008	20
4-Methoxybenzamide	0.377 ± 0.006	0.352 ± 0.002	-1.246 ± 0.011	20
3,4,5-Trimethoxybenzamide	0.386 ± 0.011	0.355 ± 0.008	-1.645 ± 0.025	22
3-Nitrobenzamide	0.302 ± 0.007	0.338 ± 0.005	-2.019 ± 0.026	26
3,5-Dinitro-4-methylbenzamide	0.378 ± 0.008	0.317 ± 0.007	-2.612 ± 0.040	22
2,3,6-Trichlorobenzamide	0.274 ± 0.005	0.279 ± 0.004	-2.704 ± 0.029	25
2,4-Dichloro-3,5-dinitrobenzamide	0.269 ± 0.008	0.282 ± 0.008	-3.053 ± 0.066	28
Equilibria of hydroxy-alkoxy-benzenes ^h				
1,3,5-Trihydroxy	0.629 ± 0.007	0.576 ± 0.006	-3.623 ± 0.032	44
1,3,5-Timethoxy	0.989 ± 0.017	0.985 ± 0.014	-5.311 ± 0.070	30
1,3-Dihydroxy-2-methyl	0.770 ± 0.015	0.775 ± 0.014	-7.518 ± 0.113	15
1,3-Dimethoxy-2-methyl	0.829 ± 0.011	0.879 ± 0.012	-8.533 ± 0.087	10
1,3-Dimethoxy	0.829 ± 0.019	0.881 ± 0.018	-8.369 ± 0.158	17
1-Hydroxy-3-methoxy	0.800 ± 0.007	0.819 ± 0.008	-8.190 ± 0.072	21
1,3-Dihydroxy	0.684 ± 0.008	0.687 ± 0.009	-7.485 ± 0.068	17
Equilibria of anions ⁱ				
Picric acid	0.731 ± 0.018	0.723 ± 0.020	-0.027 ± 0.018	22
4-(Tricyanovinyl)phenyldicyanomethane	1.000 ± 0.018	1.008 ± 0.034	+0.301 ± 0.021	15
Methyl dicyanoacetate	0.732 ± 0.014	0.776 ± 0.010	-2.734 ± 0.045	16
Hexacyanoheptatriene	0.663 ± 0.012	0.783 ± 0.019	-3.466 ± 0.067	16
Cyanoforn	0.635 ± 0.014	0.646 ± 0.011	-4.495 ± 0.065	8

* Intercepts = thermodynamic values referred to water as standard solvent; r_{ij} = $\log k_2^\circ$ values in the analysis of nitration rates; r_{ij} = $\text{p}K_{\text{BH}^+}$ values in the analysis of equilibria. † Errors estimated by least-squares technique which minimize the global error involving the whole set of experimental data. Such values are more significant, compared to those obtained by plotting Y_i versus M_C . The latter procedure gives usually smaller deviations in the r_{ij} values since it neglects the uncertainties of M_C values.

^a $\log k_{2018}$ in H₂SO₄ and HClO₄ as reported in ref. 12. ^b Refs. 8, 9; Y_i values in H₂SO₄ and HClO₄ not yet published. ^c Y_i values in H₂SO₄ from C. D. Johnson, A. R. Katritzky, and S. A. Shapiro, *J. Am. Chem. Soc.*, 1969, **91**, 6654; P. Tickle, A. G. Briggs, and J. M. Wilson, *J. Chem. Soc. B*, 1970, 65; M. J. Jorgenson and D. R. Hartter, *J. Am. Chem. Soc.*, 1963, **85**, 878. ^d Y_i values in HClO₄ from K. Yates and H. Wai, *J. Am. Chem. Soc.*, 1964, **86**, 5408; S. A. Attiga and C.H. Rochester, *J. Chem. Soc., Perkin Trans. 2*, 1974, 1624. ^e Y_i values in H₂SO₄ from E. M. Arnett and G. W. Mach, *J. Am. Chem. Soc.*, 1964, **86**, 2671. ^f Y_i values in HClO₄ from H. Wai, Ph.D. Thesis, University of Toronto, 1968; K. Yates, H. Wai, G. Welch, and R. A. McClelland, *J. Am. Chem. Soc.*, 1973, **95**, 418. ^g Y_i values in H₂SO₄ from K. Yates, J. B. Stevens, and A. R. Katritzky, *Can. J. Chem.*, 1964, **42**, 1957. ^h Y_i values in H₂SO₄ and HClO₄ from A. J. Kresge, M. J. Chen, L. E. Hakka, and J. Kouba, *J. Am. Chem. Soc.*, 1971, **93**, 6174. ⁱ Y_i values in H₂SO₄ and HClO₄ from R. H. Boyd, *J. Phys. Chem.*, 1963, **67**, 737.

analysed by the polynomial form (7). The global error to be minimized is given by (8). In order to minimize

$$Y_i = N_i f(x) + C_i \quad (6)$$

$$f^*(x) = af(x) + b \quad (6')$$

$$f(x) = \sum_K A_K x^K \quad (7)$$

$$\sum_{i,x} [Y_i(x) - (\sum_K A_K x^K) N_i - C_i]^2 \quad (8)$$

(8) various general methods were tentatively used,¹³⁻¹⁵ but the final choice was in favour of a specifically tailored procedure which turned out to be much faster.

We shall now discuss some steps in carrying out the calculations, steps taken to improve the computation and which are useful for other reasons as well.

Step (i). It can be seen in (6') that for $f(x)$ there are certain degrees of freedom (or arbitrariness) which can be reduced by using a well defined numerical path. The procedure starts by assuming $A_0 = 0$ in (7) for the specific $f(x)$ to be sought. In this way there is in (8) no possible interchange between the N_i and C_i values, while A_K and N_i are still not independent. For instance, given a solution, if the A_K values are doubled and the N_i values are halved, (8) will not change its value. (This residual arbitrariness could be removed by imposing $A_1 = 1$, but as shown later, a slightly different constraint will be used).

It is easily noticed that in (8) two groups of unknowns, the A_K values on one hand, and the N_i and C_i values on the other, can be distinguished. Thus, if one group is assumed to be known, solving for the other involves the usual linear least-squares treatment. Hence an iterative method, quickly converging to the optimal values, can be developed, where the two groups of variables (starting from an initial assumption for one of them) are alternatively estimated. From the computational point of view, the splitting of the problem produces an obvious advantage since each step involves many systems with two unknowns (as many as there are indicators) and only one linear problem of higher rank depending on the degree of (8).

Certain further features of practical calculations are now illustrated. In these studies Legendre polynomials were used because the maximum degree in (7) is not very low and interpolation by ordinary power polynomials frequently deals with ill-conditioned systems. In other words, keeping (8) unchanged, the iterative procedure was performed in a different space where calculations are less complicated, *i.e.* the space of orthogonal Legendre polynomials.

The obvious relation (9) holds, where P_j is the j th Legendre polynomial. Assuming B_1 to be unity the

$$f(x) = \sum A_K x^K = \sum B_j P_j(x) \quad (9)$$

residual arbitrariness in $f(x)$ [see (6')] was removed.

Since the use of the Legendre polynomials was only a computational choice, the final results were 'translated' to the usual symbols. Another computational advantage to be noted concerns the convergence acceleration.

Taking into account that many steps of the iterative procedure turned out to be in the same line, it was convenient to explore ahead in this direction, using jumps to save steps. If the jump arrived at a lower value of the object function [see (8)], another jump of longer extent was performed and so on.

Step (ii). The method outlined above turned out to be particularly efficient when experimental data in both sulphuric and perchloric acid were considered. In these studies additional work is required since, among the various indicators in the two acids, there are some associated bases whose basicity for vanishing values of the concentration can be checked. Thus, when all possible information is extracted by working separately in the two environments, a new estimate can be found, involving both acids. This can be accomplished by taking two object functions like that given by (8) and adding them up. As a consequence, the unifying point of the problem is that the C_i values of certain indicators in sulphuric acid will coincide with the C_K values of the corresponding indicators in the other acid.

The computational analysis was performed by using the iterative procedure outlined above, with an obvious increase in complexity. At each step, together with the ordinary 2×2 systems of each indicator free from constraints, there will be a 3×3 system for each couple of corresponding indicators, where the unknowns are N_1, N_2 , and C , with the obvious meaning for the symbols. The next step computes, in two separate systems, the A_i coefficients for the two acids.

The validity of the theoretical picture is tested by the results obtained. The values of parameters obtained by the constrained calculations should be consistent with those of the separate procedure.

Error estimate. To estimate the probable errors affecting the results, an obvious point of concern is the different amount of uncertainty brought in by the various indicators. Up to this point, the calculations were performed under the implicit assumption of an equal validity of the input data. Now, at least, something can be done since the original numbers deviate more or less from the fitting curves. Each indicator, for instance, has a certain spread around the theoretical values. The root mean square of deviations is assumed as an estimate of the intrinsic variation of the measurements for that indicator and a Monte Carlo calculation is easily organized. If the original data are perturbed with random numbers obeying the observed variance just described, a new fictitious sample is obtained, to be analysed as the original sample.

The convergence is now extremely fast, since the new optimal values of the variables will deviate very little from the 'official' ones. If this procedure (perturbation and processing) is repeated, a set of 'perturbed' solutions are obtained, yielding an estimate of how uncertain the results are.

The procedure outlined here, like most Monte Carlo methods, is an elegant trick to avoid classical difficulties.

In the present problem, difficulties were not given by

the mathematical procedure but only by a certain lack of information which prevented computation of the errors in a less empirical way. It can be seen, in fact, that in order to know, *a priori*, the uncertainty of each original number to be processed, one should know many details about the way in which each measurement was taken. Unfortunately, data come from a vast amount of work, where various methods and criteria have been used, not to mention the silence on errors. Thus any calculation based on an *a priori* estimate of errors⁵ is rather questionable.

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