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THE APPLICATION OF COMPUTER CURVE FITTING TECHNIQUES TO REGNAULT–PFAUNDLER CALCULATIONS OF CALORIMETRIC DATA

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ABSTRACT

A curve fitting programme, using a cubic-spline technique, is described for fitting the results from reaction calorimetry. The coefficients from the technique are used to determine the mean resistance and other correction terms in a Regnault–Pfaundler analysis; the results agree with hand-worked results to better the 0.5%. The difficulties of using polynomial techniques are discussed and the importance is noted of computer plotting of results in checking the behaviour of the techniques.

INTRODUCTION

In measurements of the enthalpies of reaction of transition-metal complexes by Mortimer and Evans[1], the calorimetric data have been analysed with the Regnault–Pfaundler method[2]. In this graphical procedure the results are plotted, the initial and final steady-state periods are determined and then the curve of resistance against time in the reaction period is approximated by a series of trapezia to give a value for the mean resistance for the period. The procedure has a good accuracy but it is tedious and offers scope for shortening using computer methods.

Recently Gayer and Bartel[3] offered methods for dealing with reaction curves using a straight line approximation and Dickenson's method[2], but these are not appropriate to reactions which are relatively slow.

We have investigated two curve fitting procedures for the reaction period and have found a satisfactory practical method in which the junction between the reaction and final periods is determined automatically and the reaction period curve is fitted with a cubic-spline technique[4]. The programme yields results which, within experimental error, are as good as those from graphical procedures and it has the advantage that the time required is shorter. It can also be used for calibration runs.

COMPUTER ANALYSIS

Detection of the end of the reaction period

In the graphical technique the junction between the end of the reaction period and the beginning of the final period is determined by a combination of eye and ruler, using the deviation from straightness of the final period line as the criterion. Our method is similar: the user specifies a number of experimental points which lie definitely within the final period. These are fitted to a least-squares line. Then the three points immediately prior to those specified to lie on the line are examined to see whether, to within three standard deviations, they too lie on the line. If any do, then the point immediately prior to the points on the line is added to the line and a new least-squares fit is made. The procedure is repeated, taking the two points examined previously with next prior point. When all three trial points are found to lie off the line, on the correct side for the deviation to be due to the reaction period, the last point on the straight line is taken to be the junction between the two periods. With our data, interpolation between points to find the actual junction was not necessary because the time between points was short. One method of interpolation with our technique would be to insert an interpolation point determined from the computer plot in a subsequent run. The number of standard deviations used as a criterion can be varied but the value, three, was found to work well with our data.

The inadequacy of polynomial fitting

The mean resistance for the reaction period $\bar{R}(\mathrm{RP})$ is given by:

$$\bar{R}(\mathrm{RP}) = \int_{t_2}^{t_3} R(\mathrm{RP})\mathrm{d}t/\Delta t \qquad (1)$$

where Δt $(=t_3-t_2)$ is the time of the reaction period. The first attempt to determine $\bar{R}$ was to fit the reaction period curve by a least-squares polynomial fitting routine and so determine an equation for $R(\mathrm{RP})$ from which the integral could be calculated.

Although the routine provided numerical answers, it was clear from the computer plots that the fitting was not often precise. The types of curves, for both reaction and calibration, offer difficulties to polynomial fitting: both have straight portions and there are relatively few points. Polynomials from 3rd to 6th order were tried, both in overall fits and for fitting the curve in two halves, the slopes being matched between the two. In nearly all cases the curves showed oscillations which in some cases were large enough to lead to poor numerical results. It was not possible to predict by inspection which sets of data would give poor results. The necessity of making computer plots of both points and curves was demonstrated, for it was easy to see misbehaviour in fitting, when calculated variances gave little indication of it.

The cubic-spline technique

The second, successful, approach was to use the cubic-spline technique[4]. Here each successive pair of points on the curve is fitted with a simple cubic equation. A condition is applied so that the second differentials of each of the two cubics which meet at a point are equal. Consequently there are enough data to determine the coefficients of all the cubics making up the final curve. The equations can be expressed in a matrix form which is easily handled by the computer. For both reaction and calibration curves the second differentials of the cubics at the two end points of the reaction period are each zero: the calibration curve joins smoothly at each end to a straight line; the reaction curve starts as a straight line from a discontinuity and finishes by joining to a straight line.

The technique fitted both types of curves well. It is however a *fitting* and not a *smoothing* technique; the curve is forced to go through all the points which, while it works well with good data, will not produce smooth curves from poor data. Occasionally an oscillation was noticed in the plots which could be attributed to one of two causes. Either there was an insufficient number of points in a region of sharp curvature; this could be corrected by insertion of interpolated points in a subsequent run. Or there was an overshoot, implied by the data, due to insufficient stirring in faster experiments.

RESULTS

Figures 1 and 2 show a reaction and a calibration curve. The points are experimental, the straight lines are the least-squares plots of the initial and final periods and the curve is the plot from the cubic-spline technique. Table 1 gives results from these curves, together with those from a Regnault–Pfaundler plot, a calculation for

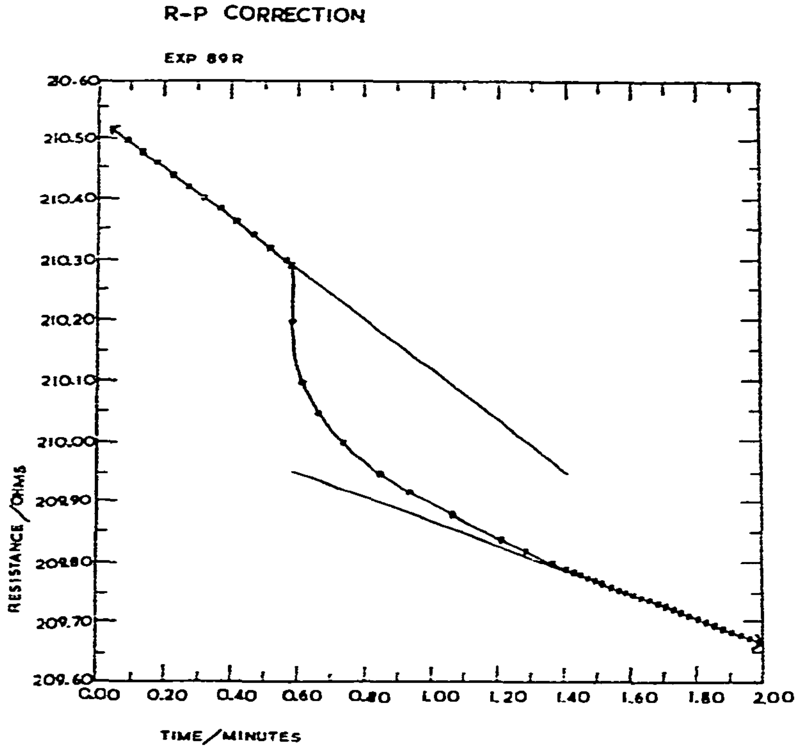

Fig. 1. Computer plot of experimental points and calculated curves for the reaction of $(Ph_3P)_2Pt(C_2H_4)$ with tetracyanoethylene. The scale figures represent the actual values multiplied by 0.1.

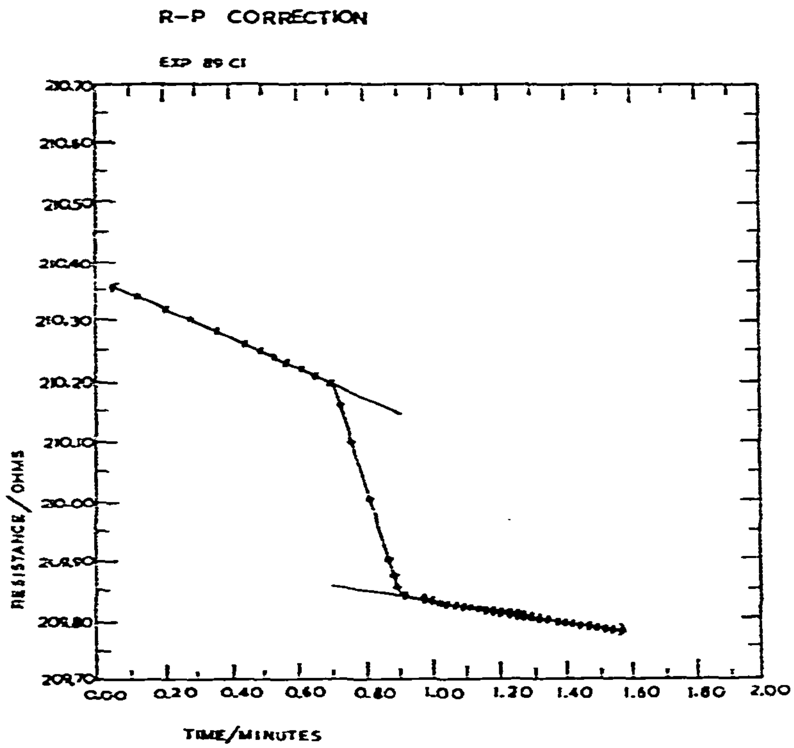

Fig. 2. Computer plot of experimental points and calculated curves for the electrical calibration for Run 89. The scale figures represent the actual values multiplied by 0.1.

TABLE 1

COMPARISON OF RESULTS FROM COMPUTER AND HAND PLOTS

	Reaction curve		*Calibration curve*	
	R–P	*Computed*	*Dickenson*	*Computed*
Mean resistance (initial) (Ω)	2104.065	2104.042	—	2102.780
Mean resistance (final) (Ω)	2097.300	2097.274	—	2098.074
Mean resistance (curve) (Ω)	2099.278	2099.186	2100.066	2100.151
Initial slope (Ω min^{-1})	−0.417	−0.416	—	−0.245
Final slope (Ω min^{-1})	−0.203	−0.207	—	−0.085
Correction resistance (Ω)	−2.187	−2.188	—	−0.331
R (experimental) (Ω)	−5.03	−5.05	—	−3.650
t (experimental) (min)	8.23	8.23	—	2.13
R (corrected) (Ω)	−2.843	−2.862	−3.308	−3.319

the reaction, and a calculation using Dickenson's method for the calibration. Agreement is to within 0.5%, which is as good as would be claimed for graphical integration.

Altogether the routine has provided a speedy and reliable method for treating these results. An important general conclusion about fitting procedures, which our experience shows, is that it is essential to plot both points and curves automatically so that the accuracy of the fit can be seen by inspection.

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