# Analysis with Microelectrodes Using Microsoft Excel Solver

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## Procedure: Part 3

In the last part of the experiment students use the expressions

$$k(T) = \left(\frac{8k_B T}{\pi\mu}\right)^{1/2} \int_0^\infty \sigma(E) f(E)\, dE \qquad (1)$$

and

$$\sigma(E) = \int_0^\infty 2\pi b P(b; E)\, db \qquad (2)$$

to calculate $k(T)$, which is a bimolecular rate constant at temperature $T$. To do this they first have to calculate a series of reaction cross sections $\sigma(E)$ at various relative translational energies, $E$. This is obtained by numerical integration of eq 2 using probabilities, $P(b; E)$, of the reaction occurring, which are calculated by the computer at chosen values of $E$ and of the impact parameter $b$. A further numerical integration of $\sigma(E)$, weighted by the Maxwell distribution of translational energies $f(E)$, which they calculate by hand, then leads them to the rate constant of interest.

In this calculation the vibrational and rotational energies are fixed and collision angle and vibrational phase are averaged over. The procedure requires a sensible choice of a range of $b$ and $E$ values by the students based on (i) their findings regarding the necessary values of $b$ in Part 2 and (ii) the fact that they are told that their $P(b; E)$ values will ultimately be used to calculate two rate constants at 300 and 500 K. Finally the students use their rate constants to calculate the Arrhenius parameters $E_a$ and $A$. The values obtained compare reasonably well with experimental values in the literature ($11$); we obtain $E_a \approx 16$ kJ mol$^{-1}$ and $A \approx 1.7 \times 10^{11}$ mol$^{-1}$ dm$^3$ s$^{-1}$, compared with $E_a = 14.64 \pm 0.13$ kJ mol$^{-1}$ and $A = (1.09 \pm 0.02) \times 10^{10}$ mol$^{-1}$ dm$^3$ s$^{-1}$ from ref $11$.

## Summary

We have described a highly student-active method of teaching molecular reaction dynamics. During the course of this computer-assisted learning process students (i) discover the relationship of the potential energy surface to the actual trajectories that atoms describe in a collision and (ii) are able to design their own experiments by choosing reaction conditions and then observe an animation of the outcome; they (iii) learn the meaning of cross sections and rate constants in terms of individual collisions and (iv) see how reaction dynamics relates to kinetics. We believe that all these factors help them in their appreciation of the nature and significance of molecular reaction dynamics.

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# Analysis with Microelectrodes Using Microsoft Excel Solver

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Considerable interest has been shown in the use of fitting experimental data to nonlinear functions as a means of introducing undergraduate students to the principle of problem solving using least-squares curve-fitting techniques (*1–5*). The purpose of this article is to demonstrate the use of a least-squares curve-fitting technique for voltammetric analysis. The problem of determining the concentrations of analytes in a solution using linear-sweep voltammetry at a microelectrode is chosen because the degree of experimental difficulty is less than, for example, in polarography, rotating disk electrochemistry, or normal pulse polarography. Furthermore, the limiting current magnitude in each of these techniques has typically been used for chemical analysis. This paper outlines a method which employs the full voltammetric curve to yield analytical information.

## Theory

The current response obtained by the application of a linear ramp waveform to a microelectrode in a solution of ferrocyanide at a sweep rate of 10 mV/s is shown in Figure 1(♦). The height of the plateau corresponds to the limiting current ($i_L$), which is proportional to the concentration of the analyte in solution. However, a problem arises in the determination of $i_L$ because only rarely is the limiting current plateau parallel to the baseline. Extrapolating the tails of the trace and measuring the perpendicular distance between them is another option, but again, a problem arises if the tails are not parallel. These conditions introduce an element of subjectiveness into the determination of $i_L$. This problem also arises in other voltammetric methods, for example, polarography, rotating disk electrochemistry, and normal pulse polarography (*6–8*). Microelectrodes were employed in this work as a model for other voltammetric techniques because they are safer to use than mercury and can be easily fabricated (*9*).

By collecting and digitally storing the current response it is possible to obtain a value for concentration ($C$) using
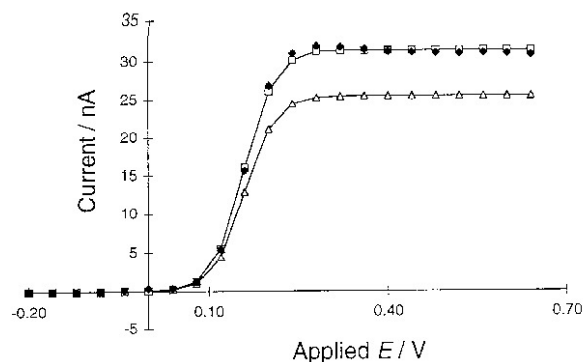
Figure 1. Current profiles corresponding to (♦) experimental data, where microelectrode radius = $2.53 \times 10^{-3}$ cm, sweep rate = 10 mV s$^{-1}$, concentration of [Fe(CN)$_6$]$^{4-}$ = 5 mM in 0.1 M KCl; (□) theoretical data set from Fig. 2 after the fitting process has been completed; and (△) theoretical data set from Fig. 2 before activating Solver. Prior to fitting, a value of $4 \times 10^{-3}$ M was used in the model for the concentration of [Fe(CN)$_6$]$^{4-}$.

| | A | B | C | D | E |
|---|---|---|---|---|---|
| 1 | n | F | r | D | C |
| 2 | E0' | nf/RT | | | |
| 3 | Applied E | Model | Data | Residuals^2 | SSR |
| 4 | -2.00E-01 | 1.67E-05 | 0.00E+00 | 2.78E-10 | 425.1851778 |
| 5 | -1.60E-01 | 8.13E-05 | 0.00E+00 | 6.60E-09 | |
| 6 | -1.20E-01 | 0.00039617 | -3.30E-02 | 1.12E-03 | |
| 7 | -8.00E-02 | 0.001931596 | 0.00E+00 | 3.73E-06 | |
| 8 | -4.00E-02 | 0.009415637 | 1.33E-01 | 1.53E-02 | |
| 9 | 0.00E+00 | 0.045844507 | 3.67E-01 | 1.03E-01 | |
| 10 | 4.00E-02 | 0.221982956 | 4.00E-01 | 3.17E-02 | |
| 11 | 8.00E-02 | 1.046903188 | 1.33E+00 | 8.01E-02 | |
| 12 | 1.20E-01 | 4.401216425 | 5.40E+00 | 9.98E-01 | |
| 13 | 1.60E-01 | 12.83551429 | 1.56E+01 | 7.64E+00 | |
| 14 | 2.00E-01 | 21.14652325 | 2.67E+01 | 3.08E+01 | |
| 15 | 2.40E-01 | 24.38466483 | 3.10E+01 | 4.38E+01 | |
| 16 | 2.80E-01 | 25.17528862 | 3.19E+01 | 4.52E+01 | |
| 17 | 3.20E-01 | 25.37865481 | 3.18E+01 | 4.12E+01 | |
| 18 | 3.60E-01 | 25.38581218 | 3.15E+01 | 3.74E+01 | |
| 19 | 4.00E-01 | 25.38728057 | 3.12E+01 | 3.38E+01 | |
| 20 | 4.40E-01 | 25.38758174 | 3.11E+01 | 3.26E+01 | |
| 21 | 4.80E-01 | 25.3876435 | 3.10E+01 | 3.15E+01 | |
| 22 | 5.20E-01 | 25.38765617 | 3.09E+01 | 3.04E+01 | |
| 23 | 5.60E-01 | 25.3876435 | 3.10E+01 | 3.15E+01 | |
| 24 | 6.00E-01 | 25.38765877 | 3.09E+01 | 3.04E+01 | |
| 25 | 6.40E-01 | 25.3876593 | 3.07E+01 | 2.82E+01 | |

Figure 2. Typical layout of the Excel spreadsheet before activating Solver. Typical values for experimental parameters and constants are $n = 1$, $F = 96,487 C$ mol$^{-1}$, $r = 2.53 \times 10^{-3}$ cm, $D = 6.5 \times 10^{-6}$ cm$^2$ s$^{-1}$, $C$ = unknown, $E^{\circ\prime} = 0.15$ V, $nF/RT = 39.608$. Columns B and C are multiplied by a factor of $10^9$ to improve the quality of the fitting process.

the complete voltammetric curve, rather than the limiting current alone. Microsoft Excel Solver provides a means of achieving this simply and effectively.

Before Microsoft Excel Solver can be used to determine unknown concentrations, a spreadsheet must be prepared that consists of a list of theoretical data and a corresponding list of experimental data. The list of experimental data is created by importing the data acquired during the experiment into the Excel spreadsheet, and the list of theoretical data is created by means of a model of the system. In this case the equation representing the microelectrode response for a reversible couple is used to generate the list of theoretical data (10):

$$ i = \frac{4 n F r D C}{1 + \exp\left(\dfrac{n F\left(E - E^{\circ\prime}\right)}{R T}\right)} $$

where, $n$ = number of electrons involved in the reaction, $F$ = Faraday's constant, $r$ = radius of the electrode, $D$ = diffusion coefficient of the analyte, $C$ = concentration of the analyte in solution, $E$ = applied potential and $E^{\circ\prime}$ = formal potential.

This equation describes the complete current–potential curve obtained under voltammetric conditions for a reversible system; the numerator determines the limiting current and the denominator determines the change in current as a function of potential. Modifying this technique to suit other voltammetric techniques requires only that the appropriate expression for the limiting current be substituted as the numerator in this equation.

## Results

The typical spreadsheet layout before fitting and a set of typical experimental parameters are given in Figure 2.

The figures in cells A1 to E1 and A2 to B2 are experimental parameters and constants, which must be entered by the student, and row 3 consists of a series of labels. A typical set of experimental parameters and constants corresponding to the conditions detailed in the experimental section is included in the figure legend. Columns A and C are filled by imported experimental data for potential and current, respectively. The

model values (column B) are generated by entering the following equation in cell B4:

=((4*$A$1*$B$1*$C$1*$D$1*$E$1)/(1+EXP($B$2*(A4-$A$2))))

The Edit →Fill→Down command is then used to create the column of data. Column D contains a list of the square of the residuals between each pair of model and experimental current data points and the number in cell E4 is the sum of squared residuals (SSR). This is the value that Solver will attempt to minimize during the curve-fitting process. Either a single variable, $C$, or two variables, $C$ and $E^{\circ\prime}$, can be optimized during this operation. At this stage the simulation is a straightforward procedure and could be included in the practical as an introductory exercise in program writing for the student. Once these columns of data have been generated, Solver is activated (1, 11).

With microelectrodes the currents involved tend to be quite small, typically nanoamps. Original attempts to fit the experimental and theoretical data sets for these experiments gave unsatisfactory results. Solver failed to fit the data sets perhaps because it was unable to process the small numbers involved. To overcome this problem both the theoretical and experimental data sets were multiplied by a factor of $10^9$. This enhanced the performance of the curve fitting to an acceptable level. On further investigation it was found that Solver was unable to function when the value of the SSR fell below $2 \times 10^{-9}$.

Figure 1(♦) shows the current profiles corresponding to the experimental data in Figure 2, Figure 1(△) is the current profile produced by the model before fitting with an initial guess by eye of the value of $C$ of $4 \times 10^{-6}$mol cm$^{-3}$, and Figure 1(□) is the current profile returned by the model on completion of the fitting process. For the reason outlined above, both the theoretical and experimental data sets were multiplied by a factor of $10^9$ before activation of Solver. In this example both $C$ and $E^{\circ\prime}$ are variable parameters. From the answer report it was seen that the SSR was reduced from 425.18 to 3.37 and that a value for $C$ of $4.94 \times 10^{-6}$ M was returned. This is a recovery of 98.8% on a standard concentration of $5.00 \times 10^{-6}$ M [Fe(CN)$_6$]$^{4-}$. The constraints that

**Table 1. Comparison of Standard Concentration Values with Values Returned by Solver**

| Standard Concn/ mol dm$^{-3}$ | Solver | | | |
|---|---|---|---|---|
| | Only $C$ Varied | | Both $C$ and $E^{o\prime}$ Varied | |
| | Concn/ mol dm$^{-3}$ | Recovery (%)[a] | Concn/ mol dm$^{-3}$ | Recovery (%)[a] |
| $1 \times 10^{-2}$ | $9.86 \times 10^{-3}$ | 98.6 | $9.89 \times 10^{-3}$ | 98.9 |
| $5 \times 10^{-3}$ | $4.86 \times 10^{-3}$ | 97.2 | $4.92 \times 10^{-3}$ | 98.4 |
| $1 \times 10^{-3}$ | $1.06 \times 10^{-3}$ | 106.0 | $1.05 \times 10^{-3}$ | 105.0 |
| $5 \times 10^{-4}$ | $5.12 \times 10^{-4}$ | 102.4 | $4.91 \times 10^{-4}$ | 98.2 |
| $1 \times 10^{-4}$ | $2.22 \times 10^{-4}$ | 45.0 | $2.22 \times 10^{-4}$ | 45.0 |

[a]Calculated as (value returned by Solver/standard concn) × 100. This is a measure of the correlation between the calculated and real concentrations.



Figure 3. The fitting of experimental data (■) to the model (smooth curve) for (a) $5 \times 10^{-4}$ M $K_4[Fe(CN)_6]$ and (b) $1 \times 10^{-4}$ M $K_4[Fe(CN)_6]$. All other experimental conditions are as in Figure 1.

were applied to the operation of the fitting process were chosen to prevent Solver from returning a negative value for concentration or formal potential.

To test the validity of this technique, a series of solutions of known concentration was prepared and analyzed using this method. Table 1 contains the nominal concentrations of the standard solutions ($C$) and the concentrations returned by Solver ($C'$). The percentage recovery is also quoted and serves as a measure of the correlation between the data sets.

It can be seen that the concentration values returned by Solver correlate well with the nominal concentrations over the range $1 \times 10^{-2}$ M to $5 \times 10^{-4}$ M. However, at lower concentrations the correlation becomes less satisfactory. Noise, although present in all the traces, becomes a problem at lower currents because it alters the overall shape of the trace, as can be seen in Figure 3. Below concentrations of $5 \times 10^{-4}$ M the experimental trace deviates from the sigmoidal shape and the model is unable to compensate for this. Obviously this greatly affects the ability of Solver to fit the experimental and theoretical data sets and therefore affects the accuracy of the results. The presence of this noise is a limitation of the potentiostat employed in this work and there appears to be no reason why lower concentrations could not be analyzed with the aid of a more noise-free system.

It was also found that fitting the experimental and theoretical data sets by allowing Solver to simultaneously vary the values of $C$ and $E^{o\prime}$ (the formal potential) resulted in concentration values closer to the nominal values than those obtained by varying only $C$, as can be seen in Table 1. In this way the information contained in the full sigmoidal shape is employed to yield an answer, rather than just the limiting current. The value of fitting the model with two variables can be clearly seen. Students should be encouraged to fit the curve with $C$ and then with $C$ and $E^{o\prime}$.

It is possible therefore to use curve-fitting techniques as a means of determining unknown concentrations for a reversible system to a high degree of accuracy, the limits of quantitation being governed by the presence of noise in the system. Any one or a combination of the other variables in the model can be determined in a similar fashion. This application of curve-fitting techniques using Microsoft Excel Solver provides a useful method of introducing students to this concept through practical experience. This method can also be adapted for use as an analytical tool with other
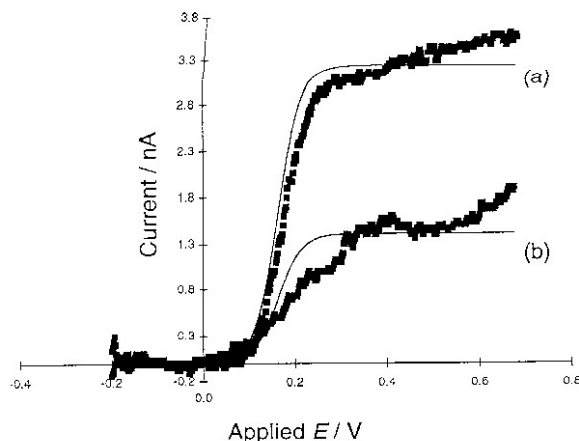
voltammetric techniques such as polarography, rotating disk electrochemistry, and normal pulse polarography, substitution of the appropriate expression for the limiting current being the only modification required.

## Experimental Details

Solutions of $K_4[Fe(CN)_6]$ were prepared in 0.1 M KCl. All solutions were degassed before collecting data, and a positive nitrogen pressure was maintained over the cell during voltammetric analysis. A three-electrode one-compartment cell with SCE as reference and a carbon rod auxiliary was employed and an EG&G M394 system was used to acquire data. The microelectrodes (9) used were fabricated in the laboratory from 50-μm platinum wire (Goodfellow). This microwire was connected to a more rigid copper wire using silver epoxy and was heat-sealed in the narrow end of a pasteur pipet. After the copper wire was secured at the open end of the pipet with an epoxy resin (Araldite), the sealed tip of the pipet was sanded and polished with 1-μm alumina until a disk of the platinum wire was exposed to solution.

## Acknowledgment

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