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CALCULATION OF NEUTRALIZATION ENTHALPIES FROM THERMOMETRIC TITRATIONS OF DIPROTIC AND TRIPROTIC ACIDS USING A LINEAR LEAST-SQUARES METHOD

C. MONGAY, M.C. GARCIA and G. RAMIS

Department of Analytical Chemistry, Faculty of Chemistry, University of Valencia, Valencia (Spain)

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ABSTRACT

The application of thermometric titrimetries to the determination of enthalpies of neutralization *of diprotic and triprotic acids using a linear least-squares method is studied critically.* The best way of fitting is investigated by analyzing the experimental data for a series of simulated titration curves of a number of acids. The conclusions are applied to the calculation of the enthalpies of maleimidedioxime, thiodipropionic and thiodiglycolic acids (diprotic systems), and citric acid.

INTRODUCTION

Thermometric titrimetries are particularly interesting for the study of acid–base systems, as it is possible to get the thermodynamic protonation parameters of these systems with them in a rapid and simple way. The study of the enthalpograms indicates that their form depends on the combined effects of the enthalpies of neutralization, of its kinetics and of the protonation constants of the system.

Several methods of calculation have been proposed for the determination of enthalpies from thermometric titration curves. In the case of a monoprotic acid, where the protonation constant is known and it is assumed that the ionic strength does not change along the titration, the calculation is immediate if the initial dissociation of the acid can be neglected [1]. If this initial dissociation is not negligible, the calculation is also immediate, but it must be considered the neutralization of the free acidity and that a part of the heat of dissociation of the acid has been liberated before the beginning of the titration. Besides, if the variation of the ionic strength is not negligible, the protonation constant of the acid must be corrected at each point of the titration [2]. Christensen and Izatt [3] have also proposed a method for the simultaneous calculation of the protonation constant and other thermodynamic parameters of a monoprotic acid.

The determination of the neutralization enthalpies of diprotic systems have been performed by the method of simple linear regression [4,5]. For polyvalent systems, Barthel et al. [6] have proposed a simple method of calculation based on the resolution of a system of equations, each of them corresponding to a determined point on the titration curve.

Other more laborious mathematical methods have been described for the calculation of the enthalpies of reaction, which take into account the propagation of the aleatory errors and their effect on the determination of the enthalpies [7]. However, these methods require the use of high speed computers and very sophisticated programs.

In this work, we undertake a critical study of the different ways of fitting the data, from a thermometric titration curve, for the determination of the enthalpies of diprotic and triprotic acids by using the methods of simple and multiple linear regression, respectively. The initial dissociation of the acid, and the variation of the protonation constants by effect of the ionic strength are considered.

In order to be able to discuss not only the precision, but also the accuracy of the method, hypothetical systems of prefixed protonation constants and enthalpies of neutralization are assumed. Since the different ways of fitting the data are not equivalent, the conditions of applicability of each of them are studied.

Finally, the conclusions are applied to the determination of the enthalpies of neutralization of real diprotic and triprotic acids. The application of the method may be carried out using a pocket programmable calculator.

TITRATION CURVES

During the titration of a diprotic acid, H_2A, with a strong base, the heat evolved arises partially from the reaction of neutralization of the free hydrogen ions in the medium

$$H^+ + OH^- \rightleftharpoons H_2O \quad \Delta H_w$$

and partially from the reaction between the diprotonated and monoprotonated species with the titrant base

$$H_2A + OH^- \rightleftharpoons HA^- + H_2O \quad \Delta H_{N2}$$

$$HA^- + OH^- \rightleftharpoons A^{2-} + H_2O \quad \Delta H_{N1}$$

(It is assumed that the dilution effect of the titrant is negligible). These enthalpies of neutralization, ΔH_N, are related to the protonation enthalpies

$$HA^- + H^+ \rightleftharpoons H_2A \quad \Delta H_{P2}$$

$$A^{2-} + H^+ \rightleftharpoons HA^- \quad \Delta H_{P1}$$

by the expression $\Delta H_N = \Delta H_w - \Delta H_P$

Thus, the heat developed during the titration in the dissociation processes of the acid is

$$-Q_1 = [([HA^-] + [A^{2-}])(V + v) - ([HA^-]_0 + [A^{2-}]_0)V](-\Delta H_{P2})$$
$$+ [[A^{2-}](V + v) - [A^{2-}]_0 V](-\Delta H_{P1}) \quad (1)$$

V being the initial volume of acid, v the volume of strong base added, and $[HA^-]_0$ and $[A^{2-}]_0$ the concentration of the monoprotonated and nonprotonated species before the beginning of the titration.

Moreover, the heat developed in the neutralization of all the hydrogen ions (those arising from the initial dissociation and those being liberated along the titration) is given by

$$-Q_2 = \left\{\left(2C_0V + \frac{K_w}{h_0}V\right) - [h(V + v) + C_0V\bar{n}_H]\right\}(\Delta H_w) \quad (2)$$

where C_0 is the initial analytical concentration of the acid, K_w the ionic product of water, h_0 and h are the concentration of the free protons at the beginning and at any point of the titration, and $\bar{n}_H$ is the average number of protons bound to the acid.

The first parenthesis in eqn. (2) represents the total acidity before the beginning of the titration, and the second one represents the total acidity of any point of the titration. The value $V \cdot K_w/h_0$ is the number of moles of hydrogen ions arising from water: this value is negligible compared with the value of C_0V.

The titration curve, $\Delta T = f(v)$ is derived from

$$Q = Q_1 + Q_2 = \Delta T(C + v\rho c')$$

where the heat developed is expressed as a function of the temperature rise from the beginning of the titration and the heat capacity of the system, which is corrected at each point of the titration, taking into account the volume added of reactant, its specific weight ρ, and its specific heat once diluted in the interior of the solution c'. Expressing the concentration of the different ionic species present as a function of the cumulative protonation constants, β_1 and β_2, results in

$$-\Delta T = \frac{C_0V}{C + v\rho c'}\left[\left(\frac{\beta_1 h + 1}{P(h)} - \frac{\beta_1 h_0 + 1}{P(h_0)}\right)\Delta H_{N2} + \left(\frac{1}{P(h)} - \frac{1}{P(h_0)}\right)\Delta H_{N1}\right]$$
$$+ \frac{1}{C + v\rho c'}\left[C_0V\frac{\beta_1 h_0 + 2}{P(h_0)} - h(V + v)\right]\Delta H_w \quad (3)$$

where $P(h) = \beta_2 h^2 + \beta_1 h + 1$ and $P(h_0) = \beta_2 h_0^2 + \beta_1 h_0 + 1$

The value of the proton concentration at each point of the titration can be calculated from the charge balance in the solution, using any iterative method

$$h - \frac{K_w}{h} + C_v \frac{v}{V+v} - C_0 \frac{V}{V+v} \frac{\beta_1 h + 2}{P(h)} = 0 \tag{4}$$

where C_v is the concentration of titrant base. Since the ionic strength changes during the titration, the values of the equilibrium constants are modified; therefore those values must be recalculated for each point. As these changes are small when the points taken from the curve are sufficiently close, the correction is done taking the constants calculated for a certain point as the initial value for the calculation of the approximated ionic strength of the next point, and thence the values of the constants at this point are obtained. Next, the values of the ionic strength and of the constants, which are used in the calculation of the enthalpies, are recalculated. (This process can be repeated if a significant difference between the two calculated ionic strengths is observed).

In the same way, the thermometric curve of neutralization of a triprotic acid, H_3A, with a strong base is given by

$$\begin{aligned} -\Delta T = \frac{C_0 V}{C + v\rho c'} \Bigg[& \left(\frac{\beta_2 h^2 + \beta_1 h + 1}{P(h)} - \frac{\beta_2 h_0^2 + \beta_1 h_0 + 1}{P(h_0)} \right) \Delta H_{N3} \\ & + \left(\frac{\beta_1 h + 1}{P(h)} - \frac{\beta_1 h_0 + 1}{P(h_0)} \right) \Delta H_{N2} + \left(\frac{1}{P(h)} - \frac{1}{P(h_0)} \right) \Delta H_{N1} \Bigg] \\ & + \frac{1}{C + v\rho c'} \left[C_0 V \frac{\beta_2 h_0^2 + 2\beta_1 h_0 + 3}{P(h_0)} - h(V+v) \right] \Delta H_w \end{aligned} \tag{5}$$

The value of the proton concentration is also calculated by the charge balance, taking into account the corrections due to the variation of the ionic strength.

Simulation of the "experimental" curves

In order to generate the "experimental" titration curves, diprotic and triprotic acids with prefixed values of their enthalpies of neutralization and protonation constants at zero ionic strength are assumed. Assuming also certain values of C_0, V and C, about 30 uniformly distributed points $(v_t, \Delta T_t)$ along the theoretical titration curve are calculated. In order to avoid values of ΔT close to zero, the first point is taken in such a way that the corresponding value of ΔT is at least the tenth part of the whole rise of temperature at the end of the titration.

From this theoretical titration curve, 15 "experimental" curves are simulated, transforming the different theoretical points $(v_t, \Delta T_t)$ into "experimental" points $(v_e, \Delta T_e)$, assigning to the former Gaussian errors by means of the expressions

$$v_e = v_t + \sigma_v z$$

$$\Delta T_e = \Delta T_t + \sigma_T z'$$

σ_v and σ_T being the standard deviations associated with each of the two variables, and z and z' aleatory numbers, which follow the normal distribution law. These values have been generated by means of a computer. following the same method used in a previous work [8].

The values taken for the different parameters have been: $V = 50$ ml. $C_v = 1$ mole l^{-1}, $C = 230$ J °C^{-1}, $\rho = 1$ g cm^{-3}, $c' = 4.184$ J g^{-1} °C^{-1} and $\Delta H_w = -55.81$ kJ mole^{-1} [9]. The assumed analytical concentration of the acid was $C_0 = 0.020$ mole l^{-1} for the diprotic systems and $C_0 = 0.015$ mole l^{-1} for the triprotic systems.

Treatment of the data

As

$$A = \frac{-C_0 V}{\Delta T(C + v\rho c') + M}\left(\frac{\beta_1 h + 1}{\mathrm{P}(h)} - \frac{\beta_1 h_0 + 1}{\mathrm{P}(h_0)}\right)$$

and

$$B = \frac{-C_0 V}{\Delta T(C + v\rho c') + M}\left(\frac{1}{\mathrm{P}(h)} - \frac{1}{\mathrm{P}(h_0)}\right)$$

where

$$M = \left[C_0 V \frac{\beta_1 h_0 + 2}{\mathrm{P}(h_0)} - h(V + v)\right]\Delta H_w$$

expression (3) may be written as the equation of a straight-line

$$Xa_0 + Ya_1 = 1 \tag{6}$$

where X and Y are functions of A and B, and the parameters a_0 and a_1 are

TABLE 1

Transformation of eqn. (3) to the form $Xa_0 + Ya_1 = 1$

Straight-line	Equation	X	Y
1	$X\Delta H_{N2} + Y\Delta H_{N1} = 1$	A	B
2	$X\frac{\Delta H_{N2}}{\Delta H_{N1}} + Y\frac{1}{\Delta H_{N1}} = 1$	$-\frac{A}{B}$	$\frac{1}{B}$
3	$X\frac{1}{\Delta H_{N2}} + Y\frac{\Delta H_{N1}}{\Delta H_{N2}} = 1$	$\frac{1}{A}$	$-\frac{B}{A}$

directly related to ΔH_{N1} and ΔH_{N2}. This equation may lead to the expressions shown in Table 1, where the values of the variables X and Y are also indicated for each case.

The 'experimental' data obtained from each one of the 15 series performed for each system are fitted according to the equations in Table 1 by the least-squares method, which leads to three regression straight-lines of X on Y and another three of Y on X. The values of ΔH_{N1} and ΔH_{N2} may be calculated from each one of the six fittings.

Similarly, for a triprotic acid, calling

$$M=\left[C_0V\frac{\beta_2h_0^2+2\beta_1h_0+3}{\mathrm{P}(h_0)}-h(V+v)\right]\Delta H_w$$

eqn. (5) may be written as the equation of a plane

$$Xa_0+Ya_1+Za_2=1 \tag{7}$$

where a_0, a_1 and a_2 are again directly related to the enthalpies of neutralization, and X, Y and Z are functions of

$$A=\frac{-C_0V}{\Delta T(C+vpc')+M}\left(\frac{\beta_2h^2+\beta_1h+1}{\mathrm{P}(h)}-\frac{\beta_2h_0^2+\beta_1h_0+1}{\mathrm{P}(h_0)}\right)$$

$$B=\frac{-C_0V}{\Delta T(C+vpc')+M}\left(\frac{\beta_1h+1}{\mathrm{P}(h)}-\frac{\beta_1h_0+1}{\mathrm{P}(h_0)}\right)$$

$$C=\frac{-C_0V}{\Delta T(C+vpc')+M}\left(\frac{1}{\mathrm{P}(h)}-\frac{1}{\mathrm{P}(h_0)}\right)$$

Thus, eq. (7) may lead to the four different forms shown in Table 2.

Each one of these equations can be treated by three different ways, giving rise to twelve regression planes, which lead to different values of the enthalpies of neutralization of the triprotic acid.

TABLE 2

Transformation of eqn (5) to the form $Xa_0+Ya_1+Za_2=1$

Plane	Equation	X	Y	Z
1	$X\Delta H_{N3}+Y\Delta H_{N2}+Z\Delta H_{N1}=1$	A	B	C
2	$X\frac{1}{\Delta H_{N3}}+Y\frac{\Delta H_{N2}}{\Delta H_{N3}}+Z\frac{\Delta H_{N1}}{\Delta H_{N3}}=1$	$\frac{1}{A}$	$-\frac{B}{A}$	$-\frac{C}{A}$
3	$X\frac{\Delta H_{N3}}{\Delta H_{N2}}+Y\frac{1}{\Delta H_{N2}}+Z\frac{\Delta H_{N1}}{\Delta H_{N2}}=1$	$-\frac{A}{B}$	$\frac{1}{B}$	$-\frac{C}{B}$
4	$X\frac{\Delta H_{N3}}{\Delta H_{N1}}+Y\frac{\Delta H_{N2}}{\Delta H_{N1}}+Z\frac{1}{\Delta H_{N1}}=1$	$-\frac{A}{C}$	$-\frac{B}{C}$	$\frac{1}{C}$

DISCUSSION AND CONCLUSIONS

Since in every thermometric titration the measurements are affected by error, the different ways of fitting the data are not equivalent, leading to diverse values of the enthalpies. This can be explained by considering that in the resolution of the systems of normal equations in the application of the least-squares method, there are, in some cases, subtraction operations between very close values, yielding a "loss of accuracy", which is bigger if the errors in the experimental data are larger. Specially when the relative error of the difference is much larger than one of the minuend or the substrahend values, the results obtained become absurd.

Diprotic acids

First of all, a study of the dependence of the results on the errors in volume and temperature has been accomplished. For this purpose, either the standard deviation associated with the temperature or the standard deviation associated with the volume has been kept constant, while the other has been modified. It can be observed that whereas the errors that affect the volume (up to a value of $\sigma_v = 0.020$) scarcely have an influence, the errors in the temperature have a more marked influence upon the results.

In Table 3 the mean values of the enthalpies and the standard deviations (given to two significant figures) obtained from 15 simulated titrations by using the different ways of fitting are indicated. This table has been obtained assuming that $\sigma_v = 0.010$. In all the tables the negative values of the neutralization enthalpies are given in kJ °C^{-1} mole^{-1}.

In this table, it may be observed that the regression of X on Y by means of straight-line 2 leads to the best results. The regression of X on Y by means of straight-line 1 gives rise to values that, though usually acceptable, are slightly more inaccurate than the former; whereas the regression of Y on X by these two straight-lines offers considerably worse results. Both regressions by straight-line 3 offer very deficient and usually unacceptable results, even for low values of the standard deviation associated with the temperature. All of it has been put in evidence, not only with the systems shown in this table, but also in all the systems, which have been studied.

In Table 4 the results from systems having a great diversity of protonation constants and enthalpies of neutralization are shown. The values of the enthalpies indicated correspond to the best way of fitting.

As expected, it is seen that when the protonation constants of the acid are smaller than 10^3 or larger than 10^{11}, the results are worse than those for other values. In addition, in general, the closer the protonation constants of the acid are, the more deficient the fitting. In this table it is assumed that $\sigma_v = 0.010$ and $\sigma_T = 0.005$.

Finally, the precision in the determination of ΔH_{N1} is worse than the

TABLE 3

Enthalpies for diprotic acids at different σ_T values

σ_T	Fitting	$-\Delta H_{N2}=45$, $-\Delta H_{N1}=40$		
		$\log K_2=2$ $\log K_1=3$	$\log K_2=5$ $\log K_1=7$	$\log K_2=8$ $\log K_1=11$
0.002	1 X on Y	45.2 ± 2.6	44.94 ± 0.41	45.00 ± 0.41
		39.3 ± 2.2	40.06 ± 0.62	39.95 ± 0.82
	Y on X	41.6 ± 2.4	44.76 ± 0.45	44.83 ± 0.46
		43.8 ± 2.1	40.88 ± 0.99	40.9 ± 1.1
	2 X on Y	45.0 ± 2 0	45.0 ± 0.38	45.05 ± 0.37
		40.0 ± 1.3	39.98 ± 0.51	39.89 ± 0.70
	Y on X	43.8 ± 1.7	44.90 ± 0.38	44.95 ± 0.39
		41.2 ± 1.1	40.31 ± 0.57	40.29 ± 0.75
	3 X on Y	47.8 ± 5.3	45.1 ± 1.9	45.3 ± 1.4
		35.7 ± 6.0	32 ± 60	−86 ± 410
	Y on X	44.8 ± 4.2	44.9 ± 1.7	45.2 ± 1.5
		40.2 ± 4.4	42 ± 49	8 ± 450
0.005	1 X on Y	47.7 ± 4.3	44.88 ± 0.88	44.93 ± 0.74
		35.5 ± 4.6	40.3 ± 1 4	40.2 ± 1.2
	Y on X	34.5 ± 9 4	44.1 ± 1.0	44.36 ± 0.91
		52 ± 10	43.8 ± 2.5	43.3 ± 2.7
	2 X on Y	45.2 ± 4.0	45.15 ± 0.82	45.10 ± 0.68
		39.8 ± 2.9	39.9 ± 1.1	39.97 ± 0.97
	Y on X	41 8 ± 3.8	44.72 ± 0.77	44.76 ± 0.71
		43.4 ± 3.0	41.3 ± 1.1	41.4 ± 1.3
	3 X on Y	54.6 ± 7.9	45 5 ± 5.3	45.0 ± 2.6
		26.0 ± 9.4	12 ± 150	−13 ± 750
	Y on X	45.2 ± 6 8	44.8 ± 5.1	44.5 ± 2.7
		39.8 ± 6.8	51 ± 140	290 ± 740
0.007	1 X on Y	44 ± 34	45.0 ± 1.1	44.48 ± 0.96
		38 ± 41	39.8 ± 1.9	40.8 ± 1.6
	Y on X	17 ± 26	44.0 ± 1.4	43.69 ± 0.99
		73 ± 31	44.4 ± 3.5	45.2 ± 2.6
	2 X on Y	44.6 ± 4.0	45.31 ± 0.97	44.73 ± 0.96
		40.3 ± 2.6	39.5 ± 1.6	40.5 ± 1.5
	Y on X	35.6 ± 4.2	44.7 ± 1.0	44.20 ± 0.84
		50.0 ± 4.4	41.5 ± 2.0	42.7 ± 1.3
	3 X on Y	72 ± 19	46.9 ± 4.0	45.5 ± 4.0
		0 ± 25	−29 ± 130	−330 ± 990
	Y on X	45.7 ± 8.9	45.9 ± 3.6	44.8 ± 3.6
		38.9 ± 9 2	22 ± 100	38 ± 820

$-\Delta H_{N2}=20$, $-\Delta H_{N1}=15$		
log $K_2=2$ log $K_1=3$	log $K_2=5$ log $K_1=7$	log $K_2=8$ log $K_1=11$
21.1 ± 1.8	19.99 ± 0.35	20.00 ± 0.20
13.1 ± 1.4	14.94 ± 0.61	15.02 ± 0.35
13.8 ± 3.6	19.71 ± 0.31	19.75 ± 0.25
22.3 ± 3.8	16.14 ± 0.70	16.31 ± 0.85
20.1 ± 1.9	20.05 ± 0.34	20.07 ± 0.20
14.9 ± 1.2	14.90 ± 0.52	14.91 ± 0.34
17.9 ± 1.6	19.88 ± 0.28	19.91 ± 0.19
17.4 ± 1.2	15.47 ± 0.36	15.58 ± 0.45
25.2 ± 3.7	20.6 ± 1.4	20.4 ± 1.4
7.4 ± 4.1	−5 ± 37	−140 ± 440
19.9 ± 3.5	20.4 ± 1.3	20.2 ± 1.4
15.3 ± 3.5	6 ± 36	−34 ± 400
8 ± 37	19.5 ± 1.1	19.70 ± 0.63
27 ± 45	15.7 ± 1.6	15.3 ± 1.1
−5 ± 14	17.5 ± 2.5	18.4 ± 1.5
45 ± 18	24.7 ± 9.2	22.4 ± 6.1
19.1 ± 3.6	20.13 ± 0.78	20.05 ± 0.53
15.5 ± 2.6	14.9 ± 1.1	14.89 ± 0.95
9.6 ± 4.5	19.06 ± 0.84	19.20 ± 0.56
25.8 ± 4.6	18.5 ± 2.2	18.4 ± 1.7
48 ± 19	21.3 ± 5.1	22.6 ± 3.7
−27 ± 30	−60 ± 160	−1100 ± 1100
18.2 ± 7.4	19.6 ± 5.0	21.5 ± 3.7
16.6 ± 7.8	32 ± 140	−430 ± 1100
50 ± 160	26 ± 26	19.43 ± 0.96
−22 ± 200	4 ± 47	15.3 ± 1.7
−14 ± 14	15.1 ± 5.0	16.9 ± 2.1
56 ± 18	34 ± 22	29.0 ± 9.0
21.1 ± 3.5	19.76 ± 0.83	20.14 ± 0.72
14.3 ± 2.5	15.4 ± 1.5	14.5 ± 1.2
0 ± 12	18.2 ± 1.1	18.5 ± 1.0
38 ± 13	20.8 ± 3.2	21.2 ± 3.4
71 ± 29	21.6 ± 4.1	23.6 ± 4.4
−59 ± 44	−100 ± 190	−1500 ± 1700
21.5 ± 8.2	18.9 ± 3.8	21.6 ± 4.0
13.7 ± 9.0	45 ± 110	−420 ± 1200

TABLE 4

Enthalpies for diprotic acids at different ΔH and $\log K$ values

	$-\Delta H_{N2}=8$ $-\Delta H_{N1}=8$	$--\Delta H_{N2}=22$ $-\Delta H_{N1}=22$	$-\Delta H_{N2}=52$ $-\Delta H_{N1}=52$	$-\Delta H_{N2}=16$ $-\Delta H_{N1}=8$
$\log K_2 = 2$	7.5 ±3.8	21.8 ±3.0	51.5 ±4.1	16 2 ±3.1
$\log K_1 = 3$	8.4 ±2.7	22.1 ±1.9	52.5 ±2.8	7.9 ±2 3
$\log K_2 = 4$	8.1 ±1 3	21.82±0.82	52.3 ±1.0	16.1 ±1.1
$\log K_1 = 5$	7.9 ±2.1	22.2 ±1.3	51.4 ±1.5	7.7±1.5
$\log K_2 = 6$	7.98±0.96	22.07±0.93	52.12±0.97	15.77±0.88
$\log K_1 = 7$	8.1 ±1.3	21.9 ±1.4	51.9 ±1.6	8.3 ±1.2
$\log K_2 = 8$	8.2 ±1 2	22.01±0.83	51.9 ±1.2	15.96±0.75
$\log K_1 = 9$	7.6 ±2.0	22 0 ±1.4	52 3 ±2 0	8.0 ±1.1
$\log K_2 = 10$	7.77±0.89	22.3 ±1 1	52.2 ±1 1	16.21±0.68
$\log K_1 = 11$	8.2 ±1.7	21.5 ±2.1	51 6 ±2.0	7.7 ±1.2
$\log K_2 = 4$	8.6 ±2.5	22.5 ±2 0	51 2 ±3 1	16.1 ±2.6
$\log K_1 = 4$	7.3 ±3 2	21.4 ±2.7	52.8 ±4.0	7.9 ±3.3
$\log K_2 = 4$	8 2 ±1.7	22.1 ±2 2	52.5 ±1.9	16.1 ±2.5
$\log K_1 = 4.25$	7.9 ±2.3	21 8 ±3 0	51.5 ±2.5	7.8 ±3.5
$\log K_2 = 4$	7.91±0.95	22.29±0 75	52.13±0.72	15 79±0.72
$\log K_1 = 6$	8.2 ±1.3	21.7 ±1.0	51 9 ±1 0	8 12±0.95
$\log K_2 = 4$	8 46±0 63	22.07±0 75	52.05±0 80	16 08±0.69
$\log K_1 = 8$	7 7 ±1.0	21.82±0.94	51 85±0.99	8.0 ±1.1
$\log K_2 = 4$	8.09±0.77	21 83±0.70	51.98±0 84	16.2 ±1.1
$\log K_1 = 11$	7 7 ±1.1	22.1 ±1 0	52 ±1.1	7.6 ±1.7
$\log K_2 = 4$	8.10±0.81	21.78±0 77	51 90±0.96	16 33±0.77
$\log K_1 = 13$	5.5 ±6.0	22.6 ±6.1	52 8 ±6 5	5.5 ±4 5

precision for ΔH_{N2} except when the second protonation constant of the acid–base system is too small.

Triprotic acids

In an analogous way, it can be observed that the standard deviation affecting the temperature has a more marked influence upon the results than the standard deviation on the volume. In Table 5 the results obtained for $\sigma_V = 0.010$ and different values of σ_T are shown. Only the treatment based upon the regressions of X on Y and Z, and of Y on X and Z according to planes 1 and 2 are indicated, since the regression of Z on X and Y by these planes and all the fittings by means of planes 3 and 4 lead to much worse

$-\Delta H_{N2}=36$ $-\Delta H_{N3}=28$	$-\Delta H_{N2}=56$ $-\Delta H_{N3}=48$	$-\Delta H_{N2}=24$ $-\Delta H_{N3}=8$	$-\Delta H_{N2}=56$ $-\Delta H_{N3}=38$
36.6 ±3.7	56.1 ±3.4	24.6 ±3.7	56.5 ±3.8
27.6 ±2.4	47.9 ±2.6	7.6 ±2.3	37.8 ±2.6
35.74±0.80	55.9 ±1.1	24.0 ±1.2	56.4 ±1.1
28.3 ±1.3	48.3 ±1.5	8.0 ±1.8	37.4 ±1.6
36.2 ±1.0	55.98±0.77	24.1 ±1.2	56.02±0.90
27.7 ±1.4	47.9 ±1.1	7.4 ±1.7	38.1 ±1.4
36.0 ±1.1	56.0 ±1.1	23.72±0.72	56.2 ±1.0
28.1 ±1.5	48.1 ±1.8	8.2 ±1.3	37.7 ±1.4
36.09±0.90	55.94±0.93	23.97±0.70	55.9 ±1.3
27.9 ±1.6	47.9 ±1.5	8.0 ±1.3	38.4 ±2.4
36.2 ±3.5	56.5 ±2.8	24.2 ±3.4	56.7 ±2.6
27.8 ±4.4	47.4 ±3.4	7.8 ±4.5	37.0 ±3.1
35.9 ±1.8	56.5 ±2.4	23.7 ±2.5	57.1 ±2.7
28.0 ±2.3	47.2 ±3.1	8.5 ±3.1	36.6 ±3.5
36.02±0.82	56.21±0.76	24.2 ±1.2	56.13±0.73
28.1 ±1.2	47.6 ±1.1	7.8 ±1.6	37.8 ±1.0
36.13±0.88	56.0 ±1.1	23.84±0.96	56.01±0.84
27.5 ±1.2	48.0 ±1.7	8.4 ±1.4	38.1 ±1.2
35.95±0.75	55.90±0.74	34.34±0.79	56.0 ±1.1
28.1 ±1.0	48.0 ±1.1	7.45±0.96	38.1 ±1.5
35.84±0.67	56.18±0.83	24.15±0.87	56.5 ±1.0
29.7 ±6.6	47.1 ±5.7	7.4 ±6.0	34.6 ±7.3

results than the former ones and are usually unacceptable.

The best values have been obtained making use of the regression of X on Y and Z by plane 2. The validity of this fitting has been tested for diverse triprotic systems; in Table 6 the values of the enthalpies assuming $\sigma_v = 0.010$ and $\sigma_T = 0.005$ are indicated.

The first fact brought out is that usually the results are somewhat worse for the triprotic acids than for the diprotic acids. It may also be observed that for the values of the protonation constants the more extreme or the closer they are, the more deficient the fitting.

Other diprotic and triprotic acids have been studied, assuming other values of the standard deviations, and all of them lead to the same conclusions.

TABLE 5

Enthalpies for triprotic acids at different σ_T values

σ_T	Fitting	$-\Delta H_{N3}=42$ $-\Delta H_{N2}=38$ $-\Delta H_{N1}=34$		$-\Delta H_{N3}=25$ $-\Delta H_{N2}=21$ $-\Delta H_{N1}=17$	
		$\log K_3=6$ $\log K_2=7$ $\log K_1=8$	$\log K_3=3$ $\log K_2=5$ $\log K_1=7$	$\log K_3=6$ $\log K_2=7$ $\log K_1=8$	$\log K_3=3$ $\log K_2=5$ $\log K_1=7$
0.002	1 *X* on *Y* and *Z*	42.01 ± 0.81	41.98 ± 0.60	25.14 ± 0.62	24.87 ± 0.83
		37.9 ± 2.1	38.03 ± 0.79	20.6 ± 1.5	21.0 ± 1.1
		34.2 ± 2.2	34.12 ± 0.55	17.4 ± 1.3	17.20 ± 0.87
	Y on *X* and *Z*	41.43 ± 0.84	41.39 ± 0.72	24.44 ± 0.63	23.9 ± 1.4
		40.1 ± 2.1	40.2 ± 1.5	23.2 ± 1.8	24.5 ± 3.7
		31.5 ± 2.1	31.4 ± 1.4	14.3 ± 2.0	12.9 ± 4.2
	2 *X* on *Y* and *Z*	42.04 ± 0.67	42.12 ± 0.52	25.15 ± 0.51	25.14 ± 0.75
		37.9 ± 1.5	37.98 ± 0.59	20.7 ± 1.0	20.75 ± 0.86
		34.1 ± 1.4	34.04 ± 0.58	17.20 ± 0.82	17.32 ± 0.56
	Y on *X* and *Z*	41.71 ± 0.68	41.83 ± 0.50	24.73 ± 0.48	24.68 ± 0.68
		39.0 ± 1.4	38.70 ± 0.65	22.1 ± 1.1	21.91 ± 0.92
		33.0 ± 1.3	33.32 ± 0.64	15.9 ± 1.1	16.15 ± 0.73
0.005	1 *X* on *Y* and *Z*	42.4 ± 1.4	40.8 ± 1.7	24.8 ± 1.5	25.4 ± 1.8
		37.2 ± 3.8	39.4 ± 2.3	20.5 ± 3.5	19.9 ± 2.6
		35.0 ± 4.2	33.0 ± 2.2	18.2 ± 3.8	18.0 ± 2.2

		40.1 ± 1.0	37.9 ± 4.1	21.3 ± 1.8	22.7 ± 2.8
	Y on *X* and *Z*	46.1 ± 3.3	50 ± 12	34.0 ± 5.5	29.3 ± 7.2
		24.3 ± 3.7	19 ± 15	2.2 ± 5.9	6.3 ± 8.2
		42.5 ± 1.2	41.6 ± 1.0	24.9 ± 1.2	26.0 ± 1.5
	2 *X* on *Y* and *Z*	37.4 ± 2.8	38.4 ± 1.2	21.0 ± 2.6	19.7 ± 1.8
		34.4 ± 2.8	33.6 ± 1.4	17.3 ± 2.7	17.7 ± 1.5
		41.14 ± 0.89	40.6 ± 1.3	22.7 ± 1.3	24.4 ± 1.5
	Y on *X* and *Z*	41.7 ± 2.2	41.0 ± 2.1	28.4 ± 3.2	23.8 ± 2.3
		30.2 ± 2.2	30.9 ± 2.2	10.1 ± 3.1	13.6 ± 2.4
0.007		42.1 ± 1.8	39.5 ± 3.0	24.8 ± 2.3	22 ± 10
	1 *X* on *Y* and *Z*	37.3 ± 4.3	40.8 ± 3.9	19.2 ± 4.0	28 ± 24
		35.1 ± 3.8	32.1 ± 3.1	19.6 ± 4.2	10 ± 25
		37.8 ± 3.0	34.3 ± 8.0	17.7 ± 5.8	17.3 ± 7.8
	Y on *X* and *Z*	54 ± 11	61 ± 26	48 ± 21	47 ± 24
		15 ± 13	6 ± 31	−15 ± 24	−15 ± 28
		42.5 ± 1.6	41.3 ± 1.5	25.3 ± 1.7	25.5 ± 2.2
	2 *X* on *Y* and *Z*	37.4 ± 3.3	38.9 ± 2.0	20.7 ± 3.5	20.7 ± 2.5
		34.6 ± 2.4	33.1 ± 2.4	16.0 ± 3.0	16.8 ± 2.1
		39.8 ± 1.6	39.4 ± 1.9	20.6 ± 2.1	22.0 ± 2.3
	Y on *X* and *Z*	46.0 ± 4.2	43.7 ± 3.4	35.9 ± 6.2	29.6 ± 3.1
		26.1 ± 4.2	28.3 ± 3.5	1.7 ± 6.1	7.9 ± 2.8

TABLE 6

Enthalpies for triprotic acids at different ΔH and $\log K$ values

	$-\Delta H_{N3}=50$ $-\Delta H_{N2}=50$ $-\Delta H_{N1}=50$	$-\Delta H_{N3}=34$ $-\Delta H_{N2}=34$ $-\Delta H_{N1}=34$	$-\Delta H_{N3}=20$ $-\Delta H_{N2}=16$ $-\Delta H_{N1}=12$	$-\Delta H_{N3}=38$ $-\Delta H_{N2}=34$ $-\Delta H_{N1}=30$
$\log K_3=2$	51.7±5.9	32.7 ± 6.3	23.1±5.5	37.5 ±5.6
$\log K_2=3$	49.0±5 3	35.3 ± 5.1	13.2±4.1	34.2 ±4.5
$\log K_1=4$	50.6±3.9	33.2 ± 2.8	13.6±2.4	29.9 ±3.3
$\log K_3=3$	49.2±2.0	34.3 ± 2.4	20.8±2.6	38.7 ±2.3
$\log K_2=4$	51.2±2.9	33.8 ± 3.6	14.3±4.5	32.9 ±3.5
$\log K_1=5$	49.5±2.2	33.7 ± 2.7	13.5±3.7	31.0 ±3.1
$\log K_3=5$	49 3±1 2	34.6 ± 1 0	19.6±1.2	38.4 ±1.3
$\log K_2=6$	51.3±2.3	33.1 ± 2.4	16.8±2.1	33.2 ±2.7
$\log K_1=7$	49.0±2 8	34.5 ± 2.4	11.4±2.0	30.9±2.8
$\log K_3=6$	49.9±1.3	34.8 ± 1.3	20.5±1.3	38.0 ±1.3
$\log K_2=7$	50.0±2.8	32 3 ± 2.6	14.9±2.9	34.0 ±2.6
$\log K_1=8$	49.9±2.2	35.0 ± 2 1	12.9±2.5	29.9 ±2.3
$\log K_3=10$	50.2±1.6	34.2 ± 1.3	19.4±1.1	38 5 ±1.4
$\log K_2=11$	49.4±3.5	33.2 ± 3.8	17.3±2.9	32.8 ±3.6
$\log K_1=12$	51 3±4.5	35.0 ± 5.5	10.0±4.9	31.7 ±5 2
$\log K_3=6.25$	51 3±4.3	34.7 ± 4 2	21.4±3.8	39.2 ±2.9
$\log K_2=6$	47.6±9.0	33 ±10	12.9±7.9	29.9 ±6.5
$\log K_1=5.75$	51.0±5.5	34.4 ± 7.5	14.0±4.9	33.7 ±4.8
$\log K_3=3$	49.6±1.0	33.8 ± 1.2	20.5±1.6	37.9 ±1.2
$\log K_2=6$	50.6±1.2	34 1 ± 1.6	15 3±2.0	34.0 ±1.2
$\log K_1=9$	49.8±1.3	34 0 ± 1.8	12.4±1.5	30.1 ±1.5
$\log K_3=4$	50.3±1.8	33.4 ± 1.4	19.4±1.9	38.4 ±1.5
$\log K_2=5$	49.8±2.4	34.9 ± 2.0	16.5±2.6	33.0 ±2.6
$\log K_1=9$	50.0±1 8	33.6 ± 1.4	11.7±1.6	30.9 ±2.2
$\log K_3=4$	50.2±1 3	34.37± 0.74	19.8±1.2	38.38±0.75
$\log K_2=8$	49.9±2.2	33.2 ± 1 2	16.2±2.7	33.2 ±1.3
$\log K_1=9$	49.7±2 0	34.6 ± 1.5	12.1±3.1	30.6 ±1.5

EXPERIMENTAL

The preceding conclusions have been applied to the calculation of the enthalpies of neutralization of diprotic and triprotic real systems.

Diprotic acids

For diprotic acids we have considered the maleinimidedioxime, whose data have been taken from Albelda et al. [5] and the thiodipropionic and

$-\Delta H_{N3}=56$ $-\Delta H_{N2}=52$ $-\Delta H_{N1}=48$	$-\Delta H_{N3}=42$ $-\Delta H_{N2}=34$ $-\Delta H_{N1}=26$	$-\Delta H_{N3}=48$ $-\Delta H_{N2}=34$ $-\Delta H_{N1}=20$	$-\Delta H_{N3}=40$ $-\Delta H_{N2}=24$ $-\Delta H_{N1}=20$	$-\Delta H_{N3}=44$ $-\Delta H_{N2}=40$ $-\Delta H_{N1}=24$
57.0±6.0	40.3 ±6.8	49.3 ±6 8	43.1±5.6	45.9±4.7
50.8±5.3	35.2 ±5.5	32.6 ±5.3	21.2±4.2	38.5±3.6
48.8±3.2	25.4 ±3.5	21.2 ±3.0	21.6±2.4	24.8±2.8
56.6±2.9	41.6 ±2.0	48.4 ±2.9	39.7±1.1	43.7±1.4
52.0±4.4	34.8 ±2.9	32.2 ±4.1	24.5±2.2	40.5±2.2
48.9±3.2	25.5 ±2.0	20.4 ±2.6	19.8±2.3	23.6±2 0
55.7±1.2	41.9 ±1.4	47.6 ±1.1	39.5±1.2	44.2±1.1
52.7±2.2	34.0 ±2.7	34.8 ±2.1	25.0±2.7	39.4±2.4
47.6±1.6	25.9 ±2.1	19.6 ±1.6	19.4±2.5	24.7±2.7
56.6±1.1	42.0 ±1.4	48.6 ±1.5	40.9±1.3	43.9±1.3
50.7±2.3	34.1 ±3.2	32.8 ±3.2	22.3±3.0	40.0±2.6
48.9±2.2	25.9 ±2.9	20.8 ±2.9	20.8±2.5	23 9±2.1
56.1±1.4	42.0 ±1.4	48.1 ±1.4	40.5±1.6	44.5±1.4
51.8±2.8	34.1 ±3.7	34.1 ±3.6	22.3±4.7	38.8±3.7
48.2±3.4	25.7 ±5.2	19.0 ±5.7	22.7±7.2	25.7±5.3
56.0±3.5	42.0 ±2.4	49.7 ±3.2	42.3±3.4	43.7±3.0
52.0±8 0	33.9 ±5.6	29.9 ±6.8	19.0±7.6	39 5±6 7
47.9±5.8	26.0 ±3.9	22.7 ±4.8	23.0±5.5	25.0±5.1
56.3±1.2	41.6 ±1 0	48 6 ±1.8	39.7±1.3	44.1±1.2
51.5±1.5	34.6 ±1.2	33.2 ±2.2	24.6±1.5	40.0±1.3
48.2±1.7	25.9 ±1.2	20.5 ±1.6	19.4±1.3	24.1±1.2
56.4±1.4	42 6 ±1.6	48.2 ±1.6	39.9±1.2	44.0±1.8
51.0±1.8	33.4 ±2 4	33.8 ±2.6	24 2±1.7	39.9±2.1
49.0±1.4	26.1 ±1.7	19.7 ±2.0	19.9±1.7	24.5±1.4
56.2±1.1	41.92±0.83	47.68±0.77	40.4±1.3	44.1±1.2
51.9±2.8	33.7 ±1.5	34.7 ±1.4	23.0±2.6	39.9±2.1
47.7±2.8	26.6 ±1.7	19.7 ±1.5	20.7±2.2	23.8±1.9

thiodiglycolic acids, taking the data cited by Borrull [1]. The mean values of the enthalpies of neutralization of these systems obtained making use of the regression of X on Y by straight-line 2 are indicated in Table 7, where they are compared with the values obtained by these authors.

In the case of the maleinimidedioxime, because of the high values of its protonation constants (log $K_1 = 11.60$ and log $K_2 = 10.41$ at 25°C, both extrapolated to zero ionic strength) it is not necessary to consider the initial dissociation, as Albelda indicates. The difference between their values and those obtained by us are mainly due to the use of different ways of fitting

TABLE 7

Enthalpies of neutralization of real diprotic systems

Substance	$-\Delta H_{N2}$	$-\Delta H_{N1}$	Ref.
Maleinimidedioxime	21.76	23.77	5
	21.89	22.84	This work
Thiodipropionic acid	52.66	68.42	1
	55.40	60.26	This work
Thiodiglycolic acid	51.14	69.98	1
	55.82	60.45	This work

and to a much lesser extent to the correction of the constants according to the ionic strength at each point.

The difference between the enthalpies indicated by Borrull for the thiodipropionic and thiodiglycolic acids and the ones determined by us are clearly larger because in addition to the application of different ways of fitting and the correction of the constants according to the ionic strength, the initial dissociation has more influence as the protonation constants of these systems are smaller (thiodipropionic acid: log $K_1 = 5.04$ and log $K_2 = 4.07$; thiodiglycolic acid: log $K_1 = 4.54$ and log $K_2 = 3.27$. All of them determined at 25°C and extrapolated to zero ionic strength).

Triprotic acids

The enthalpies of neutralization of the citric acid have been determined, taking the data from the enthalpogram given by Barthel [6] and using the protonation constants at zero ionic strength indicated by Davies and Hoyle [10]. In Table 8, the values obtained applying the regression of X on Y and Z, and of Y on X and Z according to the equations of planes 1 and 2 are

TABLE 8

Enthalpies of neutralization of citric acid

Fitting		$-\Delta H_{N3}$	$-\Delta H_{N2}$	$-\Delta H_{N1}$	References
1	X on Y and Z	49.86	55.28	57.14	This work
	Y on X and Z	49.17	57.87	53.49	
2	X on Y and Z	50.42	53.81	59.01	
	Y on X and Z	50.15	54.49	58.28	
		50.79	52.89	59.08	6
		51.72	53.45	59.25	11
		51.30	52.68	57.74	12

shown. It may be observed that the results from the fitting of X on Y and Z by plane 2 agree better with the values cited in the literature, which are also indicated in Table 8. The other ways of fitting the data lead to much more deficient or absurd values.

REFERENCES

1 F. Borrull, Licenciature Thesis, Faculty of Chemistry, University of Barcelona, 1981.
2 J.J. Christensen, R.M. Izatt, L.D. Hansen and J.A. Partridge, J Phys Chem , 70 (1966) 2003.
3 R.M. Izatt and J.J. Christensen, J. Phys. Chem., 66 (1962) 1030.
4 E. Casassas, F. Borrull, M. Esteban and V. Cerdá, Thermochim. Acta, in press.
5 M.L. Albelda, V. Cerdá and C. Mongay, J. Therm Anal., in press
6 J. Barthel, F. Becker and N.G. Schmahl, Z. Phys. Chem. N.F., 29 (1961) 58.
7 L G. Sillén, Acta Chem. Scand , 16 (1962) 159.
8 C. Mongay, G. Ramis and M.C. Garcia, Spectrochim. Acta Part A, 38 (1982) 247.
9 I. Grenthe, H. Ots and O. Ginstrup. Acta Chem. Scand., 24 (1970) 1067
10 C.W. Davies and B.E. Hoyle, J. Chem. Soc., (1953) 4134.
11 R.G. Bates and G.D Pinching, J. Am. Chem. Soc., 71 (1949) 1274.
12 G. Arena, R. Cali, M. Grasso, S. Musumeci and S. Sammartano, Thermochim. Acta, 36 (1980) 329.