The Differential Method in Chemical Kinetics

José M. Leal * and Pedro L. Domingo
Universidad de Valladolid, Departamento de Química Física, Colegio Universitario Integrado, 09001 Burgos, Spain

This paper discusses the application to kinetic data of direct methods of reduction, in an attempt to develop the capacity of differential kinetic equations. The differential method is very often relegated by the integral method in the treatment of kinetic data. Several methods are described for the obtention of reaction rates with a small margin of error at every kinetic reading; the interpolating spline function is applied and a piece-wise interpolating method with overlapping intervals is suggested. These methods have been applied to several reactions with satisfactory results, showing the usefulness of the differential method for the determination of orders of reaction and rate constants.

The processing of kinetic data with differential methods[1] is usually based on rate equation (1) where A stands for the

$$r_A = -dC_A/dt = f(C_i, \alpha_j, \ldots) \qquad (1)$$

control species, C_i for the concentration of reactants or products, and α_j for different kinetic parameters of the reacting system. A kinetic run is usually followed by the variation with time of a physical or chemical property λ which is dependent on the concentration of the control species, equation (2); α_λ being

$$C_A = g(\lambda, \alpha_\lambda) \qquad (2)$$

the corresponding parameter; for completion reactions $g(\lambda, \alpha_\lambda) = p(\lambda - \lambda_\infty)$, where p is a constant. The rate law may be written as follows, in terms of the property [equations (3) and (4)]:

$$dC_A/dt = g'(\lambda, \alpha_\lambda)(d\lambda/dt) \qquad (3)$$

where

$$r_\lambda = d\lambda/dt = F(C_i, \alpha_j, \alpha_\lambda, \ldots) \qquad (4)$$

Thus, the rate law may be written in terms of the variation with time of the property measured. The reaction rates can be obtained[2] from the tangents at different times to the plot λ/t; these tangents may be calculated either with the limit secant method,[3] or using optical instruments, as shown in the mirror method;[4,5] the same aim may be achieved with a simple prism,[6] or with certain mechanical devices,[7] but these procedures appear little in the literature. The method of finite differences converts the differentials into increments[8] equation (5), and is

$$d\lambda_n/dt = (\lambda_{n+1} - \lambda_{n-1})/(t_{n+1} - t_{n-1}) \qquad (5)$$

not interesting even if the time intervals are regularly spaced, since this approximation is too drastic.

The purpose of this work is the obtention of the rates r_λ before the introduction of any assumptions regarding the rate law or the reaction mechanism; this is the reason for rejecting differential methods based on the approximation of the derivative by numerical differentiation of kinetic readings, such as the Runge–Kutta method or predictor–corrector, *etc.*[9] The idea consists of fitting the kinetic readings to a mathematical function and obtaining the reaction rates by derivation; the λ/t trajectories are usually transcendental functions of time, so that an approximation to low degree polynomials by least-squares yields poor results. The unique way of achieving good results by minimizing the sum of deviations is to discover the function F and integrate this in order to obtain $\lambda = f(t)$, but this process would not be useful, since it is equivalent to solving the problem with the integral method before calculating the rates that enable the differential method to be used.

Interpolation is another method of fitting curves. Newton's interpolating polynomial, more sophisticated than those of Neville and Lagrange,[10] is of degree one unit lower than the number of data points and passes through all the points; it is difficult to construct if many points are used and the error of interpolation is lower the lower the degree of the polynomial; it was applied in chemical kinetics to the extrapolant formulation of the backward differentiation method for the numerical integration of stiff ordinary differential equations.[11] In the present work this method is shown to be capable of giving accurate results if the kinetic readings are regularly spaced, but in some cases leads to Legendre curves of the family points if the timing is not regular enough.

The piece-wise interpolation gives a better design of the curve; in order to interpolate the function defined in the interval (t_1, t_n), this is divided into several subintervals, in each of which a different interpolant is applied. The spline function approximation[12,13] of order m has these features and is defined from the partition p: $t_1 < \ldots t_i < \ldots < t_n$, as an application $s(t)$ of (t_1, t_n) over R (basis set of real numbers) that, restricted to the subinterval (t_i, t_{i+1}) with $i = 1, 2, \ldots n - 1$, becomes a polynomial $P_i(t) \leqslant m$. The spline function most commonly used is the cubic spline ($m = 3$), a vector of $n + 2$ dimensions of the vectorial space; to be able to determine the spline vector, the interpolating spline with two boundary conditions is included in the data processing, since there exist only n interpolation conditions (kinetic readings). The cubic spline function is introduced in chemical kinetics with the aim of improving and extending the range of application of Hilmmelbrau's method of direct integration.[14,15] This work underlines the important role of the cubic spline function for improving the differential methods, very often relegated by the integral method; also, a new type of piece-wise interpolation with overlapping time intervals is suggested, which eliminates the need for boundary conditions.

Obtention of Reaction Rates with the Cubic Spline Function.—The theory of divided differences enables the obtention of the

Table 1. Results of reaction rates $-d\lambda/dt$ obtained from simulated data of a first order reaction, $\lambda = \lambda_o \exp(-kt)$, according to different methods[a]; $\lambda_o = 1$; $k = 0.01\ \text{min}^{-1}$.

t/min	λ	Actual rate	Overinter	First spline	Second spline	Natural spline
1	0.990	9.900	9.803	9.803	9.835	9.615
10	0.905	9.050	9.046	9.050	9.041	9.103
20	0.819	8.190	8.150	8.177	8.180	8.163
30	0.741	7.410	7.450	7.440	7.439	7.444
40	0.670	6.700	6.615	6.762	6.762	6.761
50	0.606	6.060	6.065	6.010	6.010	6.011
60	0.549	5.490	5.501	5.497	5.495	5.493
70	0.496	4.960	5.009	5.001	5.006	5.017
80	0.449	4.490	4.510	4.497	4.476	4.438
90	0.406	4.060	4.010	4.010	4.087	4.231

[a] Results affected by a factor of 10^4.

polynomial $P_i(t)$ corresponding to the subinterval (t_1, t_{i+1}), as equation (6)

$$P_i(t) = \lambda_i + (t - t_i)r_{\lambda_i} + \frac{(t - t_i)^2}{\Delta t_i}(\Delta\lambda_i/\Delta t_i - r_{\lambda i}) + \frac{(t - t_i)^2(t - t_{i+1})}{\Delta t_i^2}(r_{\lambda_{i+1}} + r_{\lambda_i} - 2\Delta\lambda_i/\Delta t_i) \quad (6)$$

with $i = 1,2, \ldots n-1$; $\Delta t_i = (t_{i+1} - t_i)$; $\Delta\lambda_i = (\lambda_{i+1} - \lambda_i)$.

The cubic spline function requires the condition $P''_i(t_{i+1}) = P''_{i+1}(t_{i+1})$, with $i = 1,2 \ldots n - 2$; the two second derivatives can be obtained from equation (6) and this allows us to write equation (7); where $a_i = 1/\Delta t_i$, $c_i = 1/\Delta t_{i+1}$, $b_i = (2a_i + 2c_i)$,

$$a_i r_{\lambda_i} + b_i r_{\lambda_{i+1}} + c_i r_{\lambda_{i+2}} = d_i \; (i = 1,2, \ldots, n - 2) \quad (7)$$

and $d_i = [3c_{i+1}^2\lambda_{i+2} - (3c_{i+1}^2 - 3a_i^2)\lambda_{i+1} - 3a_i^2\lambda_i]$. There exist n indeterminates (values of r_λ at each experimental point), but only $n - 2$ equations such as equation (7) are available; then, two boundary conditions are necessary to solve the problem. Depending on the nature of the additional data coming from the boundary conditions, the cubic spline interpolants classify as follows.

(*a*) *Cubic spline with boundary conditions on the first derivative* (*first spline*). The additional information comes from the first derivative r_λ at any two of the kinetic readings, the first and last being those usually chosen; in this work they were obtained by derivation of the polynomials, fitting the first four points to a second degree polynomial, and the four last points to another polynomial; in this way, the following matrix equation (8) was

$$\begin{vmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ a_1 & b_1 & c_1 & 0 & 0 & 0 \\ 0 & a_2 & b_2 & c_2 & 0 & 0 \\ 0 & 0 & a_3 & b_3 & c_3 & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ 0 & 0 & 0 & a_{n-2} & b_{n-2} & c_{n-2} \\ 0 & 0 & 0 & 0 & 0 & 1 \end{vmatrix} \times \begin{vmatrix} r_{\lambda_1} \\ r_{\lambda_2} \\ r_{\lambda_3} \\ r_{\lambda_4} \\ \cdots \\ r_{\lambda_{n-1}} \\ r_{\lambda_n} \end{vmatrix} = \begin{vmatrix} r_{\lambda_1} \\ d_1 \\ d_2 \\ d_3 \\ \cdots \\ d_{n-2} \\ r_{\lambda_n} \end{vmatrix} \quad (8)$$

obtained: *i.e.* $C \times V = D$ and, therefore, the reaction rates may be obtained as $V = C^{-1} \times D$. The matrix of coefficients C is calculated using the successive differences between times, whereas the column matrix D depends on the successive differences between the readings of the property λ, and also on two of the derivatives.

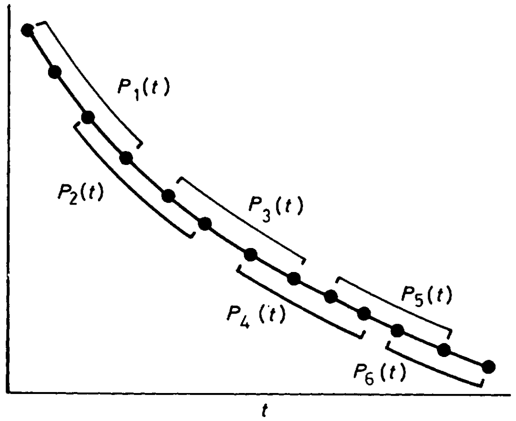

Figure 1. Decomposition of the interval of data points into several subintervals according to the overinter method.

(*b*) *Cubic spline with boundary conditions on the second derivative* (*second spline*). The additional data required are the values of the second derivative at any two of the readings, the first and last ones being chosen again; two polynomials are obtained in a manner similar to that described earlier and λ''_1 and λ''_n are determined by derivation; two conditions are applied: $\lambda''_1 = P''_1(t_1)$ and $\lambda''_n = P''_{n-1}(t_n)$, $P''_i(t)$ being obtained from equation (6). The solution of the matrix equation (9) enables the obtention of the reaction rates.

(*c*) *Natural cubic spline*. This is a particular type of the second spline, with $\lambda''_1 = \lambda''_n = 0$; it is the most commonly used, since no calculation prior to equation (9) is required.

Obtention of Reaction Rates by Piece-wise Interpolation with Overlapped Intervals (*Overinter*).—The total number of data points is distributed over several subintervals of four points each; the last interval will consist of three points if the total number is an odd number. Each interval overlaps with adjacent ones (Figure 1) and is fitted to a second degree polynomial by least squares and then $P_1(t)$, $P_2(t)$,... are obtained. The rate r_λ is deduced at every point by derivation, in such a way that all the subintervals (except the first and last ones) are solely used to obtain the derivatives at the two central points.

Results

Table 1 contains values of reaction rates obtained according to the methods described; these values come from the simulated data of a first-order reaction whose actual rates are given, and compare satisfactorily; the first spline, second spline and overinter methods provide better agreement, although none of them could be singled out; the natural spline yields poorer results due to the drastic assumption $\lambda''_1 = \lambda''_n = 0$, but it is a more manageable method; the overinter method yields better results when the subintervals are fitted to a polynomial of second degree, and no appreciable improvement was observed on increasing each subinterval to more than four points. It is to be noted that the initial and final rates are the furthest from the actual values and should be rejected as long as sufficient readings (>10) are available. Although the boundary conditions may be applied to any two points, its application to points other than the first and last ones does not improve the results. Finally, the same subroutine was always utilized with the overinter method, and became *ca.* 3.3 times faster than spline methods.

A study was also made of the influence that errors inherent to readings have on the accuracy of the methods suggested; to do this, a random alteration was made of the readings of a simulated kinetic run, in the form: $\lambda q_i = \lambda_i + qs(\lambda)$, where

$$\left|\begin{array}{cccccc} 4a_1 & 2a_1 & 0 & 0 & 0 & 0 \\ a_1 & b_1 & c_1 & 0 & 0 & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ 0 & 0 & 0 & a_{n-2} & b_{n-2} & c_{n-2} \\ 0 & 0 & 0 & 0 & 2a_{n-1} & 4a_{n-1} \end{array}\right| \times \left|\begin{array}{c} r_{\lambda_1} \\ r_{\lambda_2} \\ \cdots \\ \cdots \\ r_{\lambda_{n-1}} \\ r_{\lambda_n} \end{array}\right| = \left|\begin{array}{c} 6{}^{a2}_{1}\Delta\lambda_1 - \lambda''_1 \\ d_1 \\ \cdots \\ \cdots \\ d_{n-2} \\ 6a^2_{n-1}\Delta\lambda_{n-1} + \lambda''_n \end{array}\right| \quad (9)$$

Table 2. Determination of reaction orders from data of completion reactions by linear regression of $\ln r_\lambda = \ln K^* + n \ln P$.

Data (table number)	n	Overinter	First spline	Second spline	Natural spline
3	0.00	0.026 ± 0.015	0.025 x 0.011	0.031 ± 0.020	0.031 ± 0.021
4	0.50	0.499 ± 0.003	0.498 ± 0.003	0.498 ± 0.003	0.503 ± 0.003
5	1.00	0.999 ± 0.015	1.000 ± 0.012	1.014 ± 0.014	0.986 ± 0.015
6	1.00	1.000 ± 0.056	0.965 ± 0.057	0.960 ± 0.057	0.962 ± 0.057
7	2.00	2.133 ± 0.091	1.992 ± 0.102	1.958 ± 0.112	1.970 ± 0.111
4	2.50	2.477 ± 0.048	2.502 ± 0.022	2.494 ± 0.020	2.521 ± 0.030
8	3.00	2.933 ± 0.110	2.992 ± 0.064	2.972 ± 0.051	2.984 ± 0.050
9	4.00	4.138 ± 0.203	4.130 ± 0.175	4.109 ± 0.142	4.147 ± 0.165

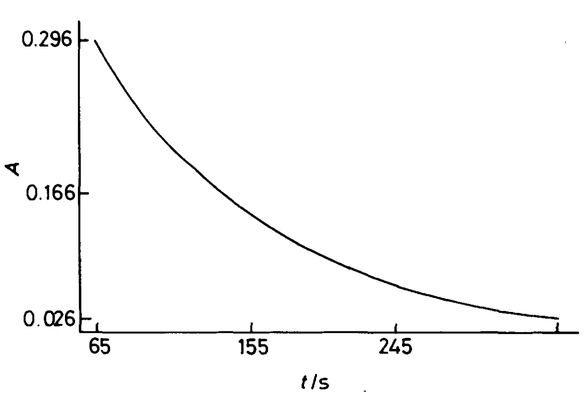

Figure 2. Absorbance–time curve obtained by application of the first spline to the kinetic readings of the oxidation of ascorbic acid by ferricyanide (Table 5).

$1 \geqslant q \geqslant -1$ and $s(\lambda)$ is the standard error of the property, which is considered to be constant during the kinetic run; good results were achieved when $s(\lambda) \leqslant 0.005\ (\lambda_1 - \lambda_\infty)$, λ_1 and λ_∞ being the first and last readings. If $s(\lambda) \geqslant 0.005(\lambda_1 - \lambda_\infty)$ the overinter method yields best results, since it minimizes the squares of deviations, whereas the cubic spline function passes through each of the points. In practice only in few cases is $s(\lambda) \geqslant 0.005(\lambda_1 - \lambda_\infty)$ and a complex version of the spline function may be utilized using weighted data and introducing an additional parameter; the trajectory λ/t can be softened so that the interpolating polynomial does not need to pass through all the points.[16]

Table 2 collects the reaction orders obtained by application of the methods described to some completion reactions, some of them carried out in our laboratory, so that equation (4) becomes equation (10).

$$(d\lambda/dt)_i = kp^{n-1}(\lambda_i - \lambda_\infty)^n = K^*(\lambda - \lambda_\infty)^n = k^*P^n \quad (10)$$

Once the reaction rates from the λ/t data have been calculated—by means of a non-linear two parametrical regression—K^* and n can be calculated, λ_∞ being a known parameter. The rate constant k is deduced from K^*. Also, a weighted linear regression can be used in the form: $\ln r_\lambda = \ln K^* + n \ln P$.

Table 3.[a] Oxidation of cysteine by ferricyanide ion in acid medium; cysteine = 0.01 mol dm^{-3}, $HClO_4$ = 0.05 mol dm^{-3}, $K_3Fe(CN)_6$ = 0.0005 mol dm^{-3}, $K_4Fe(CN)_6$ = 0.005 mol dm^{-3}, T = 25 °C.

t/s	A(416 nm)
3	0.480
7	0.420
11	0.364
15	0.310
19	0.257
23	0.204
27	0.152
31	0.099
33	0.073
35	0.048
37	0.026

[a] Ref. 17.

Discussion

Although differential rate equations are usually simpler than integral equations, the integral method provides better results in chemical kinetics if enough kinetic readings of a chemical reaction are available, since it operates directly on the kinetic readings. The integral method, however, is often difficult to use since it requires an additional parameter, which in turn derives in a more complicated model. The use of differential rate equations is advisable in the case of complex reactions; according to equation (10), if λ_∞ is unknown it would be much easier to use a non-linear three-parametrical regression; under the same circumstances the integral method would require four parameters, but a non-linear four-parametrical regression might introduce greater problems of convergence than a non-linear three-parametrical regression by the differential method. On the other hand, it is advisable to use the differential method in a first stage and obtain the integrated rate law, mainly if insufficient information is available concerning the reaction mechanism; then, in the light of the corresponding equation and the accuracy of the kinetic parameters, an easier decision can be made about the best procedure. As an example, Figure 2 shows the design corresponding to the interpolant polynomial (6) *via* first spline applied to the kinetic readings of the oxidation of ascorbic acid (Table 5) by ferricyanide.

The reactions of bromination of *o*-xylene (Table 10) and *m*-

Table 4. Kinetic data corresponding to a simulated kinetic run; $k = 0.01$, $P_o = 1$ (n = reaction order).

t	$P(n = 0.5)$	$P(n = 2.5)$
1	0.990	0.990
10	0.902	0.911
20	0.810	0.839
30	0.722	0.781
40	0.640	0.731
50	0.562	0.689
60	0.490	0.652
70	0.422	0.620
80	0.360	0.591
90	0.302	0.566

Table 5.[a] Oxidation of ascorbic acid by ferricyanide ion; ascorbic acid = 0.01 mol dm^{-3}, $HClO_4$ = 0.2 mol dm^{-3}, $K_3Fe(CN)_6$ = 0.0005 mol dm^{-3}, T = 25 °C.

t/s	A(416 nm)
65	0.296
95	0.225
125	0.171
155	0.130
185	0.100
215	0.076
245	0.058
275	0.045
305	0.034
335	0.026
365	0.020
395	0.016

[a] Ref. 17.

Table 6.[a] Decomposition of ferricyanide ion in acid medium; $K_3Fe(CN)_6$ = 0.0001 mol dm^{-3}, $HClO_4$ = 7 mol dm^{-3}, T = 60 °C.

t/s	A(416 nm)
30	0.074
60	0.062
90	0.053
120	0.044
150	0.037
180	0.032
210	0.027
240	0.023
270	0.020
300	0.017
330	0.014
390	0.010

[a] Ref. 17.

xylene (Table 11), follow the rate law given in equation (11).

$$-\mathrm{d}C_{\mathrm{Br_2}}/\mathrm{d}t = k_1 C_{\mathrm{Br_2}} + k_2 C^2_{\mathrm{Br_2}} \qquad (11)$$

Obviously, the use of the differential method is in this case equivalent to making a simple polynomial fitting. Table 12 contains the kinetic parameters of equation (11) obtained in this way; a_0 is negligible and a_1 and a_2 are in good agreement with k_1 and k_2 reported by Neyens.[21] On the other hand, integration of equation (11) leads to the less simple equation (12); where a new

$$C_{\mathrm{Br_2}} = k_1/[\exp(k_1 t - C) - k_2] \qquad (12)$$

parameter $C = \ln\,[C^{\ominus}_{\mathrm{Br_2}}/(k_1 + k_2 C^{\ominus}_{\mathrm{Br_2}})]$ is included; thus, the differential rate equation requires two parameters, whereas the integral equation requires three, which represents an additional difficulty.

Table 7.[a] Hydrochlorination of cyclohexene catalysed by $SnCl_4$; C_6H_{10} = 0.842 cm^3, $SnCl_4$ = 0.00673 mol dm^{-3}, T = 20 °C, V 670 cm^3.

t/min	$P_{\mathrm{H}}{}^{\mathrm{CL}}$/mmHg
0.5	585
1	544
1.5	517
2	477
2.5	450
3	425
3.5	404
4	385
5	350
6	323
7	297
16	176
62	57

[a] Ref. 18.

Table 8.[a] Bromination of toluene activated by nitromethane; toluene, 150 cm^3, nitromethane, 100 cm^3, T = 17 °C.

t/min	$[Br_2]$/mol dm^{-3}
2.5	0.359
6	0.320
13.5	0.268
23	0.227
29	0.210
49	0.170
78	0.141
90	0.132
135	0.111
160	0.102
200	0.092

[a] Ref. 19.

Table 9.[a] Iodination of m-xylene in nitromethane 50%, dichloroethane 40%, acetic anhydride 10%; $[m\text{-}C_8H_{10}] = [ICl]$ = 0.1078 mol dm^{-3}, T = 17 °C.

t/min	$[ICl]$/mol dm^{-3}
0.5	0.0805
2	0.0574
3.5	0.0485
5	0.0438
7.5	0.0384
10	0.0349
14	0.0312
17	0.0295
21	0.0275
27	0.0253
38	0.0226

[a] Ref. 20.

Finally, it is worth underlining that better results were obtained for kinetic runs in which standard errors of the kinetic readings are small and also for those with time intervals regularly spaced. At the present time many instruments are capable of giving kinetic readings periodically and automatically pre-selected, which is interesting for developing the procedures described. Although no data are reported here, Newton's interpolating polynomial yields very satisfactory results when the readings are regularly spaced.

Experimental

Reactants.—Potassium ferricyanide (Riedel 99%), perchloric acid (Merck 70%), ascorbic acid (Fluka 99.5%), L-cysteine (Fluka 99%), potassium ferrocyanide (Riedel 99%) were used

Table 10.[a] Bromination of *o*-xylene: [IBr] = 0.016 mol dm^{-3}; *o*-xylene, 50 cm^3; dichloroethane, 50 cm^3; T = 17 °C.

t/min	[Br_2]/mol dm^{-3}
0	0.2410
3	0.2020
6	0.1715
8	0.1540
12	0.1250
17	0.0990
21	0.0830
25	0.0690
30	0.0555
37	0.0410
43	0.0320

[a] Ref. 21.

Table 11.[a] Bromination of *m*-xylene: [IBr] = 0.0047 mol dm^{-3}; *m*-xylene, 100 cm^3; T = 17 °C.

t/min	[Br_2]/mol dm^{-3}
0	0.2550
3	0.2150
8	0.1670
11	0.1450
14	0.1280
18	0.1090
21	0.0975
24	0.0880
27	0.0795
29	0.0745
33	0.0655
41	0.0510

[a] Ref. 21.

Table 12. Parameters of the polynomial regression $-dC_{Br_2}/dt = a_0 + a_1C_{Br_2} + a_2C^2_{Br_2}$ corresponding to equation (11).

		Overinter	First spline	Second spline	Natural spline
Table 10	a_0	0.000 05 ± 0.000 16	0.000 05 ± 0.000 13	0.000 05 ± 0.000 12	0.000 05 ± 0.000 12
	a_1	0.035 04 ± 0.003 94	0.035 39 ± 0.003 12	0.035 47 ± 0.003 11	0.035 02 ± 0.002 88
	a_2	0.107 18 ± 0.021 08	0.112 09 ± 0.016 65	0.109 77 ± 0.016 60	0.114 09 ± 0.015 39
	r	0.9987	0.9992	0.9992	0.9993
Table 11	a_0	0.000 05 ± 0.000 15	0.000 04 ± 0.000 10	0.000 04 ± 0.000 09	0.000 05 ± 0.000 12
	a_1	0.017 94 ± 0.003 36	0.017 84 ± 0.002 11	0.017 81 ± 0.002 08	0.016 62 ± 0.002 66
	a_2	0.176 68 ± 0.018 40	0.182 64 ± 0.011 65	0.182 87 ± 0.011 45	0.192 89 ± 0.014 63
	R[a]	0.9982	0.9993	0.9993	0.9989

[a] R = multiple correlation coefficient.

without further purification; acid concentrations were calculated directly from molar concentrations of perchloric acid, since this species is fully ionized up to 70%. All solutions were prepared with twice distilled water as the solvent, over which nitrogen gas was made to flow before being used. In every case the solutions used were freshly prepared and kept out of the light.

Equipment.—The UV–VIS spectral curves were recorded with a Bodenseewerk Perkin-Elmer 554 Spectrophotometer with a double beam system, 1 nm slit, and a temperature-regulated cell holder adapter for 1 cm cells. Circulating water (P-Selecta Circulator) maintained the holder temperature constant to ±0.01 °C. The reference cell contained the same solvent as the sample under measurement. The kinetics of decomposition of ferricyanide, as well as the oxidation of L-cysteine and ascorbic acid by ferricyanide were followed with a Phillips Pye Unicam 8 600 spectrophotometer, furnished with a Pye Unicam cell temperature controller. The processing of data according to the methods described was carried out with computer; the program used is available on request. Battle's RNL3 program[22] was used when fitting the data points to a non-linear three parametrical regression.

Appendix

The need for good techniques for the approximation of functions arises in many settings; one of these is the numerical solution of differential rate equations in chemical kinetics. Spline functions constitute a relatively new subject in the analysis of kinetic data; during the last decade both the theory of splines and applications to the numerical analysis of data points have developed to a considerable degree. A cubic spline function is a piece-wise cubic polynomial twice continuously differentiable, and arises when trying to improve the piece-wise cubic Lagrange interpolating polynomial. On the other hand, the divided differences constitute a quite simple method for the computation of Lagrange polynomials and was used to build up the interpolating polynomial defined by equation (6), by adding the interpolation points one at a time.

The specific objective of much of the developments of splines is the fitting of a curve, providing the curve to be fitted satisfies the continuity conditions required. A detailed description of the concepts and methods used can be taken from refs. 12, 13, 23, and 24.

Acknowledgements

Thanks are due to Professor J. Casado for his useful comments.

References

1 J. H. vant Hoff, 'Etudes de Dynamique Chimique,' Muller, Amsterdam, 1884.
2 J. Casado, M. A. López, and F. M. Lorenzo, *J. Chem. Educ.*, 1986, **63**, 450.
3 H. W. Salzberg, J. I. Morrow, and S. R. Cohen, 'Laboratory Course in Physical Chemistry,' Academic Press, New York, 1966.
4 W. H. Pearlson and J. H. Simons, *J. Am. Chem. Soc.*, 1945, **67**, 352.
5 J. W. Sprauer and J. H. Simons, *J. Am. Chem. Soc.*, 1942, **64**, 648.
6 V. L. Frampton, *Science*, 1948, **107**, 323.
7 A. Weisberg, 'Techniques of Organic Chemistry,' Wiley, New York, 1961.
8 S. D. Ross, *Int. J. Chem. Kinet.*, 1982, **14**, 535.
9 D. M. Hirst, 'Mathematics for Chemists,' McMillan, Hong Kong, 1976.
10 F. Scheid, 'Análisis Numérico,' McGraw Hill, Mexico, 1972.
11 A. M. Winslow, *J. Phys. Chem.*, 1977, **81**, 2409.
12 F. García and A. Fernández, 'Diferencias Divididas. Spline,' Apuntes E. T. S. Arquitectura, San Sebastián, Spain, 1984.
13 P. M. Prenter, 'Splines and Variational Methods,' Wiley, New York, 1975.

14 Y. P. Tang, *Ind. Eng. Chem. Fundam.*, 1971, **10**, 321.
15 A. Yermakova, S. Vajda, and P. Valko, *Appl. Catal.*, 1982, **2**, 139.
16 T. N. E. Greville, 'Introduction to Spline Functions,' Academic Press, New York, 1969.
17 P. L. Domingo, Thesis, University of Valladolid Spain, 1988.
18 P. Leprince, *Rev. Inst. Pétr.*, Paris, 1959.
19 A. H. Neyens and J. C. Jungers, *Bull. Soc. Chim. Fr.*, 1959, 1482.
20 A. H. Neyens, *Bull. Soc. Chim. Fr.*, 1961, 719.
21 A. H. Neyens, *Bull. Soc. Chim. Fr.*, 1964, 1135.
22 P. Segura, 'Tratamiento de Datos y Análisis de Error,' PPU, Barcelona, Spain, 1985.
23 C. de Boor, 'A Practical Guide to Splines,' Springer, New York, 1978.
24 J. H. Ahlberg, E. N. Nilson, and J. L. Walsh, 'The Theory of Splines and Their Applications,' Academic Press, New York, 1967.

Paper 9/02673H
Received 23*rd June* 1989
Accepted 22*nd September* 1989