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<thead>
<tr>
<th>Name</th>
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<th>Date</th>
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</thead>
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</tbody>
</table>
THE DETERMINATION OF RATE CONSTANTS USING MICROELECTRODES.

PETER JOHN MAHON

B.Sc. (Hons.)

This thesis is submitted as total fulfilment of the degree of Doctor of Philosophy.

School of Sciences.
March 1992
DEAKIN UNIVERSITY

CANDIDATE'S CERTIFICATE

I certify that the thesis entitled "THE DETERMINATION OF RATE CONSTANTS USING MICROELECTRODES" and submitted for the degree of DOCTOR OF PHILOSOPHY is the result of my own research, except where otherwise acknowledged, and that this thesis (or any part of the same) has not been submitted for a higher degree to any other university or institution.

Signed

Date .........30/3/92..............
# TABLE OF CONTENTS

## SUMMARY

<table>
<thead>
<tr>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
</tr>
</tbody>
</table>

## CHAPTER ONE - GENERAL INTRODUCTION

1. INTRODUCTION

<table>
<thead>
<tr>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
</tr>
</tbody>
</table>

1.1. VOLTAMMETRY

<table>
<thead>
<tr>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
</tr>
</tbody>
</table>

1.1.1. MASS TRANSPORT IN VOLTAMMETRY

<table>
<thead>
<tr>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
</tr>
</tbody>
</table>

1.1.2. ELECTRODE KINETICS IN VOLTAMMETRY

<table>
<thead>
<tr>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
</tr>
</tbody>
</table>

1.1.3. QUANTITATION OF ELECTRODE KINETICS IN VOLTAMMETRY

<table>
<thead>
<tr>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>17</td>
</tr>
</tbody>
</table>

1.1.4. CHEMICAL MECHANISMS AND KINETICS ASSOCIATED WITH ELECTRODE PROCESSES

<table>
<thead>
<tr>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
</tr>
</tbody>
</table>

1.1.5. THE APPLICATIONS AND ADVANTAGES OF MICROELECTRODES

<table>
<thead>
<tr>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
</tr>
</tbody>
</table>

1.2. THE AIM AND SCOPE OF THIS THESIS

<table>
<thead>
<tr>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
</tr>
</tbody>
</table>

## CHAPTER TWO - VOLTAMMETRIC DATA ACQUISITION USING ANALOG AND DIGITAL INSTRUMENTATION

<table>
<thead>
<tr>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>27</td>
</tr>
</tbody>
</table>

2. INTRODUCTION

<table>
<thead>
<tr>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>28</td>
</tr>
</tbody>
</table>

2.1. INSTRUMENTATION

<table>
<thead>
<tr>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>29</td>
</tr>
</tbody>
</table>

2.1.1. THE DIGITAL STORAGE OSCILLOSCOPE

<table>
<thead>
<tr>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>29</td>
</tr>
</tbody>
</table>

2.1.2. THE FUNCTION GENERATOR

<table>
<thead>
<tr>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>34</td>
</tr>
</tbody>
</table>

2.1.3. THE POTENTIOSTAT

<table>
<thead>
<tr>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>34</td>
</tr>
</tbody>
</table>

2.1.4. THE MEASUREMENT OF CURRENT IN THE TWO ELECTRODE MODE

<table>
<thead>
<tr>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>37</td>
</tr>
</tbody>
</table>

2.1.4.1. THE MEASUREMENT OF CURRENT BETWEEN TWO ELECTRODES IN A PSEUDO-TWO ELECTRODE MODE

<table>
<thead>
<tr>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>38</td>
</tr>
</tbody>
</table>
2.2. THE ELECTRODES. 56
2.3. COMPUTER BASED DATA MANIPULATIONS. 59
2.4. CHEMICALS. 69

CHAPTER THREE - GLOBAL KINETIC ANALYSIS OF CYCLIC VOLTAMMOGRAMS AT A SPHERICAL ELECTRODE. 71
3. INTRODUCTION. 72
3.1. GENERAL THEORY. 74
3.2. BUTLER-VOLMER MODEL. 81
3.3. THE POLARIZING SIGNAL. 85
3.4. IMPLEMENTATION OF THE ANALYSIS. 86
3.5. WEIGHTED LEAST SQUARES REGRESSION ANALYSIS. 89
3.6. TESTING OF THE ANALYSIS. 91
3.7. CONCLUSION. 94

CHAPTER FOUR - INVESTIGATION OF THE INFLUENCE OF RESIDUAL UNCOMPENSATED RESISTANCE AND INCOMPLETE CHARGING CURRENT CORRECTION ON THE CALCULATION OF THE ELECTRODE KINETICS INCLUDING THE POTENTIAL DEPENDENCE OF THE CHARGE TRANSFER COEFFICIENT WHEN GLOBAL AND CONVOLUTION ANALYSIS METHODS ARE USED. 97
4. INTRODUCTION. 98
4.1. ADDITIONAL THEORY. 100
4.1.1. WEIGHTING FUNCTIONS. 101
4.2. EXPERIMENTAL. 104
4.3. RESULTS AND DISCUSSION. 106
4.4. CONCLUSION.

CHAPTER FIVE - EVALUATION OF ELECTRODE KINETICS USING THE TECHNIQUES OF NORMALISED STEADY STATE VOLTAMMETRY AND DIGITAL SIMULATION OF THE MICRODISC ELECTRODE GEOMETRY WITH THE FAST QUASI-EXPLICIT FINITE DIFFERENCE METHOD.

5. INTRODUCTION.

5.1. THE THEORY OF NORMALISED STEADY STATE VOLTAMMETRY.

5.1.1. WEIGHTING PROCEDURES USED FOR NORMALISED STEADY STATE VOLTAMMETRY.

5.2. FAST QUASI-EXPLICIT FINITE DIFFERENCE SIMULATION OF VOLTAMMOGRAMS AT AN INLAID MICRODISC ELECTRODE GEOMETRY.

5.2.1. THE TWO DIMENSIONAL EXPONENTIALLY EXPANDING SPACE GRID.

5.2.2. THE ALGORITHM FOR THE SIMULATION.

5.2.3. THE SIMULATION CONDITIONS.

5.3. RESULTS AND DISCUSSION

5.4. CONCLUSION.

CHAPTER SIX - THE VOLTAMMETRIC INVESTIGATION OF THE UNUSUAL ISOMERIC LABILITY IN BOTH OXIDATION STATES FOR THE REDOX SYSTEMS Fac/mer-[M(CO)₃(η³-P₂P')]⁺/M(CO)₃(η³-P₂P') (M = Cr, Mo, W) (P₂P' = Bis(2-Diphenylphosphinoethyl)phenylphosphine).

6. INTRODUCTION.
6.1. EXPERIMENTAL.

6.2. THE THEORY OF THE SQUARE SCHEME AND THE FQEFD SIMULATION FOR A MICRODISC ELECTRODE GEOMETRY.

6.2.1. GENERAL THEORY OF THE SQUARE SCHEME.

6.2.2. FQEFD SIMULATION OF THE SQUARE SCHEME AT A MICRODISC ELECTRODE.

6.3. RESULTS AND DISCUSSION.

6.3.1. CYCLIC VOLTAMMETRIC OXIDATION OF Cr(CO)$_3$(η$^3$ - P$_2$P') AT PLATINUM ELECTRODES IN DICHLOOROMETHANE.

6.3.1.1. CONVENTIONAL CYCLIC VOLTAMMETRIC CONDITIONS.

6.3.1.2. VOLTAMMETRY AT MICRODISC ELECTRODES.

6.3.2. CYCLIC VOLTAMMETRIC OXIDATION OF Mo(CO)$_3$(η$^3$ - P$_2$P')

6.3.2.1. CONVENTIONAL CYCLIC VOLTAMMETRIC CONDITIONS.

6.3.2.2. VOLTAMMETRY AT MICRODISC ELECTRODES.

6.3.3. CYCLIC VOLTAMMETRIC OXIDATION OF W(CO)$_3$(η$^3$ - P$_2$P')

6.3.3.1. CONVENTIONAL CYCLIC VOLTAMMETRIC CONDITIONS.

6.3.3.2. VOLTAMMETRY AT MICRODISC ELECTRODES.

6.4. GENERAL DISCUSSION OF THE STRUCTURAL EFFECTS FOR M(CO)$_3$(η$^3$ - P$_2$P')

6.5. CONCLUSION.

CHAPTER SEVEN - EFFECTS OBSERVED IN MICROELECTRODE VOLTAMMETRY AT HIGH CURRENT DENSITIES IN LOW DIELECTRIC SOLVENT SUCH AS DICHLOOROMETHANE.

7. INTRODUCTION.

7.1. EXPERIMENTAL.
7.2. THE VOLTAMMETRY OF FERROCENE IN DICHLOROMETHANE. 209

7.3. THE VOLTAMMETRY OF COBALTOCENIUM HEXAFLUOROPHOSPHATE IN DICHLOROMETHANE. 218

7.4. THE VOLTAMMETRY OF RUTHENIUM(II)-TRIS-(2,2'-BIPYRIDINE) PERCHLORATE IN DICHLOROMETHANE. 224

7.5. GENERAL IMPLICATIONS OF HIGH CURRENT DENSITIES AND ELECTROLYTE EFFECTS IN ORGANIC SOLVENTS. 233

7.6. CONCLUSIONS. 234

CHAPTER EIGHT - GENERAL CONCLUSIONS. 235

8. CONCLUSIONS. 236

APPENDIX I. 240

REFERENCES. 359
LIST OF TABLES.

2.1. The maximum scan rate available for each current setting of the Amel Model 551 potentiostat before the onset of distortion. 36

3.1. Format of the data for the spherical Global Analysis. 88

3.2. Results of subjecting simulated cyclic data to the spherical Global Analysis. 92

3.3. Kinetic and thermodynamic values calculated when simulated cyclic voltammetric data for a spherical electrode are analysed using the planar version of the Global Analysis. 93

3.4. Results of subjecting noisy simulated cyclic voltammetric data to the spherical Global Analysis. 95

4.1. Determination of electrode kinetic parameters by analysis of digitally simulated data containing a potential dependent $\alpha$. 107

4.2. Determination of electrode kinetic parameters by analysis of digitally simulated data having unequal diffusion coefficients. 109

4.3. Determination of electrode kinetic parameters by analysis of digitally simulated data having unequal diffusion coefficients. 110

4.4. Determination of electrode kinetic parameters by applying the Global Analysis method to digitally simulated data containing uncompensated resistance. 112

4.5. Determination of electrode kinetic parameters by applying the CPSV method to digitally simulated data containing uncompensated resistance. 113

4.6. Determination of electrode kinetic parameters by applying the Global Analysis method to digitally simulated data containing incomplete charging current correction. 115

4.7. Determination of electrode kinetic parameters by applying the CPSV
method to digitally simulated data containing incomplete charging
current correction.

4.8. Analysis of electrode kinetic parameters obtained by applying different
calculation methods to experimental data for the reduction of
(CH₃)₃CNO₂.

5.1. A comparison of E¹/₂-E° and E₁/₄-E₃/₄ values measured from simulated
voltammograms with values estimated from reference P₁.

5.2. The effect of k° on the analysis with σ = 71.7.

5.3. The effect of α on the analysis with σ = 71.7.

5.4. The effect of a potential dependent α on the analysis with σ = 71.7.

5.5. The effect of gaussian noise on the analysis with σ = 71.7.

5.6. The effect of k° on the calculation of E° with σ = 71.7.

5.7. The effect of α on the calculation of E° with σ = 71.7.

5.8. The effect of an errant estimation of E° on the analysis with σ = 71.7.

6.1. Thermodynamic and kinetic data for the redox systems [Cr(CO)₃(η³-
P₂P')]⁺/0,[Cr(CO)₃(OMe)₃]⁺/0 and [Mo(CO)₃(η³-P₂P')]⁺/0 in
dichloromethane.

6.2. Theoretical results from the steady state simulation (scan rate 10 mV s⁻¹)
of the square scheme using parameters E°ₐₐ = -0.085 V,
E°ₐₐ = -0.310 V and Eₜₐ = -0.122 V), other parameters as given in
Table 6.1 with k° = k°ₐₐ = k°ₐₐ and αₐₐ = αₐₐ = 0.5.

6.3. Experimental steady state results for the oxidation of Cr(CO)₃(η³-P₂P')
in dichloromethane (0.5M Bu₄NBF₄) at 20°C as a function of electrode
radius at a platinum disc microelectrode.

7.1. Ionic radii and effective charge-volume ratios for various anions and
cations.
LIST OF FIGURES.

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>The voltammetric response obtained with different values of the</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>sphericity factor.</td>
<td></td>
</tr>
<tr>
<td>1.2</td>
<td>The dependence of the cyclic voltammetric response on different values of</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>the dimensionless rate parameter.</td>
<td></td>
</tr>
<tr>
<td>1.3</td>
<td>The cyclic voltammetric response obtained with different values of the</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>charge transfer coefficient when $\Lambda = 1.0$.</td>
<td></td>
</tr>
<tr>
<td>1.4</td>
<td>The steady state voltammetric response obtained with different values of the</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>steady state normalised rate constant.</td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td>The application of semi-integration to a linear sweep voltammogram to</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>produce a time independent 'steady state' response.</td>
<td></td>
</tr>
<tr>
<td>2.1</td>
<td>Diagram of the instrumentation required for an experiment in the two</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>electrode configuration.</td>
<td></td>
</tr>
<tr>
<td>2.2</td>
<td>Diagram of the instrumentation required for an experiment in the three</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>electrode configuration.</td>
<td></td>
</tr>
<tr>
<td>2.3</td>
<td>Potential offset circuit.</td>
<td>33</td>
</tr>
<tr>
<td>2.4</td>
<td>Cell arrangement for the subtraction of the residual current in the fritted</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>cell.</td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td>Cell arrangement for the subtraction of the residual current.</td>
<td>42</td>
</tr>
<tr>
<td>2.6</td>
<td>An example of the 'spiking' that occurs due to the difference in the current</td>
<td>43</td>
</tr>
<tr>
<td></td>
<td>paths as a result of the cell configuration of Figure 2.4.</td>
<td></td>
</tr>
<tr>
<td>2.7</td>
<td>Single operational amplifier current difference measuring circuit.</td>
<td>44</td>
</tr>
<tr>
<td>2.8</td>
<td>An example of the potential error incurred when using the subtraction</td>
<td>46</td>
</tr>
<tr>
<td></td>
<td>circuit from Figure 2.7.</td>
<td></td>
</tr>
<tr>
<td>2.9</td>
<td>Current difference measuring circuit.</td>
<td>47</td>
</tr>
<tr>
<td>2.10</td>
<td>The Bode plot of the current difference amplifier from Figure 2.9 with</td>
<td>48</td>
</tr>
<tr>
<td></td>
<td>a gain of $10^6$ V A$^{-1}$.</td>
<td></td>
</tr>
</tbody>
</table>
2.11. Diagram demonstrating the various components of a voltammetric response.

2.12. An example of the current difference measuring circuit.

2.13. The process involved for the construction of microdisc electrodes.

2.14. An example of the data which is collected by the DSO.

2.15. Examples of various smoothing procedures.

3.1. Two dimensional relationship between \( i^* \) and \( E \) when the convolute \( \mu \) equals zero.

3.2. Two dimensional relationship between \( \mu^* \) and \( E \) when the current equals zero.

3.3. Linear relationship between \( i \) and \( \mu \) at any constant potential.

3.4. A plot of \( 1/\mu^* \) versus \( \exp(nFE/RT) \) from the slope and intercept of which \( M \) and \( E^{1/2}_{1/2} \) are calculated.

3.5. A plot of \( \ln i^* \) versus \( -nFE/RT \) from the slope and intercept of which \( \alpha \) and \( I \) are calculated.

3.6. Example of the relationship between \( i, \mu \) and \( E \) for cyclic voltammetric conditions.

4.1. Examples of the various weighting functions for Global Analysis.

5.1. Schematic diagram of a segment of the two dimensional expanding grid.

5.2. An example of the application of Normalised Steady State Voltammetry to simulated data.

5.3. Simulated voltammograms with \( d\alpha/dE \) equal to 0.500, \( \alpha \) equal to 0.500 and \( \kappa^0 \) equal to 10, 1.0, 0.10, 0.010.

5.4. Simulated voltammograms with \( \kappa^0 \) equal to 0.010, \( \alpha \) equal to 0.500 and \( d\alpha/dE \) equal to 0.10, 0.30, 0.50, 0.70.

6.1. The oxidation of 1 mM Cr(CO)\(_3\)(\( \eta^3 \)-P\(_2\)P') with 0.1 M Bu\(_4\)NBF\(_4\) in dichloromethane at a 0.5 mm radius Pt electrode with a scan rate of
0.1 V s\(^{-1}\) and a temperature of 20°C.

6.2. The effect of temperature for the system given in Figure 6.1.

6.3. The oxidation of 2 mM Cr(CO)\(_3\)(\(\eta^3\) - P\(_2\)P') with 0.5 M Bu\(_4\)NBF\(_4\) in dichloromethane at a 25 μm radius Pt electrode at a temperature of 20°C with various scan rates.

6.4. Simulation-experiment correlation for the oxidation of 2 mM Cr(CO)\(_3\)(\(\eta^3\) - P\(_2\)P') with 0.5 M Bu\(_4\)NBF\(_4\) in dichloromethane at a 25 μm radius Pt electrode at a temperature of 20°C with various scan rates.

6.5. The steady state oxidation of 0.5 mM Cr(CO)\(_3\)(\(\eta^3\) - P\(_2\)P') with 0.5 M Bu\(_4\)NBF\(_4\) in dichloromethane with a scan rate of 10 mV s\(^{-1}\) and a temperature of 20°C for various electrode radii.

6.6. The simulation of the steady state oxidation of Cr(CO)\(_3\)(\(\eta^3\) - P\(_2\)P') with the parameters as given in Table 6.1.

6.7. The oxidation of 2 mM Mo(CO)\(_3\)(\(\eta^3\) - P\(_2\)P') with 0.5 M Bu\(_4\)NBF\(_4\) in dichloromethane at a 25 μm radius Pt electrode at a temperature of 20°C with various scan rates.

6.8. The oxidation of 2 mM W(CO)\(_3\)(\(\eta^3\) - P\(_2\)P') with 0.5 M Bu\(_4\)NBF\(_4\) in dichloromethane at a 25 μm radius Pt electrode at a temperature of 20°C with a scan rate of 200 V s\(^{-1}\).

6.9. A simulation for the oxidation of W(CO)\(_3\)(\(\eta^3\) - P\(_2\)P') based on the parameters from Table 6.1 for Cr(CO)\(_3\)(\(\eta^3\) - P\(_2\)P').

7.1. A plot of the Specific Conductance of Bu\(_4\)NCIO\(_4\) in dichloromethane versus concentration.

7.2. Plot of the current density function versus the sphericity factor from equation (7.4).

7.3. Steady state current distribution across the surface of a microdisc.
electrode based on equation (7.5).

7.4. Simulation-experiment comparison for 2 mM Fc and 0.5 M Bu₄NBF₄ in dichloromethane.

7.5. Literature example from reference 256 showing the much broader oxidation response compared to the reductive peak shape for conditions of 4 mM Fc with 0.6 M Bu₄NClO₄ in acetonitrile at a 0.95 μm radius Pt electrode.

7.6. The concentration dependence of Fc with 0.5 M Bu₄NPF₆ in dichloromethane at a scan rate of 1 V s⁻¹.

7.7. The effect of repetitive cycling for 48.7 mM Fc with 0.5 M Bu₄NPF₆ in dichloromethane at a scan rate of 1 V s⁻¹.

7.8. The effect of a steady state experiment for 48.7 mM Fc with 0.5 M Bu₄NPF₆ in dichloromethane at a scan rate of 10 mV s⁻¹.

7.9. Simulation-experiment comparison for 1.92 mM CePF₆ and 0.5 M Bu₄NBF₄ in dichloromethane.

7.10. Voltammograms for 2 mM Ru(bipy)$_3$(ClO₄)$_2$ and 0.5 M Bu₄NBF₄ in dichloromethane at a 25 μm radius Pt electrode.

7.11. Voltammograms for 2 mM Ru(bipy)$_3$(ClO₄)$_2$ and 0.5 M Bu₄NBF₄ in dichloromethane at a 5 μm radius Pt electrode.
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PUBLICATIONS.


Alan M. Bond, Ray Colton, Stephen W. Feldberg, Peter J. Mahon and Tania Whyte, "Unusual Isomeric Lability in Both Oxidation States of the Redox Systems \textit{fac}/\textit{mer} [M(CO)\textsubscript{3}(\eta\textsuperscript{3} - P\textsubscript{2}P')]+/M(CO)\textsubscript{3}(\eta\textsuperscript{3} - P\textsubscript{2}P') (M = Cr, Mo, W; P\textsubscript{2}P' = Bis(2-(diphenylphosphino)ethyl)phenylphosphine): The First Examples Where the 17-Electron \textit{fac}\textsuperscript{+} and \textit{mer}\textsuperscript{+} Are of Comparable Stability", Organometallics 10 (1991) 3320.

Alan M. Bond, Ray Colton, Stephen W. Feldberg, Howard B. Greenhill, Peter J. Mahon and Tania White, "Instrumental, Theoretical and Experimental Aspects of Determining Thermodynamic and Kinetic Parameters from Steady State and Non-Steady State Cyclic Voltammetry at Microelectrodes in High Resistance Solvents: Application to the \textit{fac}/\textit{mer} [M(CO)\textsubscript{3}(\eta\textsuperscript{3} - Ph\textsubscript{2}PCH\textsubscript{2}CH\textsubscript{2}P(Ph)CH\textsubscript{2}CH\textsubscript{2}PPh\textsubscript{2})]^{+/0} Square Reaction Scheme in Dichloromethane.", Accepted for publication by Analytical Chemistry.
SUMMARY.

An understanding of the rate and the mechanism of reaction is of fundamental importance in the many facets of chemistry. Electrochemical systems are further complicated by the heterogeneous boundary, between the solution and the electrode, that the electron passes through before any electrochemical reaction can take place.

This thesis concerns the development of methods for analysing electrode kinetics. One part involves the further development of the Global Analysis procedure to include electrodes with a spherical geometry which are traditionally the most popular form of electrodes. Simulated data is analysed to ascertain the accuracy of the procedure and then the known artifacts of uncompensated solution resistance and charging current are added to the simulated data so that the effects can be observed. The experimental analysis of 2-methyl-2-nitropropane is undertaken and comparisons are made with the Marcus-Hush electrochemical theories concerning electrode kinetics.

A related section explores procedures for the kinetic analysis of steady state voltammetric data obtained at microdisc electrodes. A method is proposed under the name of Normalised Steady State Voltammetry and is tested using data obtained from a Fast Quasi-Explicit Finite Difference simulation of diffusion to a microdisc electrode.

In a second area of work using microelectrodes, the electrochemical behaviour of compounds of the general formula $M(CO)_3(\eta_3 - P_2P')$ where $M$ is either Cr, Mo or W and $P2P'$ is bis(2-diphenylphosphinoethyl)phenylphosphine) is elucidated. The development of instrumentation and mathematical procedures relevant to the measurement and quantitation of these systems is also investigated. The tungsten compound represents the first examples where the 17-electron $\text{fac}^+$ and $\text{mer}^+$ isomers are of comparable stability.
CHAPTER ONE

GENERAL INTRODUCTION
1. INTRODUCTION.

An understanding of the rate and the mechanism of reaction is of fundamental importance in the many facets of chemistry. In the majority of simple chemical reactions, only a single phase (solid, liquid or gas) is involved in what are termed homogeneous reactions. In even the simplest electrochemical systems involving current-potential-time relationships there is the added aspect of electron transfer across a heterogeneous boundary to a chemical species which is usually in a liquid environment. The rate at which the electrons are transferred across the interface between the electrode and the solution is dependent upon the properties of the electrode and the chemical species present. Additionally, the influence of the electron, whether it is added, as in a reduction or removed, as in an oxidation, from the electroactive species may cause further reaction(s), either in solution with other molecules or with the electrode. Therefore, the processes that occur at the electrode-solution interface and in the vicinity of the interface are inherently complicated and unravelling the various aspects related to electrochemical behaviour presents a significant challenge.

The simplest electrode process involves the transport of a species from the solution to the electrode surface. In the case of a reduction, an electron is transferred to the species and this species is transformed into a different form which is then transported back to the solution [1]. The process may be depicted as follows

\[ \text{O}_{\text{solution}} \xrightarrow{} \text{O}_{\text{electrode}} + e^- \xrightarrow{} \text{R}_{\text{electrode}} \xrightarrow{} \text{R}_{\text{solution}} \quad (1.1) \]

where O is the oxidised form and R is the reduced form of the species.

The three fundamental quantities that characterise the electrochemical process are the electrode potential, \( E \), which is referenced to a standard system, the current, \( i \), and finally there is the time (or frequency) domain in which the reaction(s) takes place. Experimentally, it is usual to control two of these quantities and to measure the third
dependent quantity [2]. For example, in voltammetry [3], the current is the dependent variable and typically the potential applied to the electrode varies linearly with time. The gradient of the applied voltage-time waveform, whose magnitude is known as the scan rate, \( v \), establishes the time domain of a voltammetric experiment [4].

1.1. VOLTAMMETRY.

Voltammetry is a derivative of the technique of polarography which was invented by Heyrovsky [5] in the early 1920's. In polarographic experiments a dropping mercury electrode is used and a constant or almost constant potential is applied during the period in which the mercury drop forms at the orifice of a capillary. The time domain of polarographic experiments is governed by the mercury drop time which is of the order of seconds [3]. Polarography still maintains a reasonable degree of popularity amongst electrochemists due to the reproducibility of the electrode surface [3]. The advent of faster recording devices such as the 'oscillograph' [6,7] enabled much shorter time domains to be investigated at a single mercury drop with scan rates in the order of 100 V s\(^{-1}\) with only a small change in area occurring during the experiment. Experimental times were much reduced with this technique referred to as linear sweep voltammetry at the dropping mercury electrode. The use of solid planar electrodes constructed from metals such as platinum or gold simplified the mathematical description of the mass transport of electroactive species to the electrode because it was no longer necessary to contend with an electrode that was changing in size during the course of an experiment [7].

1.1.1. MASS TRANSPORT IN VOLTAMMETRY.

The response obtained in linear sweep voltammetry is dependent upon a
number of variables including the size and shape of the electrode relative to the rate of mass transport to the electrode [8]. The two most popular geometries are planar inlaid disc electrodes and spherical mercury electrodes with radii ranging from nanometers to centimeters [8]. The importance of size will be discussed later. There are three modes of mass transport, namely convection, diffusion and migration. Conventionally, the experimental conditions are chosen such that diffusion is predominant and the only form of mass transport that needs to be considered. This is achieved in practice by reducing the time domain of the experiment so that natural convection is insignificant [9] and by the addition of a substantial concentration excess of indifferent electrolyte so that the electroactive analyte is not the principle charge carrier in the solution [8].

When diffusion is the only form of mass transport that needs to be considered, the voltammetric current is proportional to the fluxes of O and R at the electrode surface. Combination of the fundamentally well known Fick's first law with planar diffusion and Faraday's law gives

\[
\frac{i}{nAF} = D_O \frac{\delta c_O(x,t)}{\delta x} = -D_R \frac{\delta c_R(x,t)}{\delta x} \tag{1.2}
\]

where \( n \) is the number of electrons transferred per molecule, \( A \) is the electrode area, \( F \) is Faraday's constant, \( D_O \) and \( D_R \) are the diffusion coefficients of O and R respectively, \( c_O \) and \( c_R \) are the concentrations of O and R respectively, \( x \) is the distance normal to the electrode surface and \( t \) is time [8]. In transient voltammetric techniques, the concentration of each electroactive species at the electrode surface is often accessible from the measurement of the current and the application of semi-integral analysis [10-13]. For a planar electrode geometry with semi-infinite diffusion

\[
D_O^{1/2} (c_O^b - c_O^s) = D_R^{1/2} (c_R^s - c_R^b) = \frac{1}{nAF} \frac{d^{1/2}i}{dt^{1/2}} \tag{1.3}
\]

where the superscript on the symbol for concentration refers to the localised concentration with \( b \) signifying the bulk concentration and \( s \) denoting the electrode
surface concentration [14]. The mathematical operator \( d^{-1/2}/dt^{-1/2} \) denotes the semi-integration operator [15] which is defined generally as [8]

\[
\frac{d^{-1/2} f(t)}{dt^{-1/2}} = \frac{d^{-1/2} f(t)}{[d(t - 0)]^{-1/2}} = \frac{1}{\sqrt{\pi}} \int_{0}^{t} \frac{f(\tau)}{(t - \tau)^{1/2}} d\tau
\]

(1.4)

where \( \tau \) is an integration variable.

Fick's second law for planar diffusion conditions is given by

\[
\frac{\delta c(x,t)}{\delta t} = D \frac{\delta^2 c(x,t)}{\delta x^2}
\]

(1.5)

Thus, if a linear concentration gradient exists in solution normal to the electrode surface then the concentration at the electrode surface will become time independent and the current will be directly proportional to this concentration. This is the basis of the so-called steady state voltammetric techniques [8].

For any electrode geometry the establishment of the steady state can be achieved if lines of constant concentration flux can be formed parallel to the electrode surface. This requires, in the mathematical sense, that the electrode geometry should enable uniform accessibility as in the case of a sphere and a shrouded plane [16]. Furthermore, if the electrode has dimensions sufficiently small relative to the diffusion rate of the electroactive species then a steady state can form in a time domain less than time required for the intervention of natural convection [9]. This can be readily achieved through the use of microelectrodes having characteristic dimensions in the order of micrometers. This and other aspects of microelectrode behaviour will be discussed more fully later. In the presence of non-linear concentration gradients, behaviour resembling transient (scan rate dependent) voltammetry will be observed.

The sphericity factor, \( \sigma \), is often used to determine whether the experimental conditions will give rise to the observation of steady state or non-steady state (transient) behaviour. For an inlaid disc geometry [17]
\[ \sigma = (1/a)\sqrt{DRT/nFv} \quad (1.6) \]

where \(a\) is the radius of an electrode, \(R\) is the Universal gas constant and \(T\) is the absolute temperature. From data reported in references 18 and 19 useful criteria related to \(\sigma\) are:

\[ \begin{align*}
\sigma &\geq 40 \quad \text{steady state diffusion} \\
1/17 &< \sigma < 40 \quad \text{mixed diffusion} \\
\sigma &\leq 1/17 \quad \text{planar diffusion}
\end{align*} \quad (1.7) \]

Figure 1.1 demonstrates the voltammetric responses obtained for \(\sigma\) values of 50, 0.2, 0.05 and 0.02 which encompass the three ranges listed in equation (1.7). The planar diffusion response is characterised by a peaked appearance (\(\sigma\) equal to 0.02 for Figure 1.1(a)). At the other extreme where the steady state is predominant (Figure 1.1(d)), a sigmoidal shaped current response is observed and is characterised by the diffusion limited plateau at potentials well beyond \(E^o\). For \(\sigma\) values designated as mixed diffusion (Figure 1.1(b and c)) there are characteristics common to both the steady state and planar diffusion regimes, although the plateau current that is eventually reached at potentials beyond the peak is greater than the current that flows under purely steady state conditions [19].

More complete treatments of mass transport, including migration and convection, have been presented in most of the comprehensive electrochemical texts [1,3,20-24] and has also been reviewed relatively recently [8]. Much of the recent focus has centred on describing the concentration profiles that occur for the various microdisc [16,18,19,25-33], microsphere [25,28,34], microhemisphere [31,32], microcylinder [28,35], microline [28], microring [25,26,29,32] and microhemitoroid [32] electrode geometries [9,32,36].
Figure 1.1. The voltammetric response obtained with different values of the sphericity factor. $\sigma =$ (a) 0.02, (b) 0.05, (c) 0.2 and (d) 50.
1.1.2. ELECTRODE KINETICS IN VOLTAMMETRY.

If only the electron transfer component of equation (1.1) is considered then the process can be written as follows

\[ \text{O}_{\text{electrode}} + e^- \xrightarrow{k^0} \text{R}_{\text{electrode}} \]

(1.8)

where \( E^0 \) is the standard potential of the O/R couple, \( k^0 \) is the standard heterogeneous charge transfer rate constant at \( E^0 \) and \( \alpha \) is the charge transfer coefficient. If the kinetics of electron transfer are rapid compared to the time scale of the experiment, then the concentrations of O and R at the electrode surface can be assumed to be the equilibrium concentrations as governed by the Nernst equation (equation (1.9)) and the reaction is described as nernstian or reversible [1].

\[ E = E^0 + \frac{RT}{nF} \ln \frac{c^s_O}{c^s_R} \]

(1.9)

If \( k^0 \) is finite on the time scale of the experiment, then the electrode reaction is considered to be quasi-reversible and the electrode surface concentrations will no longer obey equation (1.9). If the time domain of the experiment is small compared with \( k^0 \) then the electrode process is considered to be irreversible.

Many approaches to the theoretical description of equation (1.8) are available in electrochemistry. The initial observation that the rate of electron transfer is potential dependent formed the basis of the empirical Tafel plot [37]. This concept was extended by Butler [38,39] and also by Erdey-Gruz and Volmer [40] to give what is now known as the Butler-Volmer equation [41]. This equation is

\[ i = i_0 \exp \left( -\alpha n F (E - E^0) \right) - \exp \left( (1 - \alpha) n F (E - E^0) \right) \]

(1.10)

where \( i_0 = nAFk^0 c^0_R c^0_O^{1-\alpha} \). The basis of equation (1.8) is that the net current is the sum
of the current from the forward and the backward reactions of equation (1.8), which in turn are dependent upon the rate of each reaction with $i_f = nAFC_{\Omega}k_f$ and $i_b = nAFC_{\Omega}k_b$. The potential dependence of each reaction rate is as follows

$$k_f = k^0 \exp\left[\frac{-\alpha nF}{RT}(E-E^\circ)\right] \quad (1.11)$$

$$k_b = k^0 \exp\left[\frac{(1-\alpha)nF}{RT}(E-E^\circ)\right] \quad (1.12)$$

where $k_f$ is the rate that the forward process proceeds in equation (1.8) and $k_b$ is the rate of the backward reaction. It is generally considered that Butler-Volmerian kinetics are obeyed if $k_f$ and $k_b$ are exponentially dependent upon potential and $\alpha$ is independent of potential. The role played by $\alpha$ can be considered from equations (1.11) and (1.12). If the driving force (i.e., $-(nF/RT)(E-E^\circ)$) is increased, then only a fraction, equivalent to $\alpha$, of the additional energy is used to increase the apparent rate constant [22]. Usually $\alpha$ is found to be close to 0.5.

Further developments of electron transfer theory were introduced by the statistical mechanics treatments of Marcus [42-45] and Hush [46-48]. In this approach, homogeneous and heterogeneous charge transfer reactions are considered to be conceptually equivalent, and the electrode is regarded as a molecule with adjustable reactivity.

With the extended theories the equations relating current, potential and reaction rate are still expressed in the traditional form equivalent to the Butler-Volmer formulation [22,49-56] to give

$$i = nAFC_k(E)\{c_{\Omega} - c_R \exp[nF(E-E^\circ)/RT]\} \quad (1.13)$$

but with

$$k(E) = k^0 \exp[(\alpha n-Z_{\Omega})F\Phi_{\lambda}/RT]\exp[-\alpha nF(E-E^\circ)/RT] \quad (1.14)$$

and

$$\alpha = \frac{1}{2} + \frac{F(E-E^\circ)\Phi_{\lambda}}{4\lambda} \quad (1.15)$$

where $k(E)$ is the potential dependent rate, $Z_{\Omega}$ is the ionic charge of species $O$, $\Phi_{\lambda}$ is the
electrical potential of the electron transfer site and this is usually considered to be close to the site of the outer Helmholtz plane (OHP). The reorganisation energy of the molecule in an electron transfer reaction is associated with changes in bond length, bond angle and solvent reorganisation and is symbolised by the term \( \lambda \) in equation (1.15). The term \( k_0 \) is the true standard heterogeneous rate constant and is related to the reorganisation energy and the collision frequency, \( Z \), as follows

\[
k_0 = Z \exp(-\lambda/4RT)
\]  

where \( Z = \sqrt{RT/2\pi M} \), with \( M \) being the molar mass of \( O \) or \( R \). The intrinsic heterogeneous rate constant is related to the true standard rate constant as follows:

\[
k^o = k_0 \exp((-\alpha n - ZO)F\phi_s/RT)
\]  

In equation (1.17) the exponential term is a double layer correction and if \( \phi_s \) is independent of potential both \( k^o \) and \( k_0 \) will be constant. The equations and discussion presented above are limited to molecules undergoing electron transfer reactions where bonds are not formed or broken either with the electrode or within the molecule in what are known as outer-sphere electron transfer reactions [44].

Quantum mechanics approaches developed by Levich [57] and Dogonadze [58] lead to a theory which has many similarities with the statistical mechanics approach. A discussion of the physical significance and interpretation of \( \alpha \) in each of the theoretical models is contained in a comprehensive monograph [59].

Inspite of the availability of sophisticated theoretical treatments, most experiments are analyzed in terms of the the apparent rate constant and the apparent transfer coefficient [60]. The potential dependence of \( \alpha \) has been investigated [50-56,61-63] with frequently conflicting results. However, molecules which are neutral and have small reorganisation energies appear to exhibit a potential dependent \( \alpha \) [52,54-54,61,62]. Neutrality ensures that the molecule is unaffected by the
electrostatic forces in the double layer and this decreases the uncertainties bought about by applying so-called double layer corrections. It follows from equation (1.15) that the smaller the reorganisation energy, the larger the potential dependence of \( \alpha \). The reorganisation energy is the sum of the inner shell and outer shell contributions [44]; the inner shell reorganisation energy is dependent on bond length and bond angle variations whereas the outer shell energy is dependent upon the solvent.

Unfortunately, from an experimental point of view the rate constant is also dependent on \( \lambda \) as can be seen from equations (1.16) and (1.17). Consequently, this means that larger potential dependencies of \( \alpha \) are predicted to occur with fast rates of electron transfer and accurate measurement of fast rate processes is difficult to achieve [54]. However, this problem is considered to be of little significance due to the relative insensitivity of the rate constant with respect to \( \lambda \) compared to the relationship between the potential dependence of \( \alpha \) and \( \lambda \) [53]. The role of the supporting electrolyte when varying the size of the tetra-alkylammonium cation [61-63], the electrode material [64-66] and the effect of varying the solvent [55,56,63,67-71] have been examined and many aspects of the problem have been reviewed relatively recently [X72].

Phenomenonologically, the presence of kinetic control in voltammetry is well documented [4,41,73-76]. Under planar diffusion conditions and for a quasi-reversible electron transfer, the peak potential for a reduction process, \( E_{pc} \), is shifted to more negative potentials than observed for a reversible reaction in linear sweep voltammetry and cyclic voltammetry. Similarly, the peak for oxidation, \( E_{po} \), is shifted to more positive potentials. The net effect in cyclic voltammetry is that peak-to-peak separation between the reduction and oxidation peaks, denoted by \( \Delta E_p \), is increased by slow electron transfer as shown in Figure 1.2.

A dimensionless rate parameter, \( \Lambda \), has been proposed [77] to indicate whether reversible, quasi reversible or irreversible voltammetry will be observed for a given transient experiment.
\[ \Lambda = k^o \sqrt{\frac{RT}{nFD\nu}} \]  \hspace{1cm} (1.18)

Under this kind of criterion, quasi-reversible type behaviour will be observed for \(10^{-3} \leq \Lambda \leq 15\) whereas reversible conditions prevail for \(\Lambda > 15\) and irreversible behaviour for \(\Lambda < 10^{-3}\) [77]. From equation (1.18) it also follows that increasing the scan rate can transform reversible behaviour into the quasi-reversible regime by reducing the time domain of the experiment.

When the charge transfer coefficient is 0.5 the reduction and oxidation peaks in cyclic voltammetry are symmetrical. For the case of a reduction with \(\alpha < 0.5\), the forward peak is rounded and the peak current is below the current observed for an \(\alpha\)-value of 0.5, in contrast the peak on the reverse cycle is more pointed and the peak current is greater than the situation with \(\alpha = 0.5\). If \(\alpha > 0.5\) then the peak profiles are reversed. Figure 1.3 shows these distinct situations for \(\alpha\) values of 0.3, 0.5 and 0.7.

Under steady state conditions, the characteristic half-wave potential, \(E_{1/2}\), is shifted from \(E^o\) to more negative potentials. Also, the slope of the waveform decreases as the degree of kinetic control increases and the measurement of this characteristic is achieved using the Tomes criteria of \(E_{1/4} - E_{3/4}\) [78]. The behaviour which results from kinetic intervention is demonstrated in Figure 1.4 for different values of the steady state normalised rate constant \(\kappa^o\). For a microdisc electrode, \(\kappa^o\) is defined as [9,79]

\[ \kappa^o = \frac{\pi k^o a}{4D} \]  \hspace{1cm} (1.19)

Useful criteria related to \(\kappa^o\) are [79]:

\[
\begin{align*}
\kappa^o &> 40 \quad \text{effectively reversible} \\
0.2 \leq \kappa^o \leq 20 & \quad \text{usefully quasi-reversible} \\
\kappa^o &< 0.1 \quad \text{effectively irreversible}
\end{align*}
\]  \hspace{1cm} (1.20)
Figure 1.2. The dependence of the cyclic voltammetric response on different values of the dimensionless rate parameter. \( \Lambda = (a) \ 50 \) and (b) 0.1.
Figure 1.3. The cyclic voltammetric response obtained with different values of the charge transfer coefficient when $\Lambda = 1.0$. $\alpha = (a) 0.3$, (b) 0.5 and (c) 0.7.
Figure 1.4. The steady state voltammetric response obtained with different values of the steady state normalised rate constant. $k^0 = (1 \text{ to } 10)$ reversible, 1, 0.1, 0.01.
1.1.3. QUANTITATION OF ELECTRODE KINETICS IN VOLTAMMETRY.

As noted in the above discussion the peak position relative to $E^0$ in linear sweep voltammetry and $ΔE_p$ in cyclic voltammetry are key indicators of $k^0$ and therefore were central to the initial efforts in the quantitation of electrode kinetics in voltammetry. For example, Nicholson [80] produced a table correlating the separation of peak potentials for cyclic voltammograms versus a dimensionless kinetic parameter equal to $Δν^{-1/2}$ and use of this table is frequently applied to calculate $k^0$ [81-85]. However, because this method is only a two point analysis of the data, it is not very accurate.

Simulation methods of the complete current-voltage curve initially developed by Feldberg [86-92] and later extended by others [93-107] also have been widely applied. The essence of the simulation technique is that the electrode geometry and the diffusion field are modelled using a grid. The diffusion process is then simulated with the grid and the concentration of each point/box in the grid is adjusted depending on the local concentration profile at another neighbouring point/box. The simulation procedure requires an *a priori* knowledge of the nature of the kinetic process. Ideally, an iterative procedure is then applied in order to find the optimum correlation between experiment and simulation. However, this can be a laborious and tedious task and so the application of optimising methods such as simplex optimisation [108], non-linear regression [109] and multi-parametric estimation [110] are often introduced to speed up this component of the analysis. In this procedure the entire curve is used and therefore it is preferred over the use of Nicholson’s tables. Many of the aspects related to digital simulation techniques were reviewed in a recent and comprehensive monograph [111].

Transformation of the transient current response to the equivalent of a 'steady-state' response via semi-integration [10-13,112-116] or convolution [117-121] also has proved to be a powerful method of calculating $k^0$ and $α$. After transformation of
the data into this format, the analysis is simplified considerably since the $t^{1/2}$ term has been removed and the problem may be linearised to calculate $k^0$ and $\alpha$. The basis for this type of procedure follows directly from the relationship of the surface concentrations of O and R to the current as portrayed by equation (1.3). A demonstration of this transformation can be seen in Figure 1.5 for a linear sweep voltammogram under quasi-reversible conditions. Comparison with Figure 1.1(d) (ignoring the absolute magnitudes) indicates why the semi-integral current is described as a pseudo-steady state. This kind of kinetic analysis was initially applied to linear sweep voltammetry [117-121] and then extended to cyclic voltammetry from which a more complete analysis was achieved under the name of Global Analysis for the planar electrode geometry [115]. This kind of approach has also been applied to the techniques of chronocoulometry and chronoamperometry with success [122]. The semi-integral may be calculated either off-line with a computer [10-13,112-122] or with an appropriate combination of resistors and capacitors to produce an analog circuit for on-line evaluation [12]. In this thesis, the semi-integration procedure will be extended for a spherical electrode geometry and applied in the form of the Global Analysis kinetic method.

Two additional procedures developed by Parker and co-workers are Derivative Cyclic Voltammetry [123,124] and Normalised Potential Sweep Voltammetry [124-127]. The advantage of using the first derivative of a cyclic voltammogram is that the peak potentials are more accurately identified because the derivative signal is zero at the potential corresponding to any current maxima or minima. This leads to the more accurate implementation of the Nicholson type procedure as previously outlined. The technique of normalising of the voltammogram with respect to a known model readily enables correlations to be performed. Deviations between the experimental and theory can then be attributed to the intrusion of an alternative mechanism to that which was considered to be the model. The disadvantages associated with this method is that an
Figure 1.5. The application of semi-integration to a linear sweep voltammogram to produce a time independent 'steady state' response.
a priori theoretical model is assumed and only a limited range of potentials are used are used in the correlation which correspond in the majority of cases to data in the range \(0.2 \leq I_N \leq 0.8\), where \(I_N\) is the normalised peak current [124,125]. Consequently, less data are used in the analysis than used in the Global method where all the data are used to calculate \(k^0\) and \(\alpha\).

The quantitation of electrode kinetics under steady state conditions is usually achieved by measuring the value of \(E_{1/2}\) relative to \(E^0\) and measuring \(E_{1/4}-E_{3/4}\). Comparison with tabulated values provides estimates of \(k^0\) and \(\alpha\) [79].

1.1.4. CHEMICAL MECHANISMS AND KINETICS ASSOCIATED WITH ELECTRODE PROCESSES.

An electrochemical process may produce a species that is stable and more useful than the original compound. This is the basis of many electrorefining and other electrochemically based synthetic methods [128,129]. Alternatively, the change in oxidation state of an electroactive species may decrease the stability of the molecular structure and this will lead to electrochemically induced reactions, which are chemical in nature, being coupled to the charge transfer process. If the product of the chemical reaction is electroactive then the mechanism and rate may be directly elucidated since its individual voltammetric responses may be observed. Also, it is possible that a species may exist in an electro-inactive state which may chemically react to form an electroactive species and this is the so-called CE mechanism [2,22,130]. In cases where chemical reactions are coupled to the charge transfer process, the current that is observed is a result of a complex juxtaposition of concentration profiles in solution and reaction rates and the time domain of the experiment is therefore integral to the accurate assessment of the mechanism(s) of electrochemical processes. Consequently, it is highly desirable to study electrode processes over the widest possible range of time.
domains [2, 22, 129-133].

There exists a myriad of possible combinations and permutations of electrochemical and chemical reactions, some which are plausible and have been observed and others that do not occur due to overwhelmingly unfavourable thermodynamic or kinetic considerations (i.e. the activation energy of the proposed mechanism is too great) [2]. The simplest electron transfer, coupled chemical reaction is the EC mechanism [2, 129-132, 134]. This may be designated as follows

\[
\begin{align*}
E^\circ & \Rightarrow \text{k} \Rightarrow \alpha \\
O + e^- & \leftrightarrow R & (E) \\
R & \rightarrow P & (C)
\end{align*}
\]

(1.21) (1.22)

where each reaction is labelled according to the nature of the step [135] (i.e. E for electrochemical and C for chemical). The species O and R are as previously defined but species R reacts at a certain rate, k, to produce P. All the same considerations of electron transfer still apply to both O and R but are further complicated by the conversion of R to P. The amount of this apparent complication is dependent upon the time domain of the experiment. If the time domain is small compared with the rate of the chemical reaction then only the electrochemical reaction (i.e. equation (1.21)) will be observed. Alternatively if the experiment takes place over a long time domain relative to k then the consumption of R will have a drastic effect on the current that is observed in techniques such as cyclic voltammetry.

One of the more interesting class of reactions relevant to work described in this thesis is the Square Scheme [136-155]. In its simplest form the square scheme contains two chemically related electroactive couples where the reduced forms exist in equilibrium as well as both the oxidised forms. The overall mechanism may be visualised in the following format:
\[ E_1^0 \ k_1^0 \ \alpha_1 \]
\[ O_1 + e^- \xrightarrow{\rightleftharpoons} R_1 \]
\[ k_{O21} = k_{O12} \quad k_{R21} = k_{R12} \]
\[ E_2^0 \ k_2^0 \ \alpha_2 \]
\[ O_2 + e^- \xrightarrow{\rightleftharpoons} R_2 \]

(1.23)

The equilibrium constants and the rates of the chemical reaction may dictate the observed voltammetry as will the potentials of the two electron transfer steps. It is also feasible that a homogeneous cross reaction may be important as in equation (1.24).

\[ O_1 + R_2 \xrightarrow{\rightleftharpoons} R_1 + O_2 \]

(1.24)

The square scheme mechanism has been demonstrated to apply for a range of organometallic complexes having cis/trans or fac/mer isomers resulting in an octahedral arrangement of ligands around the metal centre, for example, cis/trans-M(CO)\(_2\)(L-L)\(_2\) where (L-L) is a bidentate ligands or a system such as fac/mer-M(CO)\(_3\)(L)\(_3\) containing three monodentate ligands (L). In the former case the reduced form (18 electron system) commonly exists as the cis\(^0\) isomer but the oxidised form (17 electron system) is more stable as the trans\(^+\) isomer [137,138,140]. In the M(CO)\(_3\)(L)\(_3\) case, the reduced species favours the facial isomeric state whereas the meridional form is favoured for the oxidised species [146,153]. In both cases \(E^0\)-values for the isomeric couples e.g. cis\(^0\)/cis\(^+\) and trans\(^0\)/trans\(^+\), may differ by several hundred millivolts. The theory and systems reported to obey the square scheme have been recently reviewed [156-158].

1.1.5. THE APPLICATIONS AND ADVANTAGES OF MICROELECTRODES.

Application of microelectrodes has escalated in the past decade because of
inherent advantages associated with the size and in some cases the shape of these electrodes. There are essentially two modes under which these electrodes are used, the first is the steady state situation which is time independent and secondly there is the transient or time dependent case which were outlined in section 1.1.1.

The principle sources of error in voltammetric measurements are due to the presence of uncompensated solution resistance, \( R_u \), which leads to 'iR_u' drop' or ohmic distortion and the need to correct for the current arising from the charging of the double layer capacitance, \( C_d \) \([2,4,22,84,85,131,159-161]\). Both the iR_u drop and charging current terms are minimal under steady state conditions. The charging of the double layer is dynamic in nature and is therefore time dependent. Importantly, this implies that the steady state domain, which is readily accessible when using microelectrodes, is essentially unaffected by this source of error. The error due to uncompensated resistance is associated with potential control and it is equal to the product of the current and the uncompensated resistance (i.e. iR_u). Under steady state conditions the error will be constant for all sizes of microelectrodes and in most cases it is negligible in the presence of excess supporting electrolyte \([162,163]\). The independence of electrode size arises because the current is proportional to the radius of the electrode \([164]\) but the resistance is inversely proportional to the electrode radius for discs \([165]\) and spheres \([166,167]\). Consequently, the iR_u drop error is independent of the electrode size.

The data obtained under transient conditions at microelectrodes will suffer the common fate that affects more conventional sized electrodes, but to a lesser extent. Under transient conditions, the faradaic current is proportional to the area of the electrode \([4]\) whereas the resistance is inversely proportional to the radius for discs and spheres. Consequently, the iR_u drop error associated with the potential will be directly proportional to the radius \([85]\). This implies that under transient conditions, smaller electrodes will be less affected by errors associated with the potential. In contrast, the
charging current, \( i_c \), is an electrode surface phenomenon and is thus proportional to the electrode area. Therefore, no advantage will be gained from changing the electrode size because the ratio of faradaic to charging current will be constant for a given time domain. The charging current is equal to the product of the double layer capacitance and the scan rate as given by equation (1.25), therefore the use of slow scan rates will minimise the charging current.

\[
i_c = \nu C_d
\]  

(1.25)

However, with transient voltammetry, fast scan rates are required to probe shorter time domains and the charging current eventually becomes a limitation. The combined effects of \( R_u \) and \( C_d \) also produce a filter which adds a time constant to the measured current [118]. This time constant is equal to \( R_u C_d \) and therefore directly proportional to the radius. Again an advantage is gained, with respect to minimising the time constant, by reducing the electrode size.

Most advantages for the use of microelectrodes emanate from access to steady state data. Under steady state conditions where \( iR_u \) drop is minimal, voltammetry has been performed where little or no supporting electrolyte has been present [168-171], such experiments are almost impossible under transient voltammetric conditions. In view of the low \( iR_u \) drop, the use of the steady state response for kinetic studies of heterogeneous electron transfer also should produce results which are more accurate than experiments performed under transient conditions. Interestingly, results tend to indicate that the apparent rate constant is greater when measured using steady state methods [172] which may imply that complete \( iR_u \) correction in transient methods has not been achieved. In the presence of chemical reactions coupled to electron transfer, the higher rate of mass transport and the relatively reduced dimensions of the diffuse layer tend to discriminate against the products in reactions following electron transfer. This can be viewed as an advantage if only the electron transfer reaction is of interest.
as is the case in many electroanalytical methods [173,174] or as a disadvantage when compared with transient methods because some information relevant to the overall mechanism is not available. The use of microelectrodes under steady state conditions has been comprehensively reviewed [9,36].

Transient technique voltammetry has also benefited from the use of microelectrodes because of the reduced time domains that have become accessible. This enables faster rates for both heterogeneous electrode kinetics and homogeneous chemical kinetics to be investigated. In cyclic voltammetry, scan rates of megavolt per second have been achieved with microelectrodes [175,176] and the routine use of scan rates in the order of ten kilovolts per second is now common [81,177-183]. Application of microelectrodes under transient conditions has been the subject of recent review [36,184].

1.2. THE AIM AND SCOPE OF THIS THESIS.

Work described in this thesis concerns the development of methods for analysing electrode kinetics. In one part of the thesis a Global Analysis procedure for the analysis of heterogeneous electrode kinetics at mercury electrodes which have spherical geometry is described. The spherical hanging mercury drop electrode has the advantages of homogeneity and reproducibility of the electrode surface and also there exists a superior body of knowledge accumulated about the double layer properties compared to any other electrode material. The application of the method to simulated data and the 2-methyl-2-nitropropane experimental system will be demonstrated and results compared with literature data and theoretical descriptions of the electron transfer process in electrochemistry. The effect of experimental limitations of the method arising from \( R_u \) and \( C_d \) will also be investigated.

Another part of the thesis concerns the analysis of voltammograms obtained at
microdisc electrodes under steady state conditions. A method based on an empirical relationship between the current and potential will be presented and tested using simulated data created by modelling the microdisc geometry.

In a second area of work using microelectrodes, the application of transient microelectrode methods in dichloromethane, which is considered to be a difficult solvent for electrochemical measurements, will be discussed and the electrochemical behaviour of compounds of the general formula \( \text{M(CO)}_3(\eta^3 - \text{P}_2\text{P'}) \) where \( \text{P}_2\text{P'} \) is \( \text{Ph}_2\text{PCH}_2\text{CH}_2\text{P(Ph)CH}_2\text{CH}_2\text{PPPh}_2 \) and \( \text{M} \) is either \( \text{Cr} \), \( \text{Mo} \) or \( \text{W} \) will be elucidated. Development of instrumentation and mathematical procedures relevant to the measurement and quantitation of these systems will also be presented.
CHAPTER TWO

VOLTAMMETRIC DATA ACQUISITION USING ANALOG AND DIGITAL INSTRUMENTATION.
2. INTRODUCTION.

Recent advances in electrochemical instrumentation have been closely related to the development and availability of state of the art electronic components [185]. The operational amplifier which is the key component of the potentiostats which are used for the control of potential and the measurement of current in voltammetric experiments continue to be produced with faster and faster response times. This has allowed a reduction in the time domain of experiments to be achieved without any impediment to accuracy brought about by the slow response of the instrumentation. The application of microprocessor based technology for the execution and control of experiments has introduced enormous flexibility and sophistication into electrochemical instrumentation [186].

In modern electrochemical instrumentation, it is now very common for the excitation waveform to be computer generated in a digital format which is then converted into an analog waveform using a digital-to-analog (D/A) converter [187,188]. This digital signal is then presented to the analog potentiostat circuit and then to the electrochemical cell. The resultant analog waveform from the experiment is converted to a digital data set using an analog-to-digital (A/D) converter [187,188] and the data is transferred back to the computer for analysis and/or storage. This procedure may take place using various linked components or by using an integrated approach [189].

The advantages of microprocessor based instruments include the low cost and the versatility of techniques that are available compared with the use of analog instruments capable of only a few techniques due to the lack of a general analog circuit for complex waveform generation [185]. Additionally, the analysis of the data is more efficient and enables the ready implementation of simple background subtraction methods and more complex mathematical procedures such as Fourier analysis [190] as
well as semi-integration which was discussed in Section 1.1.3.

The general instrumental considerations and procedures that were used throughout the experimental component of this work are outlined below.

2.1. INSTRUMENTATION.

Electrochemical experiments are usually performed using either a two electrode or a three electrode configuration. The two electrode format consists of a working electrode and a reference electrode [191], and naturally is instrumentally less complicated than the three electrode system. It is used when uncompensated resistance is considered to be negligible and the additional electrode and potentiostat circuitry only serve to introduce noise, as is the case in the application of microelectrodes. A diagram of the two electrode configuration is given in Figure 2.1. The three electrode format includes a working electrode, reference electrode and auxiliary electrode [191] and a diagram of this configuration is presented in Figure 2.2.

2.1.1. THE DIGITAL STORAGE OSCILLOSCOPE.

In figures 2.1 and 2.2 a digital storage oscilloscope (DSO) is used for the acquisition of the data in either configuration. The Gould Digital Storage Oscilloscope 4035 (Gould Inc., Hainault, Essex, England) used in this work contains dual 20 MHz A/D converters which maintain the storage specification for timebases ranging between 50 seconds per division and 5 microseconds per division with sensitivities ranging between 10 volts per division and 2 millivolts per division [192]. The digital facilities available with the DSO enabled 1 kilobyte of 8 bit data to be stored which translates to a vertical resolution of 1 in 256 and a horizontal resolution of 1 in 1024.

The practice of measuring the voltage which is proportional to the current using
Figure 2.1. Diagram of the instrumentation required for an experiment in the two electrode configuration.
Figure 2.2. Diagram of the instrumentation required for an experiment in the three electrode configuration.
Channel 1 and the applied potential using Channel 2 was adopted in this work. The data window of the DSO contained eight divisions and because the applied potential range of most experiment was less than 800 mV, a sensitivity setting of 100 mV div\(^{-1}\) or less was used in most instances. In cases where parts or all of the applied potential range was outside the data window, an external offset provided by a Wavetek Function Generator (Wavetek, San Diego, California, USA) was summed to the applied potential as demonstrated in Figure 2.3. In this way adequate resolution was retained for all experiments. The external offset device was prevented from loading the PAR 175 Function Generator (Princeton Applied Research Corp., Princeton, New Jersey, USA) through the use of the resistors shown in Figure 2.3 and consequently had no effect on the applied potential except for the desired offset adjustment.

The output of experimental data from the DSO based system could be in the form of an analog plot to a Houston 100 XY recorder (Houston Instruments, Austin, Texas, USA), a digital plot to a digital graphics plotter (not used) or by transferral via the General Purpose Interface Bus (GPIB) using the IEEE-488 interface (National Instruments, Austin, Texas, USA) to a computer which was the preferred option. The computer was an IBM/PC compatible MicroDos personal computer equipped with a 4 MHz 8086 microprocessor and an IEEE-488 interface board. The computer program "DSO CONTROLLER" written in QUICKBASIC 4.0 (Microsoft, Redmond, Washington, USA) is listed in Appendix I. The program was executed in the interpreted QUICKBASIC environment in order to communicate with the oscilloscope. The DSO settings could either be adjusted manually or by software. However, it was found that manual adjustment was faster and more generally preferable in an experimental situation.

The data transfer facility enables the data to be represented in four numeric bases which are binary, octal, hexadecimal and decimal [192]. Direct decimal representation of the data was only possible if the data was transferred directly from the
Figure 2.3. Potential offset circuit. All resistances are given as ohms (Ω)
DSO to magnetic disk [193], which then requires that the data has to be retrieved from the disk and plotted on the screen for initial observation. This was very time consuming due to the requirement to initially store the data and the need for two disk operations before inspection of the data. The preferred and faster alternative was to transfer the data to arrays and then convert the hexadecimal data to decimal prior to plotting onto the computer screen, at which time the option to either store the data or reject the data was then available with a minimal time loss. Off-line scaling and analysis of the data was undertaken with an Olivetti M24 PC (Ing C. Olivetti and Co., Ivrea, Italy) equipped with an 8 MHz 8086 microprocessor and 8087 math co-processor.

2.1.2. THE FUNCTION GENERATOR.

The function generator was a PAR 175 Function Generator which produces either single or multiple triangular and pulse voltage waveforms and is therefore ideally suited to provide the potential ramps required in linear sweep and cyclic voltammetry. The maximum scan rate using this function generator is 11000 V s\(^{-1}\) [194]. In the single scan mode, a signal pulse is available which coincides with the beginning of the scan. This pulse was used to trigger the DSO through the external trigger input of the DSO. The signal waveform was applied directly to the electrochemical cell in the two electrode configuration and to the external voltage input of the potentiostat for the three electrode configuration.

2.1.3. THE POTENTIOSTAT.

An Amel Model 551 potentiostat (AMEL, Milan, Italy) which has current ranges between 1 \(\mu\)A V\(^{-1}\) to 1 A V\(^{-1}\) as well as positive feedback uncompensated
resistance correction capabilities was used in the three electrode mode [195]. The response time of this potentiostat was determined using a method similar to that described in reference 175. The electrochemical cell is replaced by a dummy cell consisting of a resistor and the auxiliary and reference channels are shorted together. The current flowing in the resistor is measured and compared to the applied potential after taking into account the current scale and the value of the resistance. The time domain is then reduced by increasing the scan rate until a discernible separation in the forward and reverse sweeps of a cyclic potential sweep program is apparent. The separation arises from instrumental distortion due to an inadequate response time under the conditions at which it is observed and the time domain for this observation provides a measure of the response time. For convenience, the resistance is usually taken to be equal to the inverse of the current scale measured in A V\(^{-1}\) (i.e. from Ohm's law \(1/R = I/V\)). If the value of the resistor is reduced for a constant current gain scale, then a faster scan rate can be employed before distortion is evident because this is equivalent to a reduction in gain for the amplifier and the gain-bandwidth product is a constant for a particular amplifier [196]. Therefore, operating with lower currents for a particular current scale setting will result in less amplifier distortion but there is a penalty in the form of an increase in the relative noise. Table 2.1 contains data for the fastest applicable scan rate for each current gain setting of the Amel Model 551 potentiostat for two resistance values corresponding to gains of 100 mV V\(^{-1}\) and 1 V V\(^{-1}\). The expected behaviour is demonstrated with the faster scan rates being available at lower gains.

The correction for uncompensated resistance was achieved by following the recommendations of Whitson, VandenBor and Evans [197] in which a compound with well established reversible behaviour under the same conditions of solvent, electrolyte, electrode material and cell geometry is used to calibrate the application of positive feedback to the test compound. This method will be discussed in more detail
Table 2.1. The maximum scan rates available for each current setting of the Amel Model 551 potentiostat before the onset of distortion.

<table>
<thead>
<tr>
<th>Current Setting (A V⁻¹)</th>
<th>Dummy Cell Resistance (Ω)</th>
<th>Voltage Gain (V V⁻¹)</th>
<th>Maximum Scan Rate (V s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10⁻⁶</td>
<td>10⁷</td>
<td>0.1</td>
<td>1000</td>
</tr>
<tr>
<td></td>
<td>10⁶</td>
<td>1</td>
<td>100</td>
</tr>
<tr>
<td>10⁻⁵</td>
<td>10⁶</td>
<td>0.1</td>
<td>2500</td>
</tr>
<tr>
<td></td>
<td>10⁵</td>
<td>1</td>
<td>1000</td>
</tr>
<tr>
<td>10⁻⁴</td>
<td>10⁵</td>
<td>0.1</td>
<td>11000</td>
</tr>
<tr>
<td></td>
<td>10⁴</td>
<td>1</td>
<td>5000</td>
</tr>
<tr>
<td>10⁻³</td>
<td>10⁴</td>
<td>0.1</td>
<td>&gt;11000</td>
</tr>
<tr>
<td></td>
<td>10³</td>
<td>1</td>
<td>5000</td>
</tr>
<tr>
<td>10⁻²</td>
<td>10³</td>
<td>0.1</td>
<td>11000</td>
</tr>
<tr>
<td></td>
<td>10²</td>
<td>1</td>
<td>5000</td>
</tr>
<tr>
<td>10⁻¹</td>
<td>10²</td>
<td>0.1</td>
<td>5000</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>1</td>
<td>1000</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>0.1</td>
<td>2500</td>
</tr>
</tbody>
</table>
at a later stage of the thesis.

2.1.4. THE MEASUREMENT OF CURRENT IN THE TWO ELECTRODE MODE.

In the two electrode mode, the current was measured using an ammeter which outputs a voltage proportional to the measured current. The ammeter is designated as the I to V converter in Figure 2.1. The characteristics required for the I to V converter are dependent on the time domain and the magnitude of the current that needs to be measured.

Under steady state conditions at microelectrodes, the need to measure small currents ranging between picoamps and nanoamps are common and so noise can be a problem. The use of filtering to discriminate against high frequency noise is possible due to the relatively long time scale of this kind of steady state experiment and many commercial instruments are available which are suitable for this purpose. The Keithley Model 614 Electrometer (Keithley Instruments Inc., Cleveland, Ohio, USA) was chosen in this work because it has the advantage that it has a rechargable battery power supply and therefore can be used inside a faraday cage without the introduction of mains induced noise.

The measurement of transient currents obtained at microelectrodes was achieved through the use of circuits based on the use of current to voltage amplifiers that are well suited to converting small currents to an easily measured proportional voltage [196]. The experimental conditions dictate that the operational amplifier should have the widest possible bandwidth in order that the data obtained at the faster scan rates are unaffected by non-lineairities in the amplifier's frequency response. The other general considerations of high input and low output impedance are readily obtained in commercially available operational amplifiers when used in the current to voltage configuration [196]. All the circuits were battery powered to minimise the
noise. The gain was varied by altering the plug-in feedback resistor of the feedback loop and switches were avoided due to the possibility of introducing capacitance, from the switch contacts, into the feedback loop which would reduce the amplifier's bandwidth. Originally, an OPA-37 (Burr-Brown Corp., Tuscon, Arizona, USA) operational amplifier was used with gains in the range of $10^5$ - $10^6$ V A$^{-1}$. This was superseded in later studies by a circuit containing an AD3554AM (Analog Devices, Norwood, Massachusetts, USA) operational amplifier which had a greater gain-bandwidth product (1.7 GHz). This feature meant that faster scan rates were available for similar sensitivities or that greater sensitivities were possible using similar scan rates. Alternative devices described in the next section were used in circuits developed to discriminate against charging currents that result at high scan rates in transient voltammetric experiments.

2.1.4.1. THE MEASUREMENT OF CURRENT BETWEEN TWO WORKING ELECTRODES IN A PSEUDO-TWO ELECTRODE MODE.

Under transient voltammetric conditions and low analyte concentration or high scan rate conditions, the residual current, $i_r$, contribution to a voltammogram can be quite significant due to it being derived from the charging current which is directly proportional to the scan rate [4] whereas the faradaic current, $i_f$, is proportional to the square root of the scan rate [4] under the conditions of planar diffusion. Another consideration is that when $i_r > i_f$, the residual current is the major term causing $iR_u$ drop problems. Thus the $i_r$ term significantly reduces the ease with which mechanistic information may be extracted from voltammograms.

There are three commonly used procedures for the minimisation of the effects of residual current in cyclic voltammetry. (a) The use of high analyte concentrations in excess of the millimolar level has typically been used in fast scan rate experiments.
Unfortunately this procedure gives rise to a larger iR
 drop problem due to the increased current associated with a higher concentration of electroactive species so that this method is not very useful in high resistance solvents where, if anything, lower concentrations of analyte would be preferable to minimise iR
 drop. (b) A second method involves the post experimental subtraction of a blank electrolyte solution obtained under identical conditions to the analyte/electrolyte voltammogram [198]. Usually these voltammograms are recorded digitally with a fixed current 'window' and under this subtraction procedure the residual current proportion is a wasted component of this window, although this problem can be minimised using an analog offset [177]. A further disadvantage of this method is that this subtraction procedure doubles the recorded noise. (c) The third common procedure for background subtraction is the use of dual cells and the measurement of the difference in current between the analyte/electrolyte cell and the electrolyte cell [199,200]. For this to be successful there are three important conditions that must be satisfied [199]:

1) the concentration of supporting electrolyte must be identical in each cell

2) the electroactive analyte must not significantly influence the double layer capacity

3) the working electrodes must have identical area and surface characteristics.

Fortunately, the use of microelectrodes substantially reduces the problem of achieving equal potential control at both electrodes because of the decreased ohmic iR
 drop and lower sensitivity to the cell geometry due to the relative size of the electrode compared to the dimensions of the cell.

In this thesis, new efficient procedures for subtraction of the residual current obtained at microelectrodes were explored. Two microelectrodes of the same radius were used, one in electrolyte alone and one in the test solution, the difference in their responses was measured by a differential amplifier circuit. Initial developments were based on the cell configuration shown in Figure 2.4 in which the cell containing the
Figure 2.4. Cell arrangement for the subtraction of the residual current in the fritted cell where CE is the counter electrode with W1 and W2 the two working electrodes.
supporting electrolyte alone was separated from the analyte/electrolyte solution by a porous Vycor frit. This was superseded by the cell arrangement in Figure 2.5 because of the problems introduced by the use of the porous frit. The major problem with the first design arises due to the difference in resistance for the two current paths through the cell with the resistance between W2 and CE greater than the resistance between W1 and CE. This was most apparent at the beginning of a voltammogram and after the switching potential of a cyclic voltammogram where the current is essentially dependent upon the product of the resistance and the capacitance. In the absence of faradaic current [1]

\[ i = uC_d - vC_d \exp(-vRC_d) \] (2.1)

where \( t \) is the time transpired from the beginning of the potential sweep and \( R \) is the resistance of the current path. The result of the difference in resistance was that the \( RC_d \) time constant was smaller for the direct current path (i.e. between W1 and the reference electrode) and therefore the capacitive current was reached more rapidly. Under these conditions subtraction resulted in the observation of large spikes at the initial and switching potentials as can be seen in Figure 2.6. The use of the cell arrangement of Figure 2.5 eliminated this problem because the current paths are now equal.

The development of electronic circuits for the current difference measurements began with a circuit frequently used in photo-multiplier applications [201] which is represented in Figure 2.7. The basis of this circuit is the current to voltage amplifier circuit with the modification of a second current input which is divided between the positive input of the operation amplifier, in this case the AD3554AM, and a resistor connected to earth with a resistance equal to the feedback loop resistor which sets the gain.

The problem that becomes apparent when the circuit is applied in voltammetry
Figure 2.5. Cell arrangement for the subtraction of the residual current where CE is the counter electrode with W1 and W2 the two working electrodes.
Figure 2.6. An example of the 'spiking' that occurs due to the difference in the current paths as a result of using the cell configuration of Figure 2.4. Scan rate = 2000 V s$^{-1}$. 
Figure 2.7. Single operational amplifier current difference measuring circuit.
is that the current flowing through the resistor connected to earth changes the potential of the virtual earth at the negative input of the operational amplifier to a value equal to I_2R_f. This changes the potential difference between the working electrode W1 and the reference electrode. For photo-multiplier applications this variation in potential is insignificant due to the magnitude of the applied voltages being in the kV range. However, in voltammetry where the object of the current amplifier is to produce a signal in the range of 100 mV to 1 V at the output, this results in a potential error of this magnitude. Furthermore, this error is also potential dependent. The error introduced by this circuit is demonstrated in Figure 2.8 for a cyclic voltammogram measured with the standard current to voltage amplifier circuit and the circuit given in Figure 2.7.

Since a single operational amplifier circuit was not suitable, a multi-stage amplifier was then developed using a circuit constructed from a high performance monolithic quad operational amplifier OPA404 (Burr-Brown Corp., Tuscon, Arizona, USA) which was also battery powered to reduce noise. This circuit is given in Figure 2.9 and contains two current to voltage amplifiers with variable gain (10^5 - 10^8 V A^{-1}) produced by changing the feedback resistors (10^5 - 10^8 \Omega). The resistors were matched in order to produce identical voltages at the outputs of the initial stage, the difference between the two voltages was then obtained at the final stage. The final stage was operated at unity gain in order to maintain the widest possible bandwidth.

The current difference measuring device has a second order component as can be seen in the Bode plot in Figure 2.10 which was obtained by applying a sinusoidal waveform through a dummy cell consisting of a resistor (which was 10^6 \Omega for a gain of 10^6 V A^{-1}) and measuring the ratio of the measured voltage as compared to the input waveform over the range of frequencies given in Figure 2.10. Problems with the second order component may be avoided by using scan rates much lower than the frequency where any significant non-linearity would be introduced. The maximum
Figure 2.8. An example of the potential error incurred when using the subtraction circuit from Figure 2.7. (a) The voltammogram without the resistor connected between the positive input of the operational amplifier and the earth. (b) With the resistor connected, $R_f = 10^8 \, \Omega$. 
Figure 2.9. Current difference measuring circuit.
Figure 2.10. The Bode plot of the current difference amplifier from Figure 2.9 with a gain of $10^6$ V A$^{-1}$. 
scan rate available for use can be estimated from the following equation [202]

$$\nu = \frac{f}{5n}$$  \hspace{1cm} (2.2)

where $f$ is the cut-off frequency and $n$ is the number of electrons in the reaction. An alternative approach used was to correct for the non-linearity by converting the voltammogram into the frequency domain via a Fast Fourier Transform and applying a correction based on the frequency response of the amplifier [203] as given in Figure 2.10. An inverse transform is then applied and the corrected voltammogram is then generated, this procedure will be discussed in more detail later with the other computer based methods. It was generally observed that due to the dependence of the current on the scan rate, a reduction of the gain was necessary at faster scan rates in order to avoid saturation of the amplifier. This has the benefit of increasing the frequency response of the amplifier thereby enabling higher scan rates to be used. Consequently, the first method was applied in most instances.

The use of the current subtraction circuit enables improved resolution of the faradaic signal from the total current but in the presence of significant $iR_d$ drop the result will not be the actual faradaic current. The voltammograms at fast scan rates will have been affected by both the uncompensated solution resistance and the double layer capacitance to a varying degree dependent on the magnitude of the total current and the cell time constant $R_dC_d$ [118]. If one considers that the background current may not be totally due to the current that flows as a result of charging the double layer (i.e. as in the case of impurities or due to the solvent limit) then the faradaic current at each potential can be calculated after taking into account the various contributions to the current as demonstrated in Figure 2.11.

The voltammogram of the solvent containing electrolyte known commonly as the 'blank' will have current contributions from the charging current, $i_c$, and possibly faradaic currents from other electroactive species present either in the solvent or the
Figure 2.11. Diagram demonstrating the various components of a voltammetric response.
electrolyte, \(i_r\). In this case \(i_r\) will symbolise the residual current ignoring the charging current component and will contribute to both the blank and the analyte voltammograms. Therefore the current observed for the blank will be

\[
i_{\text{blank}} = i_r + i_c = i_r - C_d \frac{dE}{dt}
\]  

(2.3)

where \(dE/dt\) is the scan rate distorted by the presence of \(R_u\) and \(C_d\) with

\[
E' = E - ut + R_u i_{\text{blank}}
\]  

(2.4)

where \(E\) is the applied potential and \(E'\) is the actual potential which includes a term for ohmic losses.

From equation (2.4), the distorted scan rate is obtained

\[
\frac{dE'}{dt} = -u + R_u \frac{di_{\text{blank}}}{dt}
\]  

(2.5)

When this result is combined with equation (2.3), the capacitance at each potential can be calculated as follows:

\[
C_d(E) = (i_{\text{blank}} - i_r)/(u - R_u \frac{di_{\text{blank}}}{dt})
\]  

(2.6)

If \(C_d\) is potential dependent, then the actual \(C_d(E)\) can only be measured if \(i_r\) is known which will seldom be the case. In the majority of cases \(di_{\text{blank}}/dt\) may be ignored and under these conditions equation (2.6) will reduce to equation (2.3) with the potential being the applied potential \(E\) without the need to consider any errors introduced by \(R_u\) and \(C_d\).

In the analyte

\[
i_{\text{total}} = i_r + i_r + i_c = i_r + i_r - C_d \frac{dE''}{dt}
\]  

(2.7)

where \(E''\) is the actual potential at the electrode and is affected by \(R_u\) as follows

\[
E'' = E - ut + R_u i_{\text{total}}
\]  

(2.8)
and the resultant effective scan rate is

\[ \frac{dE'}{dt} = -\nu + R_u \frac{di_{\text{total}}}{dt} \]  \hspace{1cm} (2.9)

When combined with equation (2.7), an alternative expression for the total current can be obtained as follows

\[ i_{\text{total}} = i_r + i_r + C_d(\nu - R_u \frac{di_{\text{total}}}{dt}) \]  \hspace{1cm} (2.10)

or in terms of the faradaic current

\[ i_f = i_{\text{total}} - i_r - \nu C_d + R_u C_d \frac{di_{\text{total}}}{dt} \]  \hspace{1cm} (2.11)

and \( \nu C_d \) can be converted to \( i_c \) based on the previous assumptions regarding the distortion (or lack of distortion) of the scan rate in the blank. It then follows that

\[ i_r = i_{\text{total}} - i_r - i_c + R_u C_d \frac{di_{\text{total}}}{dt} \]  \hspace{1cm} (2.12)

\[ i_f = i_{\text{diff}} + R_u C_d \frac{di_{\text{total}}}{dt} \]  \hspace{1cm} (2.13)

where \( i_{\text{diff}} \) is equal to the total current minus the current due to the blank as given by equation (2.3) and is directly measured by the current difference circuit.

The actual potential at the electrode surface in this work was calculated from the applied potential, \( E \), as follows

\[ E' = E + R_u i_{\text{total}} \]  \hspace{1cm} (2.14)

The potential scale was then linearly interpolated so that the potential increment on the potential scale was again constant. This procedure for correcting the potential axis will be discussed in more detail later in this thesis.

The capacitance in equation (2.13) cannot be truly evaluated in the presence of residual current as a function of the applied potential. Thus, it was assumed to be constant over the potential range needed for the characterisation of an electroactive
couple. Additionally, equation (2.13) indicates that the presence of current that doesn't result either from faradaic or capacitive sources can be subtracted directly from the total current of the analyte cell and that the correction procedure only requires that $i_{\text{total}}$ can be obtained. This is readily achieved by recombining the current difference signal with the separately measured blank voltammogram. The advantage of the cell arrangement is that the blank can be directly measured when the electrode from the analyte cell is disconnected. However, because only one input of the current measuring device is used, the noise in the blank experiment was found to be greater than when a true differential input was used.

The experimental procedure used to provide voltammograms was to measure the current difference voltammogram and store the result on computer disk. After this, the measurement and storage of the blank voltammogram was achieved by disconnecting the lead to the analyte working electrode. With this method there is no need to change solutions or alter the electrode configuration as required with other subtraction procedures discussed earlier in this section. The corrections for $R_u$ and $C_d$ were applied off-line with $di_{\text{total}}/dt$ being calculated using a Savitsky-Golay quadratic least squares operation [204]. The minimum number of points used for the calculation of this derivative was seven but this was varied so that the time interval of the convolute (i.e. the product of the number of points and the time increment between points) was greater than the $R_uC_d$ time constant of the cell. If this condition was not satisfied then wild oscillations appeared in the corrected data.

The need for the background current subtraction procedure and $iR_u$ correction at fast scan rates even when using microelectrodes is presented in Figure 2.12(a,b,c,d). At a scan rate of 2000 V s$^{-1}$ there is a substantial residual current which causes significant distortion of the voltammogram and additionally there is considerable ohmic distortion (Figure 2.12(a)). The voltammogram from the cell containing only electrolyte is shown in Figure 2.12(b) and it can be seen that there
Figure 2.12. (a) A voltammogram of $2 \text{mM} \text{Cr} (\text{CO})_3 (\eta^3 - \text{P}_2 \text{P}^')$ with $0.5 \text{ M} \text{Bu}_4 \text{NBF}_4$ in dichloromethane at a scan rate of 2000 V s$^{-1}$. (b) The 'blank' voltammogram of 0.5 M \text{Bu}_4 \text{NBF}_4 in dichloromethane at a scan rate of 2000 V s$^{-1}$.
Figure 2.12(continuation). (c) The current difference voltammogram plotted with the same scales as Figures 2.12(a) and (b) obtained using the current difference circuit of Figure 2.9. (d) (---) As for (c) but replotted with the corrected voltammogram (-----) obtained from the procedures described in this thesis.
exists non-linearities in the shape of this voltammogram which makes it necessary to ensure that the background current is properly subtracted. The differential current is plotted in Figure 2.12(c) using the same scale as for Figures 2.12(a) and (b) to show what proportion of the total current was due to the electroactive species. In Figure 2.12(d) the corrected current is plotted in comparison with the differential current and shows the degree of ohmic distortion that is introduced under the conditions that the voltammogram was recorded. The correction procedure increases the noise because of the step involving the differentiation of the total current-time curve (equation (2.13)) and the slight ripple in the corrected voltammogram is a result of this. However, the voltammogram that is finally obtained after employing these procedures is of a quality required for quantitative studies which are based on theories which assume the absence of background current and iRₚ drop.

A related procedure [181] requires that the scan rate at each potential be calculated after adjusting the potential scale for the iRₚ error as for equation (2.14) and adding a current component at each potential equal to the product of the double layer capacitance and the difference between the applied scan rate and the actual scan rate. This procedure was also investigated but was found to be difficult to implement because the noise in the current data affected the accuracy for the evaluation of the actual scan rate. Additionally, the recommended procedure performed equally if not better than this other procedure, even when noise was not a problem.

2.2. THE ELECTRODES.

The microdisc electrodes were constructed in two ways, the larger electrodes of 10, 25, 50 and 100 μm diameter Au and Pt are relatively easily constructed from microwires (Goodfellow Metal, England) of the requisite size scaled in scrupulously cleaned 1.5 mm I.D. soda glass capillary using a Multipole burner (Analite, Australia).
Electrical contact was made by melting the low melting point (= 68°C) Woods metal alloy (Ajax Chemicals, Melbourne, Victoria, Australia) that had been placed inside the electrode body and then pushing a snugly fitting wire down the electrode body into the molten metal which was then allowed to cool. The exposed microwire was then removed and the glass was initially ground using a smooth polishing stone, followed by successive grades of emery paper and then successive grades of alumina slurried in water until a mirror finish on the exposed plane was observed. The lowest grade of alumina used was 0.05 μm and this grade was used subsequently to maintain the condition of all the microdisc electrode surfaces. This process is demonstrated in Figure 2.13.

For the smaller microdisc electrodes of 0.6, 1, 2 and 5 μm diameter the overall process is identical to that previously outlined but these microwires (Goodfellows Metal, England) are Wollaston wires and as such are only available as platinum wires coated with silver. Also, the connecting wire is attached in the initial stage and contains a series of coils that act as springs to absorb shock and prevent the delicate wire from breaking. The silver is removed with 6 M nitric acid and the exposed microwire is washed carefully with distilled water and then acetone, the wire is then sealed. All electrodes were calibrated based on the limiting current under steady state conditions [164] using a 1.00 mM ferrocene solution (where D = 2.4 x 10⁻⁵ cm² s⁻¹) in acetonitrile containing 0.1 M tetraethylammonium perchlorate as supporting electrolyte.

A conventional Metrohm E410 Hanging Mercury Drop Electrode (Metrohm, Herisau, Switzerland), with a drop surface area of 0.019 ± 0.0001 cm² obtained by dialing the control plunger 3 divisions, was also used. The electrode area was determined by measuring the mass of ten mercury spheres. The capillary of the electrode was maintained in good working condition by using the silicone coating treatment outlined in reference 205.
Figure 2.13. The process involved for the construction of microdisc electrodes.
The reference electrodes used depended upon the solvent and the circumstances. For conventional experiments with the three electrode potentiostat, the reference electrode for acetonitrile was a 0.010 M AgNO₃ solution containing 0.100 M tetraethylammonium perchlorate as the electrolyte and a Ag coil with a porous glass frit at the liquid junction. This represents the standard Ag⁺/Ag reference which is recommended for acetonitrile [206]. In dichloromethane, a Ag/AgCl (saturated LiCl) reference with 0.1M tetrabutylammonium perchlorate as the electrolyte was used. Both reference electrodes were used in conjunction with salt bridges containing electrolyte solutions for the solvent corresponding to the reference electrode and the analyte solution.

The impedance of these reference electrodes was found to be too great when used in a two electrode format with fast scan rates. In those circumstances, a lower resistance Pt or Ag wire coil was used as a pseudo-reference electrode and was frequently calibrated against the reversible potential for the oxidation of ferrocene [207]. For steady state measurements, the conventional reference electrodes could be used without any problems since the currents are low and the frequency response is less important.

2.3. COMPUTER BASED DATA MANIPULATIONS.

Ultimately, all of the computer programs developed were written in QUICKBASIC 4.0 and were executed on an Olivetti M24 PC, although at various stages they were written in Pascal or FORTRAN for use on a DEC-20 (Digital Equipment Corporation, Maynard, Massachusetts, USA) mainframe computer using the TOPS-20 operating system. When the data was originally collected on a PC and transferred to the more powerful mainframe computer, restrictions on the access and storage of the data resulting from the time-share nature of this machine caused
problems. Also the graphics capabilities and flexibility available with the PC provides a much more friendly (although slower) environment compared to the more rigid structural requirements connected with the use of the mainframe computer.

The program "DSO CONTROLLER" fully listed in Appendix I was developed to transfer the digitised data from the oscilloscope to the PC where further simple data treatments such as the subtraction of one waveform from another, serial averaging of waveforms and smoothing of the waveforms using a moving window average could be applied in a pseudo on-line environment. These methods are easily implemented and based on well established and simple data manipulation methods and therefore require no further discussion, also more sophisticated methods were developed and applied in an off-line environment.

The data collected from the storage oscilloscope has the form of two files with one containing the potential data and the other containing the current data. The data in the files was in a decimal format and in the range -127 to 128. The first procedure in the off-line analysis is the truncation and subsequent scaling of the data into the more familiar units of Volts and Amps. Use of a data-time window led to the storage of useless information that only increased the size of the final data file. The original data was always retained and only the processed data was truncated which means that the integrity of the original was maintained at all times.

Figure 2.14 shows the characteristics of the original data. To identify the times corresponding to the three most important potentials in a cyclic voltammogram, namely the initial, switching and final potentials, the following strategy was used:

1) Identify the maximum value representing the potential and find the average time corresponding to this potential. This corresponds to the time of the potential switch.

2) Work backwards to the time where the first potential point is equal to the overall minimum. This point corresponds to the time that the potential scan commenced. All data before this point are rejected.
Figure 2.14. An example of the data which is collected by the DSO, displayed on the screen of the DSO and then transferred to the computer.
3) Work forwards from the time corresponding to the switching potential and identify where the next minimum occurs. This point corresponds to the time where the experiment finished. All data after this point is rejected.

Once the above process of identifying the three key potentials was completed, scaling of the data was possible. The potential was scaled on a time basis rather than using the potential as measured after digitisation by the oscilloscope. The latter process created large steps in the potential data arising from the 8-bit resolution of the A/D converter. Since a smooth analog ramp was actually applied during the experiment it was considered legitimate to interpolate firstly between the initial and switching times to calculate the potentials at each point on the forward scan and then between the switching and final points on the reverse scan to regain the potential waveform that was originally applied. The exact potentials of the initial, switching and final potentials were measured using a digital voltmeter and these were the values used when scaling the potential data.

The current, $i_j$, was scaled from the digitised data, $i_{j(DSO)}$, using the following formula based on the calibration of the A/D converters as given in the oscilloscope manual [192] and the settings of the oscilloscope, $s_{DSO} (V \text{ div}^{-1})$, and the current to voltage converters, $s_{CV} (A \text{ V}^{-1})$.

$$i_j = [0.346 s_{CV} s_{DSO} i_{j(DSO)}] - i_0$$  \hspace{1cm} (2.15)

There is no absolute zero current available in this method and therefore the zero current, $i_0$, was estimated using the linear least squares method over a range of no fewer than 50 data points either before the scan commenced or after the current had reached zero at the very end of the data collecting window. The discarded data therefore provides a vital role before it is finally removed. The final data is then stored as one file containing two columns of data with the potential in Volts with the corresponding current in Amps stored side-by-side.
A requirement of the Global Analysis developed in this work dictates that the data from the cyclic voltammogram should contain current pairs obtained at identical potentials on the forward and reverse sweeps. Due to a small asymmetry in the potential waveform (i.e. less than 1%) it became necessary to linearly interpolate the potentials during the reverse sweep so that they coincided with the potentials of the forward sweep. This was implemented as follows:

1) Set the potential increment
2) Increment the potential if less than the final potential
3) Find the data points either side of this potential i.e. E_{0j} and E_{0j+1}
4) Interpolate the original current, io, to obtain the current, i, at the desired potential, E, as follows

\[ i = io_j + (io_{j+1} - io_j)(E - E_{0j})/(E_{0j+1} - E_{0j}) \]  

(2.16)

5) Go back to 2) and continue in the same way for the remaining data.

It should be noted that the difference between scan rates for the forward and reverse sweeps bought about by the asymmetry in the waveform is well within the experimental error attributable to the measurement of the scan rate.

The digitised data contained varying degrees of noise which arose from many factors. Consequently, several methods of data smoothing were tested. However, the overriding consideration is that only minimal distortion of the waveform should occur and as such the smoothing that was applied was mostly cosmetic. Simulated data with superimposed 'noise' (see later) was used to test the various smoothing methods and this is demonstrated in Figure 2.15. The first method considered was a three-point triangular method [208] (Figure 2.15(c)) of the following form

\[ i_j = io_j/2 + (io_{j-1} + io_{j+1})/4 \]  

(2.17)

However, since this method was only active on the very high frequency components
Figure 2.15. (a) A voltammogram consisting of 900 points. (b) As for (a) with 'noise' equal to 2% of the forward peak current. (c) As for (b) after the three-point triangular smoothing.
Figure 2.15 (cont.). (d) As for (b) after the 50 transform Fourier smoothing. (e) As for (b) after the 100 transform Fourier smoothing. (f) As for (b) after the 200 transform Fourier smoothing.
Figure 2.15 (cont.). (g) As for (b) after the nine-point Savitsky-Golay smoothing.
due to the relatively small time frame of the smoothing window i.e. 3 points in 700-900 data points, little if any improvement was gained from implementation of this method. Fourier smoothing without using the Fast Fourier Transform [209] was implemented for use on cyclic voltammetric data. The data set was considerably greater than the data set of the derivative neopolarograms in the original work and an uncertainty as to whether oversmoothing had occurred was introduced which is a problem when the waveform integrity is of paramount importance. Three examples of this smoothing are presented in Figures 2.15(d),(e) and (f). When the noisy voltammogram is represented by 50 sine wave components (Figure 2.15(d)), there is substantial oversmoothing. With 100 transforms (Figure 2.15(e)), the voltammogram is reasonably noise-free but with 200 transforms only the very high frequency components have been removed. The most useful method employed was a nine-point cubic least squares moving average procedure [204] (Figure 2.15(g)) which is a commonly employed method for the smoothing of electrochemical data [209] and very simple to implement.

In order to test the smoothing procedures and to examine the effect of noise on the data during analysis, an algorithm for the addition of gaussian noise was written based on reference 122. A randomness chi-square test [210] was applied to the data and the algorithm was found to produce noise that was completely random based on this statistical test.

The 'correction' of the charging current error was introduced in order to determine its effect during the analysis of the cyclic voltammetric data and was implemented by displacing the current data either positively or negatively during the reverse sweep of the cyclic voltammogram. Only the reverse sweep was adjusted because, as already explained, only an arbitrary zero current line can be draw and this always corresponded to the plateau current that occurred before the onset of any faradaic current flowing on the forward sweep. Consequently, any offset due to either
overcorrection or undercorrection only affects the reverse sweep current data. In most cases the error is less than 5% and any non-linearities in the background are reasonably well subtracted, therefore the error can be modelled as a constant current which is independent of potential. The procedure involves identifying the switching potential and then adding an arbitrary constant current component based on a percentage of the forward peak current.

An \( iR_u \) drop correction subroutine was written which only considers the effect of the potential error and assumes that there are no capacitive contributions to the potential error. The new potential, \( E_j \), is calculated from the original potential, \( E_{0j} \), based on an arbitrary constant uncompensated resistance, \( R_u \), as follows

\[
E_j = E_{0j} + i_j R_u
\]  

(2.17)

the potential scale is then linearised as described previously to produce potential pairs. This procedure was not used for the correction of \( iR_u \) potential errors in experimental work due to its idealised basis, but it was frequently used to add \( iR_u \) potential errors to simulated data in order to test the effect of uncompensated resistance.

The implementation of the correction of the faradaic current obtained from the current difference method as discussed in Section 2.1.4.1. requires that the separately measured background voltammogram is added to the difference voltammogram in order to obtain the total voltammogram. In order to correct for extremely small differences in the potential programs of each constituent voltammogram it was necessary to interpolate the background voltammogram to find the background current corresponding to each potential of the difference voltammogram before the addition to obtain the total current. The remaining correction considered in Section 2.1.4.1 is based on equation (2.14) and this was followed by linearisation of the potential scale and interpolation as discussed above.

Correction for the slow response of the current transducer may be achieved by
converting the voltammogram into the frequency domain by using a Fast Fourier Transform. The first step in this method is to find the time increment, $\Delta t$, between data points and this is calculated from the scan rate, the potential range and the number of data points, $J$, as follows

$$\Delta t = 2(E_{\text{switch}} - E_{\text{initial}})/(vJ) \quad (2.18)$$

The transformation of the data into the frequency domain required that the number of data points is equal to $2^n$ and 1024 data points were used in this work. Zero filling of the remaining data points may be used if the number of experimental points is less than $2^n$. However, this procedure may create errors due to the introduction of data discontinuities [209] and therefore an alternative filling method was employed. The procedure involved assigning the final data point of the transform window (i.e. data point 1024) a value of zero corresponding to the value of the first experimental point (i.e. data point 1). A line connecting the final experimental data point to the final data point of the transform window was then calculated and the remaining empty data points were then filled based on the calculated line. Due to the periodic nature of the transform no discontinuity was introduced. This method worked well and no discernible difference was observed for data, that was transformed and then had the inverse transform applied, and the original data. The correction was applied in the frequency domain based on the Bode plot of the transducer and then the inverse transform was applied. The Fourier transform and inverse Fourier transform software as well as a range of modulating windows for the reduction of spectral leakage were obtained from reference 211.

2.4. CHEMICALS.

The solvents were acetonitrile (Mallinckrodt Aust., Clayton, Victoria,
Australia) which was ChromAR-HPLC grade and distilled daily from calcium hydride (BDH Chemicals, Poole, England) and dichloromethane (Mallinckrodt Aust., Clayton, Victoria, Australia) which was also ChromAR-HPLC grade but used as supplied. The p-nitrotoluene was recrystallized from aqueous methanol and the 2-methyl-2-nitropropane (Aldrich Chemical Co., Milwaukee, Wisconsin, USA) was used as supplied. The electrolytes tetra-n-butylammonium tetrafluoroborate (Bu$_4$NBF$_4$) (Southwestern Analytical Chemicals Inc., Austin, Texas, USA) and tetra-n-butylammonium hexafluorophosphate (Bu$_4$NPF$_6$) (Southwestern Analytical Chemicals Inc., Austin, Texas, USA) were used as supplied, the tetraethylammonium perchlorate (Et$_4$NClO$_4$) (Southwestern Analytical Chemicals Inc., Austin, Texas, USA) was recrystallized from ChromAR-HPLC grade methanol (Mallinckrodt Aust., Clayton, Victoria, Australia), dried in vacuo at 60°C and stored over phosphorous pentoxide (Merck, Darmstadt, Germany). The silver nitrate (Ajax Chemicals, Sydney, New South Wales, Australia) and lithium chloride (Ajax Chemicals, Sydney, New South Wales, Australia) were analytical grade and used as supplied. The substituted metal carbonyl compounds M(CO)$_3$Ph$_2$PCH$_2$CH$_2$PCH$_2$CH$_2$PPPh$_2$ where M = Cr, Mo and W and Ph = phenyl were kindly prepared and supplied by Dr. Ray Colton and Tanya Whyte formerly of the Inorganic Section of the Department of Chemistry at Melbourne University, Parkville 3052, Victoria, Australia and presently at the Department of Chemistry, LaTrobe University, Bundoora 3058, Victoria, Australia.
CHAPTER THREE

GLOBAL KINETIC ANALYSIS OF CYCLIC VOLTAMMOGRAMS AT A SPHERICAL ELECTRODE.
3. INTRODUCTION.

Several years ago, a three dimensional method for studying electrochemical processes controlled jointly by diffusion and kinetics was reported. The so-called "Global Analysis" [115], based on a concept pioneered by Reinmuth [212], provides a unique surface in (m, i, E) space that is independent of the details of the experimental method selected (m is the temporal semi-integral of i).

The Global Analysis has been demonstrated to be an efficient method for determining the standard heterogeneous charge-transfer rate constant, the charge transfer coefficient, and the reversible halfwave potential for a simple electrode reaction, as well as the diffusion coefficient of the electroactive species. More recently [213], the Global Analysis has been extended to accommodate electrode reactions complicated by homogeneous chemical reactions. Three advantages exist for this technique compared with alternative electrochemical methods of evaluating kinetic and thermodynamic parameters.

Firstly, the Global Analysis uses all the data from a cyclic voltammogram, thus affording high precision. In contrast, the traditional technique employed for cyclic voltammetric data analysis [4] relies on the separation of the two peaks of each sweep of the voltammogram and as such the majority of the experimental data remains unused. Similarly potentiostatic methods [112,114,122,214] access the kinetics at only one or two potentials in a single experiment. A related convolution method [60] processes only half of the acquired experimental data.

Secondly, the Global Analysis is based on fundamental electrochemical diffusive transport and kinetic principles that are familiar to most experimental electrochemists. Moreover, the global procedure can be easily programmed allowing rapid on-line calculation of kinetic and thermodynamic parameters by digital computer. The simplicity and speed of the global procedure are distinct advantages over the more
laborious simulation optimisation approach [55,61,62,65] or complex non-linear fitting techniques [109,110,215] which are of a complexity that will appeal to few electrochemists. Similar in objective, though distinct in concept, is the three dimensional procedure advocated by Parker [124] under the name Normalized Potential Sweep Voltammetry.

Finally, the global method is not based on any particular model of electrode kinetics. It is usual in electrode kinetic studies to assume that the rate of the electrode reaction is related to the electrode potential and the surface concentrations of oxidised and reduced species via the well-known Butler-Volmer equations as presented in Section 1.1.2. This assumption, which underlies semi-integral linear sweep [13,113] and most other methods of determining kinetic parameters is not necessary in the global approach. Thus, kinetic and thermodynamic parameters can be determined without the prejudice of a pre-assumed relationship between the rate constant and potential. In fact, the three-dimensional method provides a useful diagnosis of whether the Butler-Volmer kinetic model is appropriate in a particular electrode reaction.

A limitation of the Global Analysis to the present time is that the method is restricted to the evaluation of data acquired at planar electrodes. For reasons of mathematical simplicity, shrouded planar electrodes are assumed in most voltammetric derivations of the theory even when a mercury drop electrode is used experimentally. Unfortunately, these spherical mercury electrodes cannot always be approximated adequately by a planar model [14,216-225].

The purpose of this chapter is to modify the Global Analysis method so that it may be applied to spherical electrodes. The procedure is then tested on simulated data. The presence of noise and the application of smoothing are also examined.
3.1. GENERAL THEORY.

Consider a stationary spherical electrode of radius \( r_0 \) which, for times \( t < 0 \) is held at a potential such that no reaction occurs. Subsequent to \( t = 0 \), potentials are encountered such that the \( n \)-electron reduction

\[
O_{\text{soln}}^+ + n e^- \rightarrow R_{\text{soln}}
\]  
(3.1)

occurs. In this section we will not prescribe any particular polarizing signal, though later a triangular potential ramp will be considered. The electroreactant \( O \) is initially present at a bulk concentration \( c^b_O \) but the product \( R \) is initially absent, so that \( c^b_R = 0 \). Both species are soluble only in the electrolyte solution which is unstirred and contains excess supporting electrolyte to ensure that diffusion is the sole transport mode.

Reaction (3.1) is assumed to occur bidirectionally with the forward rate proportional to \( c^b_O \), the concentration of species \( O \) present at the electrode surface, and the backward rate proportional to \( c^b_R \), the concentration of species \( R \) at the electrode surface. The net rate of the electron-transfer reaction, measured by the current according to Faraday's law, can be equated to the difference between these two first order reaction rates

\[
\frac{i}{nAF} = \text{rate} = k_f c^8_O - k_b c^8_R
\]  
(3.2)

where \( A \) is the surface area of the spherical electrode and \( k_f \) and \( k_b \) are the two rate constants. These two constants are expected to depend on potential in the sense that \( k_f \) will become larger, but \( k_b \) small, as the potential is made more negative. If equation (3.2) is to apply at equilibrium, then the two rate constants must be in the ratio

\[
k_b/k_f = \exp((nF/RT)(E-E^\circ))
\]  
(3.3)

where \( E^\circ \) is the standard (more strictly the formal, or conditional) potential, in order
that the Nerst equation be obeyed when the rate is zero.

Being soluble in the electrolyte solution, O and R diffuse in a transport field bounded by a convex spherical surface, the electrode. Under such circumstances, it has been demonstrated [226] that the faradaic current is related to the concentration of O and R at the electrode surface by

\[ i = nAF\sqrt{D_O} \frac{d^{1/2}}{dt^{1/2}} (c_O^b - c_O^s) + \frac{nAFDO}{r_0} (c_O^b - c_O^s) = nAF\sqrt{D_R} \frac{d^{1/2}}{dt^{1/2}} c_R^s + \frac{nAFDO}{r_0} c_R^s \]  \hspace{1cm} (3.4)

where \( \frac{d^{1/2}}{dt^{1/2}} \) represents the semi-differentiation operator with respect to time \( t \). Each term involving \( r_0 \) is a correction for the curvature of the electrode. Laplace transformation [15] of equation (3.4) leads to

\[ L\{i\} = nAF\sqrt{D_O} \left[ \sqrt{s} + \frac{\sqrt{D_O}}{r_0} \right] L\{c_O^b - c_O^s\} = nAF\sqrt{D_R} \left[ \sqrt{s} + \frac{\sqrt{D_R}}{r_0} \right] L\{c_R^s\} \]  \hspace{1cm} (3.5)

We now make the approximation that, in the correction terms only, we can ignore the difference between \( D_O \) and \( D_R \), so that

\[ \frac{L\{i\}}{\sqrt{s} + \sqrt{D}/r_0} = nAF\sqrt{D_O} L\{c_O^b - c_O^s\} = nAF\sqrt{D_R} L\{c_R^s\} \]  \hspace{1cm} (3.6)

where \( D \) represents some mean diffusion coefficient. Laplace inversion of the factor that multiplies \( L\{i\} \) in the left-hand side of equation (3.6) gives [14]

\[ L^{-1}\left( \frac{1}{\sqrt{s} + \frac{\sqrt{D}}{r_0}} \right) = \frac{1}{\sqrt{\pi t}} \cdot \frac{\sqrt{D}}{r_0} \exp\left( \frac{\sqrt{D}x}{r_0^2} \right) \text{erfc}\left( \frac{\sqrt{D}x}{r_0^2} \right) \]  \hspace{1cm} (3.7)

where the function \( f \) is defined by

\[ f(x) = \frac{1}{\sqrt{\pi x}} - \exp(x) \text{erfc}(\sqrt{x}) \]  \hspace{1cm} (3.8)

Hence, making use of the convolution theorem [227], we are led to
\[
\frac{L(i)}{\sqrt{s} + \sqrt{D}/r_o} = L \left\{ \frac{\sqrt{D}}{r_o} \int_0^t i(\tau) f \left( \frac{D(t - \tau)}{r_o^2} \right) d\tau \right\}
\]

(3.9)

After combination with equation (3.6), Laplace inversion produces

\[
nAF\sqrt{D_O} (c_O^b - c_O^s) = nAF\sqrt{D_R} c_R^s = \frac{\sqrt{D}}{r_o} \int_0^t i(\tau) f \left( \frac{D(t - \tau)}{r_o^2} \right) d\tau = \mu
\]

(3.10)

The integrals in equations (3.9) and (3.10) is technically known as a convolution integral, the procedure which uses it has been call 'spherical convolution' [14,116]. The symbol \( \mu \) is used to represent the spherical convolution integral in equation (3.10) and can be considered equivalent to, \( m \), the temporal semi-integral of the current for a planar geometry. This equation relates the concentration of \( O \) and \( R \) at the surface of a spherical electrode to the faradaic current. By combining equations (3.2), (3.3) and (3.10) to eliminate \( c_O^s \) and \( c_R^s \), one arrives at the universal equation

\[
\frac{i}{k_f} = nAFc_O^b \cdot \mu \left[ \frac{1}{\sqrt{D_O}} + \frac{\exp( (nF/RT)[E-E^0] )}{\sqrt{D_R}} \right]
\]

(3.11)

which provides a unique relationship between \( i \), \( \mu \) and \( E \), irrespective of the experimental technique employed.

Special cases of equation (3.11) arise when \( \mu \) or \( i \) is equal to zero. When \( \mu = 0 \), \( i \) adopts the special value

\[
\dot{i} = nAFc_O^b k_f
\]

(3.12)

where \( \dot{i} \) represents the faradaic current that would have flowed across the spherical working electrode at potential \( E \) if there were no transport impediments whatsoever. Also, because \( k_f \) depends on potential there is a two-dimensional relationship between the current and potential at \( \mu = 0 \), as illustrated in Figure 3.1, which contains purely
Figure 3.1. Two-dimensional relationship between $i^*$ and $E$ when the convolute $\mu$ equals zero.
kinetic information. Similarly, when \( i = 0 \), \( \mu \) adopts the special value

\[
\mu^* = nAFCO\left[\frac{1}{\sqrt{D_0}} + \exp\left(\frac{nF/R}{\sqrt{D_R}}(E - E^*)\right)\right]^{-1}
\] (3.13)

where \( \mu^*/nAFC\sqrt{D_R} \) expresses the concentrations that \( R \) would have attained at the spherical electrode surface in the absence of kinetic impediments to the electrode reaction. Figure 3.2, containing purely transport and thermodynamic information, illustrates the two-dimensional relationship between \( \mu^* \) and \( E \) at \( i = 0 \). Substitution of equations (3.12) and (3.13) into equation (3.11) leads to the very simple relationship

\[
i/i^* + \mu/\mu^* = 1
\] (3.14)

at any constant potential \( E \). This predicted linear interdependency of \( i \) and \( \mu \) is shown graphically as Figure 3.3. Thus values of \( i^* \) and \( \mu^* \) may be determined as the intercepts of a plot of \( i \) versus the \( \mu \) value at the same potential. As a result of two non-coincident points determining a unique straight line, any experiment that generates two \( (i, \mu) \) pairs at a common potential can be used to determine the intercepts \( i^* \) and \( \mu^* \).

Graphs similar to Figures 3.1 and 3.2 can then be constructed by determining \( i^* \) and \( \mu^* \) values at several potentials. Though the potential \( E \) may be varied in many ways, a later section will consider one of the simplest means of scanning the useful potential range.

One should appreciate that no particular dependence of the electron-transfer rate upon potential was presupposed in the derivation of equations (3.11) - (3.14), although first-order kinetics were specified in equation (3.14). A test of this first-order kinetic assumption is provided by rearranging equation (3.13) to

\[
\frac{1}{\mu^*} = \frac{1}{nAFCO\sqrt{D_0}} + \exp\left(\frac{-nF}{RT}\right)\exp(nFE/RT)
\] (3.15)

which predicts that a plot of \( 1/\mu^* \) versus \( \exp(nFE/RT) \) will be linear. Turning to equation (3.12), \( k_f \), can be calculated from values of \( i^* \) at several potentials as
Figure 3.2. Two-dimensional relationship between $\mu^*$ and $E$ when the current equals zero.
Figure 3.3. Linear relationship between $i$ and $\mu$ at any constant potential.
i^*/nAFc_0^b thus permitting its potential dependence to be determined. Equation (3.3) then provides a route for investigating the potential dependence of k_b. The dependence of k_f and k_b on potential is exponential only if Butler-Volmer kinetics are obeyed with a constant transfer coefficient. In such a case, a plot of ln i^* versus E will be linear. In the next section, expressions (3.11), (3.12) and (3.15) will be recast in terms of the Butler-Volmer model.

3.2. BUTLER-VOLMER MODEL.

The Butler-Volmer equations

\[ k_f = k^0 \exp \left( -\alpha nF/RT \left[ E-E^0 \right] \right) \]  \hspace{1cm} (3.16)

and

\[ k_b = k^0 \exp \left( (1-\alpha)nF/RT \left[ E-E^0 \right] \right) \]  \hspace{1cm} (3.17)

are almost universally believed to express the dependence of the reaction rate constants on potential, though there is not unanimity on whether the charge transfer coefficient should be regarded as constant.

Substituting equation (3.16) for k_f in the general equation (3.11) leads to

\[ i = \frac{nAFc_0^b}{I} \exp \left( \frac{\alpha nF}{RT} \left[ E-E_{1/2} \right] \right) \left( 1 - \frac{\mu}{M} \right) \exp \left( \frac{\mu nF}{RT} \left[ E-E_{1/2} \right] \right) \]  \hspace{1cm} (3.18)

where we define

\[ I = nAFc_0^b k^0 (D_O/D_R)^{\alpha/2} \]  \hspace{1cm} (3.19)

\[ M = nAFc_0^b \sqrt{D_O} \]  \hspace{1cm} (3.20)

and the reversible halfwave potential

\[ E_{1/2} = E^0 + (RT/2nF) \ln ((D_R/D_O)) \]  \hspace{1cm} (3.21)
The significance of these three new constants in the relationships of \( i^* \) and \( \mu^* \) to the potential are shown in Figures 3.1 and 3.2. Usually only approximate values for \( M \) and \( E_{1/2} \) are available, \emph{a priori}, because of the wide variation in diffusion coefficient and standard potential values reported in the literature. In spherical Global Analysis, no value of \( E_{1/2} \) is required and only a crude diffusion coefficient. The crude diffusion coefficient is used during the correction for the sphricity and a more accurate diffusion coefficient can be calculated from the experimental voltammogram through the use of equation (3.20) and the calculated value of \( M \) (see later).

In terms of Butler-Volmer kinetics, equations (3.12) and (3.13) can be rewritten in forms that emphasize the linear relationships

\[
\ln i^* = \ln I + \alpha n F E_{1/2}/RT - \alpha n F /RT \tag{3.22}
\]

between \( \ln i^* \) and \(-nF/RT\), and for

\[
\frac{1}{\mu^*} = \frac{1}{M} + \frac{\exp(-nF E_{1/2}/RT)}{M} \exp(nF/RT) \tag{3.23}
\]

between \( 1/\mu^* \) and \exp(nF/RT). These relationships are illustrated in Figures 3.4 and 3.5. Hence a plot (or least squares regression calculation) of \( 1/\mu^* \) versus \exp(nF/RT) will give a straight line of intercept \( 1/M \) and gradient \exp(-nF E_{1/2}/RT)/M. The \( M \) and \( E_{1/2} \) values are then found from

\[
M = 1/\text{intercept} \tag{3.24}
\]

and

\[
E_{1/2} = \frac{RT}{nF} \ln \left( \frac{\text{intercept}}{\text{slope}} \right) \tag{3.25}
\]

as shown in Figure 3.4.

Similarly, a plot (or a corresponding calculation) of \( \ln i^* \) versus \(-nF/RT\) will give a straight line (if \( \alpha \) is a potential-independent constant) of slope \( \alpha \) and intercept \( \ln I \). The kinetically significant result is the \( I/M \) ratio, equal to
Figure 3.4. A plot of $1/\mu^*$ versus $\exp(nFE/RT)$ from the slope and intercept of which $M$ and $E_{1/2}$ are calculated.
Figure 3.5. A plot of $\ln i^*$ versus $-nFE/RT$ from the slope and intercept of which $\alpha$ and $I$ are determined.
\[ I/M = I/nAFc_{O}^{b} \sqrt{D_{O}} = k^{o}D_{O}^{(\alpha-1)/2}D_{R}^{\alpha/2} \quad (3.26) \]

Usually \( D_{O} \gg D_{R} \) so that the \( I/nAFc_{O}^{b} \) ratio will be within experimental error of the standard rate constant \( k^{o} \).

3.3. THE POLARIZING SIGNAL.

The simplest means of scanning all useful potentials and obtaining two \((i,\mu)\) pairs at each potential is via cyclic voltammetry, as illustrated in Figure 3.6. The applied signal consists of a negative-going ramp with slope \(-\nu\) and starting at an initial potential of \( E_{0} \) where the current is negligible, so that

\[ E = E_{0} - \nu t \quad 0 \leq t \leq \theta/2 \quad (3.27) \]

where \( \theta \) is the duration of the experiment. The ramp continues until time \( \theta/2 \) by which time \( E \) has reached a value about 100/n mV more negative than \( E_{PC} \) the forward peak potential. The ramp direction is then reversed, so that

\[ E = E_{0} - \nu(\theta - t) \quad \theta/2 \leq t \leq \theta \quad (3.28) \]

Useful data will cease to be collected once the potential ramp has passed a value of 100/n mV more positive than \( E_{PA} \), though the potential ramp could conveniently return to \( E_{0} \). If the ramp is simulated by a staircase, voltage increments should be as small and numerous as possible.

If \( \mu^{+} \) and \( \mu^{-} \) are the values of \( i \) and \( \mu \) at some potential on the forward sweep with \( \mu^{+} \) and \( \mu^{-} \) as the corresponding values at the same potential during the reverse sweep, then the following equations

\[ i^{+} = (\mu^{+} - \mu^{-}) / (\mu - \mu) \quad (3.29) \]

and

\[ \mu^{+} = (\mu^{+} - \mu^{-}) / (i - i) \quad (3.30) \]
may be used to calculate \( i^* \) and \( \mu^* \) from two data pairs. The terms \( i^* \) and \( \mu^* \) are, in fact, the quantities appearing in equations (3.22) and (3.23) and are defined in Figure 3.3.

3.4. IMPLEMENTATION OF THE ANALYSIS.

Modern voltammetric instrumentation provides digital current data at a set of equally spaced time intervals. We let \( \Delta \) represent the time interval between data and the odd number \( 2N+1 \) be the total number of current data \( i_0, i_1, i_2, \ldots, i_j, \ldots, i_{2N-2}, i_{2N-1}, i_{2N} \). Hence \( 2N\Delta = \Theta \). The initial potential is selected so that the initial current \( i_0 \) is zero. The potential program provides \( E_j \) data at times corresponding to each \( i_j \). Thus, for a cyclic voltammetric experiment, the results take the form of Table 3.1. Hence \( i_j \) and \( i_{2N-j} \) are currents measured at the same potential \( E_j \); they correspond to an \( \langle \vec{t}, \vec{i} \rangle \) pair in the notation consistent with equations (3.29) and (3.30) and shown in Figure 3.6.

The fourth column of Table 3.1 illustrates values of \( \mu \) which results from convolving the current data of the third column while the seventh column results from the conjoined third and sixth columns. The entries \( \mu_j \) and \( \mu_{2N-j} \) constitute a \( \langle \vec{\mu}, \vec{\mu} \rangle \) pair in equations (3.29) and (3.30) and as also illustrated in Figure 3.6. The convolution integral given in equation (3.10) is computed using a published algorithm [14] which utilizes the equations

\[
\mu_J = \frac{\sqrt{D}}{r_0} \int_{0}^{t} i(\tau) f \left( \frac{D(t - \tau)}{r_0^2} \right) d\tau = \frac{\Delta \sqrt{D}}{r_0 b^2} \sum_{j=0}^{J-1} i_{J-j} h_j \quad J = 1, 2, 3, \ldots, 2N \quad (3.31)
\]

where \( \mu_J \) is a member of the \( \mu \) family when \( J < N \) and a member of the \( \mu \) when \( J > N \). The \( h \) coefficients are given by
Figure 3.6. (a) Potential versus time (b) current versus potential and (c) convoluted current versus potential graphs for cyclic voltammetry. (—) $\overrightarrow{i}$, $\overrightarrow{i}$, $\overrightarrow{\mu}$ and $\overrightarrow{\mu}$ at a specific potential.
Table 3.1. Format of the data for the spherical Global Analysis. The symbol \( \mathbf{\tilde{t}} \) represents the time at each potential during the forward sweep, \( \mathbf{\tilde{t}} \), the time at each potential during the backward sweep.

<table>
<thead>
<tr>
<th>( E )</th>
<th>( \mathbf{\tilde{t}} )</th>
<th>( \mathbf{\tilde{t}}' )</th>
<th>( \mathbf{\tilde{t}}'' )</th>
<th>( \mathbf{\tilde{t}}''' )</th>
<th>( \mathbf{\tilde{t}}'''' )</th>
<th>( \mathbf{\tilde{t}}''''' )</th>
<th>( \mathbf{\tilde{t}}''''''' )</th>
<th>( \mathbf{\tilde{t}}''''''''' )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_0 )</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( E_1 )</td>
<td>( \Delta )</td>
<td>( \mathbf{i}_1 )</td>
<td>( \mu_1 )</td>
<td>( (2N-1)\Delta )</td>
<td>( \mathbf{i}_{2N-1} )</td>
<td>( \mu_{2N-1} )</td>
<td>( \mathbf{i}_1^* )</td>
<td>( \mu_1^* )</td>
</tr>
<tr>
<td>( E_2 )</td>
<td>2( \Delta )</td>
<td>( \mathbf{i}_2 )</td>
<td>( \mu_2 )</td>
<td>( (2N-2)\Delta )</td>
<td>( \mathbf{i}_{2N-2} )</td>
<td>( \mu_{2N-2} )</td>
<td>( \mathbf{i}_2^* )</td>
<td>( \mu_2^* )</td>
</tr>
<tr>
<td>( \vdots )</td>
<td>( \vdots )</td>
<td>( \vdots )</td>
<td>( \vdots )</td>
<td>( \vdots )</td>
<td>( \vdots )</td>
<td>( \vdots )</td>
<td>( \vdots )</td>
<td>( \vdots )</td>
</tr>
<tr>
<td>( E_j )</td>
<td>( j\Delta )</td>
<td>( \mathbf{i}_j )</td>
<td>( \mu_j )</td>
<td>( (2N-j)\Delta )</td>
<td>( \mathbf{i}_{2N-j} )</td>
<td>( \mu_{2N-j} )</td>
<td>( \mathbf{i}_j^* )</td>
<td>( \mu_j^* )</td>
</tr>
<tr>
<td>( \vdots )</td>
<td>( \vdots )</td>
<td>( \vdots )</td>
<td>( \vdots )</td>
<td>( \vdots )</td>
<td>( \vdots )</td>
<td>( \vdots )</td>
<td>( \vdots )</td>
<td>( \vdots )</td>
</tr>
<tr>
<td>( E_{N-2} )</td>
<td>( (N-2)\Delta )</td>
<td>( \mathbf{i}_{N-2} )</td>
<td>( \mu_{N-2} )</td>
<td>( (N+2)\Delta )</td>
<td>( \mathbf{i}_{N+2} )</td>
<td>( \mu_{N+2} )</td>
<td>( \mathbf{i}_{N-2}^* )</td>
<td>( \mu_{N-2}^* )</td>
</tr>
<tr>
<td>( E_{N-1} )</td>
<td>( (N-1)\Delta )</td>
<td>( \mathbf{i}_{N-1} )</td>
<td>( \mu_{N-1} )</td>
<td>( (N+1)\Delta )</td>
<td>( \mathbf{i}_{N+1} )</td>
<td>( \mu_{N+1} )</td>
<td>( \mathbf{i}_{N-1}^* )</td>
<td>( \mu_{N-1}^* )</td>
</tr>
<tr>
<td>( E_N )</td>
<td>( N\Delta )</td>
<td>( \mathbf{i}_N )</td>
<td>( \mu_N )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
\[ h_j = -2 \sqrt{\frac{jb-b}{\pi}} \exp(jb-b) \text{erfc}\sqrt{jb-b} + 4 \sqrt{\frac{jb}{\pi}} + 2 \exp(jb) \text{erfc}\sqrt{jb} \]

\[ -2 \sqrt{\frac{jb+b}{\pi}} \exp(jb+b) \text{erfc}\sqrt{jb+b} \quad 1 \leq j \leq J-1 \]  

(3.32)

and

\[ h_0 = 1 - 2 \sqrt{\frac{b}{\pi}} + b - \exp(b) \text{erfc}\sqrt{b} \]  

(3.33)

with \( b = D\Delta/\tau_0^2 \). The referenced algorithm, and the computer program "BHOSCPSV.BAS" (found in Appendix I) which was based on it were adapted for the present work with the only change being replacement by "Set \( a = \Delta\sqrt{D/\tau_0 b^2} \)" of the command "Set \( a = \Delta/(289455nVb^2) \)" found in the original (Appendix B of reference [14]).

Data processing initially makes use of equations (3.29) and (3.30) in the form

\[ i_j^* = \frac{\mu_{2N-j} \cdot i_{1-j} - \mu_j \cdot i_{1-j}}{\mu_{2N-j} \cdot \mu_j} \quad J = 1,2,3,...N \]  

(3.34)

and

\[ \mu_j^* = \frac{\mu_{2N-j} \cdot i_{1-j} - \mu_j \cdot i_{1-j}}{i_{1-j} \cdot \mu_{2N-j}} \]  

(3.35)

which are the algebraic equivalents of the graphical extrapolations shown in Figure 3.3. Next, from a plot of \( 1/\mu_j^* \) versus \( \exp(nFE_j/RT) \) similar to Figure 3.4, one finds values for \( M \) and \( E_{1/2}^r \) according to equations (3.24) and (3.25). Similarly, \( \alpha \) and \( l \) are easily found from a plot of \( \ln i_j^* \) versus \( -nFE_j/RT \) as in Figure 3.5. Finally, the standard rate constant \( k^0 \) is found from the I/M ratio given by equation (3.26).

3.5. WEIGHTED LEAST SQUARES REGRESSION ANALYSIS.

With the advent of computer based analysis of experimental data, the analyst has become separated from some of the more mundane aspects, but as a result of this lack of 'hands-on' checking for the reliability of the data, it is necessary to provide
some sort of mechanism to discriminate against the possibility of imprecision. The many points used in the construction Figures 3.4 and 3.5 have a wide range of inherent reliabilities and require some form of weighting in order to fit the 'best' line through all the available data. A weighted least squares procedure [115,227,228] was used for this purpose.

The weighting has been described for Global Analysis [115] and the method prescribes an individual weighting function for each of the regression analyses and they are

$$w(\ln i^*) = \frac{(\tilde{\mu} - \mu)^2}{\epsilon^2 + \frac{\Delta}{\pi} \ln(180 \, \frac{\mu}{i^*} + (i^*)^{-2} \, \epsilon^2 \, \Omega)}$$

(3.36)

for equation (3.22) and the following for equation (3.23)

$$w(1/\mu^*) = \frac{(\tilde{\mu} - \mu)^2}{2\epsilon^2 + (\mu^*)^{-2} \, \epsilon^2 \, \Omega}$$

(3.37)

where

$$\Omega = \left[ \tilde{\mu} - \frac{4}{3} \sqrt{\frac{\Delta}{\pi}} \, \iota \right]^2 + \left[ \tilde{\mu} - \frac{4}{3} \sqrt{\frac{\Delta}{\pi}} \, \iota \right]^2 + \frac{\Delta}{\pi} \left[ (\iota)^2 \ln(2.27 \, \iota) + (\iota)^2 \ln(2.27 \, \iota) \right],$$

$\epsilon$ is the standard error which is arbitrary because of the relative nature of the weighting and $J$ is the index of each data point in the array.

For the application of linear least squares the following equations were used to evaluate the slope, $m$, and the intercept, $c$, for a linear equation of the form $y = mx + c$

$$m = \frac{\sum w_j \sum w_j x_j y_j - \sum w_j x_j \sum w_j y_j}{\sum w_j \sum w_j x_j^2 - (\sum w_j x_j)^2}$$

(3.38)

$$c = \frac{-\sum w_j x_j \sum w_j x_j y_j - \sum w_j y_j \sum w_j x_j^2}{\sum w_j \sum w_j x_j^2 - (\sum w_j x_j)^2}$$

(3.39)
between unity and the total number of points in the analysis.

Application of weighted quadratic least squares involved the evaluation of the coefficients \(a, b\) and \(c\) of the quadratic equation \(y = ax^2 + bx + c\) from the following set of simultaneous equations

\[
\begin{align*}
a \sum w_j x_j^2 + b \sum w_j x_j + c \sum w_j &= \sum w_j y_j \\
a \sum w_j x_j^3 + b \sum w_j x_j^2 + c \sum w_j x_j &= \sum w_j x_j y_j \\
a \sum w_j x_j^4 + b \sum w_j x_j^3 + c \sum w_j x_j^2 &= \sum w_j x_j^2 y_j
\end{align*}
\]  

(3.40)

This was achieved through the use of a published algorithm incorporating the gaussian elimination method [229].

3.6. TESTING OF THE ANALYSIS.

To verify the spherical Global Analysis concept, the analysis of simulated cyclic voltammograms was undertaken, the simulations were generated using the program "SPOLO.FOR" [230] in Appendix I which employs the explicit finite difference technique [87] and initially assumed Butler-Volmer kinetics and semi-infinite spherical diffusion. Table 3.2 summarizes the results of subjecting the simulated current data to the spherical Global Analysis. The table considers three values of \(k^o\) for each value of the sphericity factor \(\sigma\). The \(\sigma\) values of 0.0010, 0.0100 and 0.1000 correspond to a spherical radius of 8.014x10^{-4} m, 8.014 x10^{-5} m and 8.014x10^{-6} m respectively under the conditions assumed in Table 3.2. Inspection of this table illustrates the success of the spherical Global Analysis in determining kinetic and thermodynamic parameters of an electrode reaction over a range of electrode sizes and rate constant values. The need to take sphericity into account in the Global Analysis is established in Table 3.3. This table lists the results when simulated spherical data are processed using the Global Analysis based on a planar geometry.
Table 3.2. Results of subjecting simulated cyclic voltammetric data to the spherical Global Analysis. The simulations assumed values of $\alpha = 0.5000$, $D_0 = D_R = 2.500 \times 10^{-9}$ m$^2$ s$^{-1}$, $E_{1/2} = -0.05000$ V, $v = 100.000$ V s$^{-1}$ and $T = 298.15$ K. Three sphericities $\sigma$ and three rate constants $k^a$ are considered.

<table>
<thead>
<tr>
<th>Values assumed</th>
<th>Values recovered</th>
<th>$10^2 k^a /$m s$^{-1}$</th>
<th>$10^9 D /$m$^2$ s$^{-1}$</th>
<th>$E_{1/2} /$V</th>
<th>$\alpha$</th>
<th>$10^2 k^a /$m s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0.0010$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0550</td>
<td></td>
<td>2.500</td>
<td>-0.05000</td>
<td>0.4999</td>
<td>0.05500</td>
<td></td>
</tr>
<tr>
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<td></td>
<td>2.502</td>
<td>-0.05005</td>
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<td>0.5506</td>
<td></td>
</tr>
<tr>
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<td>2.503</td>
<td>-0.05006</td>
<td>0.5110</td>
<td>5.528</td>
<td></td>
</tr>
<tr>
<td>$0.0100$</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>0.0550</td>
<td></td>
<td>2.500</td>
<td>-0.05000</td>
<td>0.5000</td>
<td>0.05501</td>
<td></td>
</tr>
<tr>
<td>0.5500</td>
<td></td>
<td>2.501</td>
<td>-0.05005</td>
<td>0.5009</td>
<td>0.5510</td>
<td></td>
</tr>
<tr>
<td>5.5000</td>
<td></td>
<td>2.502</td>
<td>-0.05006</td>
<td>0.5086</td>
<td>5.558</td>
<td></td>
</tr>
<tr>
<td>$0.1000$</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>0.0550</td>
<td></td>
<td>2.495</td>
<td>-0.05002</td>
<td>0.5006</td>
<td>0.05502</td>
<td></td>
</tr>
<tr>
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<td></td>
<td>2.498</td>
<td>-0.05007</td>
<td>0.4999</td>
<td>0.5537</td>
<td></td>
</tr>
<tr>
<td>5.5000</td>
<td></td>
<td>2.499</td>
<td>-0.05008</td>
<td>0.4968</td>
<td>5.814</td>
<td></td>
</tr>
</tbody>
</table>
Table 3.3. Kinetic and thermodynamic values calculated when simulated cyclic voltammetric data for a spherical electrode are analysed using the *planar* version of the Global Analysis. Simulation parameters are identical to those listed in Table 3.2. A rate constant of $0.5500 \times 10^{-2}$ m s$^{-1}$ was used in these simulations.

<table>
<thead>
<tr>
<th>$\sigma$</th>
<th>$10^9$ D/m$^2$ s$^{-1}$</th>
<th>$E_{1/2}$ /V</th>
<th>$\alpha$</th>
<th>$10^2$ k$^2$ /m s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0010</td>
<td>2.680</td>
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<td>0.5120</td>
<td>0.4439</td>
</tr>
<tr>
<td>0.0100</td>
<td>3.116</td>
<td>-0.04777</td>
<td>0.4733</td>
<td>0.3277</td>
</tr>
<tr>
<td>0.1000</td>
<td>4.968</td>
<td>-0.04481</td>
<td>0.3883</td>
<td>0.2174</td>
</tr>
</tbody>
</table>
[115] using the computer program "BHOPCPSV.BAS" in Appendix I. As the sphericity factor $\alpha$ decreases (corresponding to a decrease in electrode curvature), the variables $D$, $E_1$, $P$, $\alpha$, and $k^*$ take values which are numerically closer to the input values used in the simulations.

Of experimental interest is the question of how well the spherical Global Analysis is able to cope with current data that contain extraneous contributions, such as spurious 'noise'. To investigate such a situation, data sets were created by adding to each $i_j$ in Table 3.1 a gaussian noise component distributed about a mean of zero with a root-mean-square of 2% of the forward peak current of each cyclic voltammogram. The gaussian noise was generated pseudorandomly using a standard method [122,227] as outlined in Section 2.1.6. The effect of subjecting the resulting noisy data to the spherical Global Analysis is tabulated in Table 3.4. Evidently, the analysis is able to extract kinetic parameters containing only modest errors, even when the faradaic data are contaminated by noise. Smoothing of the current data using the three-point triangular and the nine-point weighted moving-average as outlined in section 2.1.6, resulted in retrieved kinetic and thermodynamic values which were slightly better than those without the benefit of smoothing. The noisy voltammograms that were closer to reversibility were less affected by the noise and also showed no improvement with either smoothing procedure, the more irreversible voltammograms were more affected by the noise but responded to the application of smoothing with the nine-point Savitsky-Golay method the most effective.

3.7. CONCLUSION.

The Global Analysis has been redeveloped to accommodate curvature inherent in spherical electrodes and includes the advantages of the planar counterpart. These are: (1) All the data from a single experiment are used which improves the accuracy
Table 3.4. Results of subjecting noisy simulated cyclic voltammetric data to the spherical Global Analysis. Simulation parameters were identical to those listed in Table 3.2. A sphericity of $\sigma = 0.1000$ was used. The expected value for $M$ is $1.947 \times 10^9$ $A \text{s}^{1/2}$ and the values of $I$ are $2.142 \times 10^{-8}$ $A$, $2.142 \times 10^{-7}$ $A$ and $2.142 \times 10^{-6}$ $A$ respectively.

<table>
<thead>
<tr>
<th>Values assumed</th>
<th>Values recovered</th>
<th>$10^2 k^0 / m \text{s}^{-1}$</th>
<th>$10^9 D / m^2 \text{s}^{-1}$</th>
<th>$E_{1/2} / V$</th>
<th>$\alpha$</th>
<th>$10^2 k^0 / m \text{s}^{-1}$</th>
<th>$10^9 M / A \text{s}^{1/2}$</th>
<th>$10^6 I / A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2% noise</td>
<td>0.0550</td>
<td>2.363</td>
<td>-0.03712</td>
<td>0.4887</td>
<td>0.04459</td>
<td>1.893</td>
<td>0.01736</td>
<td></td>
</tr>
<tr>
<td>3pt. smooth</td>
<td></td>
<td>2.464</td>
<td>-0.04634</td>
<td>0.4919</td>
<td>0.05250</td>
<td>1.933</td>
<td>0.02044</td>
<td></td>
</tr>
<tr>
<td>9pt. smooth</td>
<td></td>
<td>2.475</td>
<td>-0.04719</td>
<td>0.4925</td>
<td>0.05326</td>
<td>1.937</td>
<td>0.02074</td>
<td></td>
</tr>
<tr>
<td>2% noise</td>
<td>0.5500</td>
<td>2.423</td>
<td>-0.04890</td>
<td>0.5039</td>
<td>0.5563</td>
<td>1.917</td>
<td>0.2166</td>
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<tr>
<td>3pt. smooth</td>
<td></td>
<td>2.426</td>
<td>-0.04896</td>
<td>0.5038</td>
<td>0.5576</td>
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<td>0.2171</td>
<td></td>
</tr>
<tr>
<td>9pt. smooth</td>
<td></td>
<td>2.430</td>
<td>-0.04903</td>
<td>0.5040</td>
<td>0.5583</td>
<td>1.920</td>
<td>0.2174</td>
<td></td>
</tr>
<tr>
<td>2% noise</td>
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<td>2.447</td>
<td>-0.04931</td>
<td>0.5126</td>
<td>5.724</td>
<td>1.926</td>
<td>2.229</td>
<td></td>
</tr>
<tr>
<td>3pt. smooth</td>
<td></td>
<td>2.446</td>
<td>-0.04929</td>
<td>0.4911</td>
<td>5.924</td>
<td>1.926</td>
<td>2.307</td>
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</tr>
<tr>
<td>9pt. smooth</td>
<td></td>
<td>2.447</td>
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<td>0.4895</td>
<td>5.943</td>
<td>1.926</td>
<td>2.314</td>
<td></td>
</tr>
</tbody>
</table>
and minimises noise effects; (2) All parameters are calculated from a single experiment so that irreducibilities between experiments are avoided and as a result the irreducibilities become more obvious; (3) The analysis is objective and, unlike simulation-curve-fitting methods, requires no recursive operations or subjective judgements; (4) The analysis provides an internal check on the validity of Butler-Volmer kinetics.

The Global Analysis shares with other electrochemical methods of determining transport, kinetic and thermodynamic parameters the requirement of accurate, albeit non-trivial, compensation for capacitance and uncompensated resistance, as well as the absence of homogeneous kinetics. These considerations will be integral to the analysis of an actual electrochemical system.
CHAPTER FOUR

INVESTIGATION OF THE INFLUENCE OF RESIDUAL UNCOMPENSATED RESISTANCE AND INCOMPLETE CHARGING CURRENT CORRECTION ON THE CALCULATION OF THE ELECTRODE KINETICS INCLUDING THE POTENTIAL DEPENDENCE OF THE CHARGE TRANSFER COEFFICIENT WHEN GLOBAL AND CONVOLUTION ANALYSIS METHODS ARE USED.
4. INTRODUCTION.

The Global Analysis procedure for a spherical electrode was developed and then demonstrated to be a powerful and accurate method for the analysis of quasi-reversible electron transfer in Chapter Three. A related technique is Convolution Potential Sweep Voltammetry (CPSV) [117-121], this has the same objective as Global Analysis but only uses the relationship between the potential and the resultant semi-integral of the current for the forward sweep of a cyclic voltammogram. This procedure also provides estimations of $k^0$ and $\alpha$. The reversible half-wave potential is calculable but the degree of precision is lower because it is only evaluated at one potential on the reverse sweep of a cyclic voltammogram. Also, the accuracy of this determination may suffer as the kinetics become more irreversible [120].

The successful application of both the Global Analysis and CPSV procedures requires that the applied electrochemical experiment provides an accurate representation of the faradaic current, which is free from any artifact. The influence of uncompensated solution resistance can be greatly reduced by the use of potentiostats [159,176,197,231-235] particularly when coupled with additional software and/or hardware methodology to further minimise the problem [117,159,161,176,197,232-236]. However, the problem of uncompensated resistance is still not eliminated and in cyclic voltammetry it increases the peak separation [83,84,235,236] in a manner that could be mistaken for an apparently slow rate of electron transfer based on the Nicholson procedure [80] of analysis. The effect in CPSV is to decrease the slope of the characteristic logarithmic plot used to calculate the electrode kinetic parameters and this could also be mistaken for apparently slow rates of electron transfer [118].

In cyclic voltammetry, the analysis of the electrode kinetics for fast electron transfer processes involves entering the kinetic (quasi-reversible) regime by decreasing the time scale of the experiment. This is achieved by increasing the potential scan rate,
which combined with the double layer capacitance produces a current according to equation (1.25). This charging current adds to the faradaic current and therefore to the resistance induced potential error. Additionally, the product of the capacitance and the resistance \((R_u C_d)\) introduces a time constant which dilates the voltammogram [83, 118]. In the event of complete potentiostatic compensation of the solution resistance (i.e. \(R_u = 0\)), the only major effect of the charging current will be to offset the forward and the reverse branches of the voltammogram. Under this condition the offset may be subtracted from the voltammogram [52, 55, 61, 117, 197, 237] under the assumption that the presence or absence of the electroactive species has no effect on the behaviour of the electrode-solution (electrolyte) interface. Alternative techniques such as the application of a non-linear ramp followed by semi-integral analysis have been used for analytical purposes but not yet in kinetic measurements [238]. Again, as in the case of uncompensated resistance, subtraction of the charging current is unlikely to be perfect.

In this chapter, an investigation of the effects of residual uncompensated resistance and incomplete charging current correction for simulated data with respect to all the parameters calculable in both the Global Analysis and CPSV procedures will be presented. These factors are considered in conjunction with the influence of unequal diffusion coefficients for O and R. After examination of these factors a final objective is to examine the historically controversial question of the potential dependence of \(\alpha\) [44, 50, 52, 55, 61, 62, 120, 237, 239, 240] based on a knowledge of the magnitude of the errors introduced by the possible interferences of \(R_u\) and \(C_d\). This will be verified by the analysis of experimental data for the well-studied [52, 55, 60, 62, 66, 241, 242] reduction of 2-methyl-2-nitropropane to its radical anion in acetonitrile (equation (4.1)).

\[
(CH_3)_3CNO_2 + e^- \rightleftharpoons (CH_3)_3CNO_2^- \quad (4.1)
\]
4.1. ADDITIONAL THEORY.

The theory of Global Analysis has been comprehensively presented in Sections 3.1, 3.2 and 3.3 of Chapter Three, but the inclusion of a potential dependent $\alpha$ requires further development of the analysis. If $\alpha$ is allowed to vary linearly with potential [44,50,52-55,61,62,120,237,239,240] as given in equation (4.2) [237]

$$\alpha = \alpha_0 + d\alpha/dE(E - E^0)$$

(4.2)

where $\alpha_0$ is the value of the charge transfer coefficient at the standard potential, then equation (3.22) must take into account equation (4.2) and be recast as follows

$$\ln i^* = -d\alpha/dE)nF/RT(E - E_{1/2}^{r})^2 - \alpha_0nF/RT(E - E_{1/2}^{r}) + \ln I$$

(4.3)

In this case quadratic regression analysis is now required, with the potential dependence of $\alpha$ being calculated from the quadratic coefficient.

The equivalent equations for CPSV as presented for Global Analysis may be derived from references 117-129. Under quasi-reversible conditions, with constant $\alpha$, the following relationship applies

$$\frac{RT}{nF} \ln \Phi = \alpha(E - E_{1/2}^{r}) + \frac{RT}{nF} \ln \frac{k^o}{D^o}$$

(4.4)

where $\Phi = \frac{M - \mu[1 + (D_0/D_R)^{1/2}\exp(nF/RT)(E - E_{1/2}^{r})]}{i}$. Linear regression analysis of $(RT/nF) \ln \Phi$ versus $E - E_{1/2}^{r}$ therefore enables $\alpha$ to be calculated from the slope and $k^o$ to be calculated from the intercept. The determination of the value of $E_{1/2}^{r}$ is obtained from the measurement of a single data point using equation (4.5)

$$E_{1/2}^{r} = E_{i=0} - \frac{RT}{nF} \ln \frac{M - \mu_{i=0}}{\mu_{i=0}}$$

(4.5)

where $E_{i=0}$ is the potential at which the current cuts the zero current axis on the reverse
sweep of the cyclic voltammogram and \( \mu_{i=0} \) is the convoluted current at this potential. If \( \alpha \) varies with potential as in equation (4.2) then equation (4.4) must also be recast to give

\[
\frac{RT}{nF} \ln \Phi = \frac{d\alpha}{dE}(E - E_{1/2})^2 + \alpha_0 (E - E_{1/2}) - \frac{RT}{nF} \ln \frac{k^*}{\sqrt{D_0}} \tag{4.6}
\]

In which case quadratic regression analysis will again enable the value of \( d\alpha/dE \) to be estimated.

4.1.1. WEIGHTING FUNCTIONS.

Two types of weighting have been described for Global Analysis. The first method has been described in Section 3.4. The second and less complicated approach used involves a restriction of the usable data to a window between the 5\% and 95\% limits of \( M \) [237]. This is a weighting procedure in the sense that the data obtained outside the limits may be considered to have a weighting of zero, with the remaining data being equally weighted. This method is referred to as Window weighting in this chapter but suffers from the need to arbitrarily choose the size of the central portion.

In CPSV, the weighting has been determined in terms of the log-plot analysis [228] and the weights are assigned inversely proportional to the variances as follows.

\[
w = i^2 (M - \mu)^2 \tag{4.7}
\]

Figure 4.1 shows a comparison of each form of weighting for two sets of kinetic parameters. The procedures required for implementing weighted linear regression analyses incorporating the weighting functions has been previously described in Section 3.4.
Figure 4.1. I) Simulated cyclic voltammogram for $\Lambda = 1.40$. II) Convoluted current of I. III) Weighting functions: (a) CPSV weighting as given by equation (4.7). (b) Global Analysis weighting as given by equation (3.36). (c) Global Analysis weighting as given by equation (3.37). (d) Window weighting.
Figure 4.1 (cont.). I) Simulated cyclic voltammogram for $\Lambda = 0.0700$. II) Convoluted current of I. III) Weighting functions: (a) CPSV weighting as given by equation (4.7). (b) Global Analysis weighting as given by equation (3.36). (c) Global Analysis weighting as given by equation (3.37). (d) Window weighting.
4.2. EXPERIMENTAL.

Solutions of 0.500 mM (CH₃)₃CNO₂ with 0.100 M Et₄NClO₄ were prepared in acetonitrile which was freshly distilled daily from calcium hydride. Bubbling with nitrogen prior to each experiment was used to deoxygenate the solutions. The water-jacketed cell was thermostated to 20.0 ± 0.1°C for each experiment and all experiments were performed in a faraday cage.

A three electrode configuration was used and the electrodes were the Metrohm E410 hanging mercury drop electrode serving as the working, a platinum ring serving as the counter electrode and the standard Ag⁺/Ag reference electrode system for acetonitrile. These electrodes are described in greater detail in Section 2.2. The function generator was as described in Section 2.2.2. The potentiostat was an Amel 551 (as described in Section 2.1.3.) and positive feedback was applied in all experiments. The degree of compensation was adjusted until the cyclic voltammogram of p-nitrotoluene, under identical experimental conditions, exhibited a reversible shape. This method of R compensation has been suggested by Whitson et al. [197]. Data were acquired at time intervals corresponding to 1 mV increments using the Gould Model 4035 digital storage oscilloscope as described in Section 2.1.1.

Experiments performed on blank solutions of supporting electrolyte only, or on solutions containing both supporting electrolyte and 2-methyl-2-nitropropane, were replicated three times and the averaged currents were stored serially. Current data were background corrected, interpolated and smoothed using the nine-point cubic least squares procedure of Savitsky and Golay [204].

The simulation program "SPOLO.FOR" in Appendix I was altered to include a potential dependent α as given in equation (4.2). To simulate the distortion created by uncompensated resistance, the simulated voltammetric data was processed by adding in the potential error [83] as follows
\[ E' = E \pm iR_u \quad (4.8) \]

where \( E' \) is the potential with the resistive error added. The sign of the error is dependent on whether undercompensation (negative) or overcompensation (positive) of the potentiostat was simulated. The data was then linearly interpolated so that a set of matched data pairs for the forward and reverse sweeps was obtained, this is a requirement of the Global Analysis.

The use of a potentiostat under positive feedback conditions requires careful adjustment to achieve the correct degree of compensation of the potential error. Correct adjustment is usually detected via oscillation in the circuit network. However, instability of the feedback circuitry may restrict full compensation leading to undercompensation. Alternatively, the addition of capacitive elements to the feedback loop or other factors may repress the onset of potentiostat oscillation [231] and it is then possible to use greater compensation than is required [197] which corresponds to overcompensation.

The simulation of incomplete correction of the charging current was achieved by applying a constant current offset to the reverse sweep of the voltammogram based on a percentage of the forward peak current. A positive or negative offset may be applied which corresponds to overcorrection and undercorrection respectively. Experimentally both situations may arise. The reason why only the reverse half of the voltammogram is treated in this manner is due to way in which the experimental data is acquired. A digital storage oscilloscope was used to collect the raw current data and consequently only an arbitrary zero current line can be derived for the voltage-time window during post-acquisition scaling and analysis. The zero line was chosen to occur, in the absence of faradaic current, at the beginning of the voltammogram with 50-100 data points being treated by linear regression analysis. The background voltammogram collected in the presence of supporting electrolyte alone was treated in exactly the same manner and subtracted from the data set obtained in the presence of
the electroactive species. Although this method may appear to lack precision due to the possibility of introducing systematic error, a benefit of this approach is that the forward sweep used for the CPSV method is unaffected by any error that may or may not be introduced by this data treatment. In an absolute zero current method, if charging current subtraction errors occur, then both the forward and reverse sweeps are affected so then neither Global Analysis or CPSV may be used. If an offset is then applied to counteract this error, then a similar result to the arbitrary zero current approach is achieved.

4.3. RESULTS AND DISCUSSION.

A series of simulated voltammograms relevant to an electrode of spherical geometry was generated in order to test the accuracy of the analysis procedures, the weighting methods and source of errors discussed above. The parameters were selected based on the experimental parameters related to the test system of 2-methyl-2-nitropropane. In the analyses, the heterogeneous rate constant is expressed as the dimensionless rate parameter, $\Lambda$, defined by equation (1.18) with the lowest value considered approximating the 2-methyl-2 nitropropane system at a scan rate of 100 V s$^{-1}$.

Normally $\alpha$ is assumed to be independent of potential, but this need not be the case. To test the accuracy of the procedures, simulated voltammograms were calculated based on equation (4.2) using the parameters $D = 3.33 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, $\alpha = 0.425$, $E^0 = -2.000 \text{ V}$ and $\Lambda$ in the range of 0.0700 to 1.40. The three values of $d\alpha/dE$ tested were 0.1, 0.2, and 0.3 V$^{-1}$, these values cover the range of values for $d\alpha/dE$ found previously and the results are presented in Table 4.1. It can be seen that a linear analysis in the presence of a potential dependent $\alpha$ will result in an underestimation of $\alpha$. However, estimation of $\alpha$ by quadratic regression analysis is
<table>
<thead>
<tr>
<th>Potential</th>
<th>Value</th>
<th>( \Lambda = 0.0700 )</th>
<th>( \Lambda = 0.140 )</th>
<th>( \Lambda = 0.700 )</th>
<th>( \Lambda = 1.40 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{d}^2 \text{e} / \text{d} \text{E} ) = 0.1 V(^{-1}) (Linear)</td>
<td>( \Lambda )</td>
<td>0.0710</td>
<td>0.0697</td>
<td>0.0715</td>
<td>0.137</td>
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<tr>
<td></td>
<td>( \alpha )</td>
<td>0.406</td>
<td>0.411</td>
<td>0.406</td>
<td>0.411</td>
</tr>
<tr>
<td></td>
<td>( E_{1/2} ) (V)</td>
<td>-1.999</td>
<td>-2.000</td>
<td>-2.000</td>
<td>-2.000</td>
</tr>
<tr>
<td>( \text{d} \alpha / \text{d} \text{E} ) (Quadratic)</td>
<td>( \Lambda )</td>
<td>0.0692</td>
<td>0.0692</td>
<td>0.0698</td>
<td>0.136</td>
</tr>
<tr>
<td></td>
<td>( \alpha )</td>
<td>0.425</td>
<td>0.426</td>
<td>0.425</td>
<td>0.426</td>
</tr>
<tr>
<td></td>
<td>( \text{d} \alpha / \text{d} \text{E} )</td>
<td>0.101</td>
<td>0.103</td>
<td>0.102</td>
<td>0.104</td>
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<td>( \Lambda )</td>
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<td>0.0701</td>
<td>0.0733</td>
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</tr>
<tr>
<td></td>
<td>( \alpha )</td>
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<td>0.398</td>
<td>0.387</td>
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<tr>
<td></td>
<td>( E_{1/2} ) (V)</td>
<td>-1.999</td>
<td>-2.000</td>
<td>-2.000</td>
<td>-2.000</td>
</tr>
<tr>
<td>( \text{d} \alpha / \text{d} \text{E} ) (Quadratic)</td>
<td>( \Lambda )</td>
<td>0.0692</td>
<td>0.0692</td>
<td>0.0698</td>
<td>0.136</td>
</tr>
<tr>
<td></td>
<td>( \alpha )</td>
<td>0.425</td>
<td>0.426</td>
<td>0.425</td>
<td>0.426</td>
</tr>
<tr>
<td></td>
<td>( \text{d} \alpha / \text{d} \text{E} )</td>
<td>0.201</td>
<td>0.202</td>
<td>0.202</td>
<td>0.203</td>
</tr>
<tr>
<td>( \text{d} \alpha / \text{d} \text{E} ) = 0.3 V(^{-1}) (Linear)</td>
<td>( \Lambda )</td>
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<td>0.0702</td>
<td>0.0754</td>
<td>0.140</td>
</tr>
<tr>
<td></td>
<td>( \alpha )</td>
<td>0.367</td>
<td>0.386</td>
<td>0.366</td>
<td>0.381</td>
</tr>
<tr>
<td></td>
<td>( E_{1/2} ) (V)</td>
<td>-1.999</td>
<td>-2.000</td>
<td>-2.000</td>
<td>-2.000</td>
</tr>
<tr>
<td>( \text{d} \alpha / \text{d} \text{E} ) (Quadratic)</td>
<td>( \Lambda )</td>
<td>0.0693</td>
<td>0.0692</td>
<td>0.0699</td>
<td>0.136</td>
</tr>
<tr>
<td></td>
<td>( \alpha )</td>
<td>0.426</td>
<td>0.426</td>
<td>0.425</td>
<td>0.426</td>
</tr>
<tr>
<td></td>
<td>( \text{d} \alpha / \text{d} \text{E} )</td>
<td>0.301</td>
<td>0.302</td>
<td>0.301</td>
<td>0.303</td>
</tr>
</tbody>
</table>

Simulation parameters \( D = 3.33 \times 10^{-9} \text{ m}^2 \text{ s}^{-1} \), \( \alpha = 0.425 \), \( E_{1/2} \) = -2.000 V, \( T = 293 \text{ K} \) and electrode area = 0.019 cm\(^2\). \( \text{d} \alpha / \text{d} \text{E} \) given as V\(^{-1}\).
quite accurate due to the use of analysis equations which are more appropriate to this model. Linear analysis produces a consistently higher value for $\Lambda$ over the quadratic analysis and therefore failure to include a potential dependent $\alpha$ will result in the overestimation of $k^e$. Also, as the kinetics approach the reversible limit, the difference between the linear and quadratic analyses decreases and this is most likely due to a reduction in the influence of the kinetics and this corresponds to a reduction in the sensitivity to any kinetic effect. Overall it appears that the most accurate analysis will occur if $\Lambda$ is maintained below unity.

Normally, the values of $D_O$ and $D_R$ are assumed to be equal. However, in practice this assumption may not be valid. The influence of unequal diffusion coefficients for O and R was therefore examined in order to determine if neglect of this factor would have an effect on the calculation of $k^e$ and $\alpha$. The possibility of introducing an error in the method of Global Analysis at spherical electrodes may be significant because of the assumption made that the diffusion coefficient of O and R be equivalent when applying the spherical correction (See Section 3.1).

With unequal diffusion coefficients, the kinetic parameter may be redefined as given by equation (4.9) [4].

$$\Psi = \left(\frac{D_O}{D_R}\right)^{\alpha/2} \frac{\Lambda}{\sqrt{\pi}} \quad (4.9)$$

Voltammetric curves with two values of $\Psi$, each with three differing degrees of electrode sphericity, $\sigma_{\text{sphere}}$, defined as [224]

$$\sigma_{\text{sphere}} = (1/r_0)\sqrt{\frac{DRT}{nF\varphi}} \quad (4.10)$$

where $r_0$ is the spherical electrode radius, were simulated and then analysed. Results with $D_O = 2D_R$ (i.e. $(D_O/D_R)^{\alpha/2} = 1.190$ where $\alpha = 0.5$) and with $D_O = 2/3D_R$ (i.e. $(D_O/D_R)^{\alpha/2} = 0.904$ where $\alpha = 0.5$) are presented in Table 4.2 and Table 4.3, respectively. The values of $\Lambda\pi^{1/2}$ for the two cases correspond to approximate values.
Table 4.2. Determination of electrode kinetic parameters by analysis of digitally simulated data having unequal diffusion coefficients of $D_O=2.500 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ and $D_R=1.250 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$

<table>
<thead>
<tr>
<th>Sphericity Factor (Calculation)</th>
<th>Calculated Value</th>
<th>$\Psi=0.118$</th>
<th>$\Lambda \pi^{1/2}=0.0995$</th>
<th>$\Psi=1.18$</th>
<th>$\Lambda \pi^{1/2}=0.995$</th>
</tr>
</thead>
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<tr>
<td></td>
<td></td>
<td>Global</td>
<td>Window</td>
<td>CPSV</td>
<td>Global</td>
</tr>
<tr>
<td>$\sigma_{\text{sphere}}=0.0010$ (Linear)</td>
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<td>0.118</td>
<td>0.118</td>
<td>1.19</td>
</tr>
<tr>
<td></td>
<td>$\alpha$</td>
<td>0.500</td>
<td>0.500</td>
<td>0.501</td>
<td>0.498</td>
</tr>
<tr>
<td></td>
<td>$D_O (10^9 \text{ m}^2 \text{ s}^{-1})$</td>
<td>2.501</td>
<td>2.501</td>
<td>#</td>
<td>2.503</td>
</tr>
<tr>
<td></td>
<td>$E_{1/2}^I$ (V)</td>
<td>-2.009</td>
<td>-2.009</td>
<td>-2.009</td>
<td>-2.009</td>
</tr>
<tr>
<td>(Quadratic)</td>
<td>$\Psi$</td>
<td>0.118</td>
<td>0.118</td>
<td>0.118</td>
<td>1.19</td>
</tr>
<tr>
<td></td>
<td>$\alpha$</td>
<td>0.500</td>
<td>0.500</td>
<td>0.501</td>
<td>0.498</td>
</tr>
<tr>
<td></td>
<td>$d\alpha/dE (\text{V}^{-1})$</td>
<td>-0.001</td>
<td>0.000</td>
<td>-0.005</td>
<td>-0.035</td>
</tr>
<tr>
<td>$\sigma_{\text{sphere}}=0.0100$ (Linear)</td>
<td>$\Psi$</td>
<td>0.118</td>
<td>0.114</td>
<td>0.120</td>
<td>1.24</td>
</tr>
<tr>
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<td>$D_O (10^9 \text{ m}^2 \text{ s}^{-1})$</td>
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<td>2.505</td>
<td>#</td>
<td>2.513</td>
</tr>
<tr>
<td></td>
<td>$E_{1/2}^I$ (V)</td>
<td>-2.009</td>
<td>-2.009</td>
<td>-2.009</td>
<td>-2.010</td>
</tr>
<tr>
<td>(Quadratic)</td>
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<td>0.114</td>
<td>0.120</td>
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<tr>
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<td>$\alpha$</td>
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<td>0.498</td>
<td>0.475</td>
</tr>
<tr>
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<td>$d\alpha/dE (\text{V}^{-1})$</td>
<td>-0.019</td>
<td>-0.011</td>
<td>-0.009</td>
<td>-0.419</td>
</tr>
<tr>
<td>$\sigma_{\text{sphere}}=0.0100$ (Linear)</td>
<td>$\Psi$</td>
<td>0.133</td>
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<td>0.131</td>
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<td>$E_{1/2}^I$ (V)</td>
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<td>0.132</td>
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<td>0.486</td>
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<td>-0.035</td>
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</tbody>
</table>

Simulation parameters $\alpha = 0.500$, $E_{1/2}^I = -2.000$ V, $T = 293$ K and electrode area = 0.019 cm$^2$.

# CPSV unable to calculate a value for $D_O$ directly.
<table>
<thead>
<tr>
<th>Sphericity Factor</th>
<th>Calculation</th>
<th>Calculated Value</th>
<th>$\Psi=0.0899$</th>
<th>$\Psi=0.899$</th>
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<tr>
<td></td>
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<td>$\Delta \pi^{-1/2}=0.0995$</td>
<td>$\Delta \pi^{-1/2}=0.995$</td>
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<td></td>
<td></td>
<td>Global</td>
<td>Window</td>
<td>CPSV</td>
</tr>
<tr>
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<td>0.0899</td>
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<td></td>
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<td>0.0899</td>
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<td></td>
<td></td>
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<td>0.500</td>
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<tr>
<td></td>
<td></td>
<td>$\Delta \alpha/\Delta E \ (\text{V}^{-1})$</td>
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<td>0.001</td>
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<td>$\sigma_{sphere}=0.0100$</td>
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<td>0.0890</td>
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<td>-1.994</td>
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<td>(Quadratic)</td>
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<td>0.0890</td>
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<tr>
<td></td>
<td></td>
<td>$\alpha$</td>
<td>0.502</td>
<td>0.501</td>
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<tr>
<td></td>
<td></td>
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<td>0.006</td>
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<td>$\sigma_{sphere}=0.0100$</td>
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<td>$\alpha$</td>
<td>0.504</td>
<td>0.504</td>
</tr>
<tr>
<td></td>
<td></td>
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<td>2.483</td>
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<td>$E_{1/2} \ (\text{V})$</td>
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<td>-1.992</td>
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<td>(Quadratic)</td>
<td>$\Psi$</td>
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<td>0.0837</td>
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<td>0.507</td>
</tr>
<tr>
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<td>$\Delta \alpha/\Delta E \ (\text{V}^{-1})$</td>
<td>0.035</td>
<td>0.024</td>
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</table>

Simulation parameters $\alpha = 0.500$, $E_{1/2} = -2.000 \text{ V}$, $T = 293 \text{ K}$ and electrode area = 0.019 cm$^2$.

# CPSV unable to calculate a value for $D_Q$ directly.
of 0.1 and 1. The value used for $E^o$ in the simulations was -2.000V and the theoretical $E_{1/2}^i$ value expected from the analyses of the data will be offset from $E^o$ by a constant equal to $(RT/2nF) \ln(D_R/D_O)$. Therefore, the expected $E_{1/2}^i$ values are respectively equal to -2.009 V and -1.995 V in Tables 4.2 and 4.3. Data in Tables 4.2 and 4.3 for the lower value of $\Psi$ reveal that as the degree of sphericity increases, the estimation of $\Psi$ becomes slightly inaccurate whereas the evaluation of $\alpha$ is almost unaffected with only a minimal apparent $d\alpha/dE$ being introduced. In fact, the sign of $d\alpha/dE$ as determined in the analyses was found to be negative for $D_O > D_R$ which cannot be equated to any reported potential dependence found previously. At the larger value of $\Psi$ where the process approaches reversibility, the errors becomes much more significant as expected from the previous discussion but for reasons predominantly arising from factors unrelated to unequal diffusion coefficients. Since very large differences between $D_O$ and $D_R$ were used in order to demonstrate the effect on the analysis, it is concluded that the effect of unequal diffusion coefficients will not be significant on the analysis of most experimental data. Errors introduced from this factor only become apparent at electrodes of very small radius and large differences in diffusion coefficients.

The influence of uncompensated resistance on the analysis of data in both Global Analysis and CPSV is summarised in Tables 4.4 and 4.5. Only the Global Analysis weighting is reported since the results are essentially the same as those obtained with the Window weighting method. For an electrode of spherical geometry, the uncompensated resistance between the working and reference electrodes is described in equation (4.11) [36,166,167]

$$R_u = \frac{\rho}{4\pi} \left[ \frac{1}{r_0} + \frac{1}{d} \right]$$  \hspace{1cm} (4.11)

where $d$ is the distance between the working and the reference electrodes. In acetonitrile with 0.1 M $\text{Et}_4\text{NClO}_4$, the specific resistivity, $\rho$, is 128 $\Omega$ cm [197].
<table>
<thead>
<tr>
<th>Resistance Error</th>
<th>( \Lambda = 0.0700 )</th>
<th>( \Lambda = 0.140 )</th>
<th>( \Lambda = 0.700 )</th>
<th>( \Lambda = 1.40 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha )</td>
<td>0.0680</td>
<td>0.0693</td>
<td>0.134</td>
<td>0.138</td>
</tr>
<tr>
<td>( \beta )</td>
<td>0.421</td>
<td>0.425</td>
<td>0.413</td>
<td>0.415</td>
</tr>
<tr>
<td>( da/dE )</td>
<td>-0.041</td>
<td>-0.054</td>
<td>-0.078</td>
<td>-0.066</td>
</tr>
<tr>
<td>( E_{1/2} )</td>
<td>-2.000</td>
<td>-2.000</td>
<td>-2.000</td>
<td>-2.000</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Resistance Error</th>
<th>( \Lambda = 0.0700 )</th>
<th>( \Lambda = 0.140 )</th>
<th>( \Lambda = 0.700 )</th>
<th>( \Lambda = 1.40 )</th>
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</thead>
<tbody>
<tr>
<td>( \alpha )</td>
<td>0.0683</td>
<td>0.0694</td>
<td>0.135</td>
<td>0.136</td>
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<tr>
<td>( \beta )</td>
<td>0.423</td>
<td>0.426</td>
<td>0.415</td>
<td>0.417</td>
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<tr>
<td>( da/dE )</td>
<td>-0.051</td>
<td>-0.066</td>
<td>-0.070</td>
<td>-0.066</td>
</tr>
<tr>
<td>( E_{1/2} )</td>
<td>-2.000</td>
<td>-2.000</td>
<td>-2.000</td>
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</table>

<table>
<thead>
<tr>
<th>Resistance Error</th>
<th>( \Lambda = 0.0700 )</th>
<th>( \Lambda = 0.140 )</th>
<th>( \Lambda = 0.700 )</th>
<th>( \Lambda = 1.40 )</th>
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<td>0.0698</td>
<td>0.136</td>
<td>0.138</td>
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<td>( \beta )</td>
<td>0.428</td>
<td>0.428</td>
<td>0.420</td>
<td>0.422</td>
</tr>
<tr>
<td>( da/dE )</td>
<td>-0.058</td>
<td>-0.062</td>
<td>-0.066</td>
<td>-0.074</td>
</tr>
<tr>
<td>( E_{1/2} )</td>
<td>-2.000</td>
<td>-2.000</td>
<td>-2.000</td>
<td>-2.000</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Resistance Error</th>
<th>( \Lambda = 0.0700 )</th>
<th>( \Lambda = 0.140 )</th>
<th>( \Lambda = 0.700 )</th>
<th>( \Lambda = 1.40 )</th>
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<tbody>
<tr>
<td>( \alpha )</td>
<td>0.0692</td>
<td>0.0692</td>
<td>0.138</td>
<td>0.138</td>
</tr>
<tr>
<td>( \beta )</td>
<td>0.425</td>
<td>0.425</td>
<td>0.426</td>
<td>0.426</td>
</tr>
<tr>
<td>( da/dE )</td>
<td>0.002</td>
<td>-0.005</td>
<td>-0.005</td>
<td>-0.003</td>
</tr>
<tr>
<td>( E_{1/2} )</td>
<td>-1.999</td>
<td>-2.000</td>
<td>-2.000</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Resistance Error</th>
<th>( \Lambda = 0.0700 )</th>
<th>( \Lambda = 0.140 )</th>
<th>( \Lambda = 0.700 )</th>
<th>( \Lambda = 1.40 )</th>
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<tbody>
<tr>
<td>( \alpha )</td>
<td>0.0693</td>
<td>0.0704</td>
<td>0.141</td>
<td>0.141</td>
</tr>
<tr>
<td>( \beta )</td>
<td>0.433</td>
<td>0.431</td>
<td>0.424</td>
<td>0.424</td>
</tr>
<tr>
<td>( da/dE )</td>
<td>-0.065</td>
<td>-0.055</td>
<td>-0.055</td>
<td>-0.041</td>
</tr>
<tr>
<td>( E_{1/2} )</td>
<td>-2.000</td>
<td>-2.000</td>
<td>-2.000</td>
<td>-2.000</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Resistance Error</th>
<th>( \Lambda = 0.0700 )</th>
<th>( \Lambda = 0.140 )</th>
<th>( \Lambda = 0.700 )</th>
<th>( \Lambda = 1.40 )</th>
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<td>0.0707</td>
<td>0.142</td>
<td>0.143</td>
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<tr>
<td>( \beta )</td>
<td>0.435</td>
<td>0.433</td>
<td>0.426</td>
<td>0.426</td>
</tr>
<tr>
<td>( da/dE )</td>
<td>-0.068</td>
<td>-0.051</td>
<td>-0.051</td>
<td>-0.047</td>
</tr>
<tr>
<td>( E_{1/2} )</td>
<td>-2.000</td>
<td>-2.000</td>
<td>-2.000</td>
<td>-2.000</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Resistance Error</th>
<th>( \Lambda = 0.0700 )</th>
<th>( \Lambda = 0.140 )</th>
<th>( \Lambda = 0.700 )</th>
<th>( \Lambda = 1.40 )</th>
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<tr>
<td>( \alpha )</td>
<td>0.0699</td>
<td>0.0711</td>
<td>0.144</td>
<td>0.144</td>
</tr>
<tr>
<td>( \beta )</td>
<td>0.438</td>
<td>0.434</td>
<td>0.428</td>
<td>0.428</td>
</tr>
<tr>
<td>( da/dE )</td>
<td>-0.072</td>
<td>-0.047</td>
<td>-0.047</td>
<td>-0.047</td>
</tr>
<tr>
<td>( E_{1/2} )</td>
<td>-2.000</td>
<td>-2.000</td>
<td>-2.000</td>
<td>-2.000</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Resistance Error</th>
<th>( \Lambda = 0.0700 )</th>
<th>( \Lambda = 0.140 )</th>
<th>( \Lambda = 0.700 )</th>
<th>( \Lambda = 1.40 )</th>
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<tr>
<td>( \alpha )</td>
<td>0.0702</td>
<td>0.0714</td>
<td>0.145</td>
<td>0.146</td>
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<tr>
<td>( \beta )</td>
<td>0.441</td>
<td>0.436</td>
<td>0.430</td>
<td>0.430</td>
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<tr>
<td>( da/dE )</td>
<td>-0.077</td>
<td>-0.043</td>
<td>-0.043</td>
<td>-0.043</td>
</tr>
<tr>
<td>( E_{1/2} )</td>
<td>-2.000</td>
<td>-2.000</td>
<td>-2.000</td>
<td>-2.000</td>
</tr>
</tbody>
</table>

Simulation parameters \( D = 3.33 \times 10^{-9} \) m² s⁻¹, \( \alpha = 0.425 \), \( E_{1/2} = -2.000 \) V, \( T = 293 \) K and electrode area = 0.019 cm². All potentials given as Volts and \( da/dE \) given as V⁻¹.
Table 4.5. Determination of electrode kinetic parameters by applying the CPSV method to digitally simulated data containing uncompensated resistance with $E_{1/2}^r$ calculated from equation (4.5)

<table>
<thead>
<tr>
<th>Resistance Error</th>
<th>Value</th>
<th>$\Lambda=0.0700$</th>
<th>$\Lambda=0.140$</th>
<th>$\Lambda=0.700$</th>
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<td></td>
<td></td>
<td>Linear</td>
<td>Quadratic</td>
<td>Linear</td>
<td>Quadratic</td>
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<tr>
<td>-40 ohm</td>
<td>$\Lambda$</td>
<td>0.0680</td>
<td>0.0697</td>
<td>0.135</td>
<td>0.136</td>
</tr>
<tr>
<td></td>
<td>$\alpha$</td>
<td>0.423</td>
<td>0.414</td>
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</tr>
<tr>
<td></td>
<td>$d\alpha/dE$</td>
<td>-0.040</td>
<td>-0.070</td>
<td>-0.070</td>
<td>-0.070</td>
</tr>
<tr>
<td></td>
<td>$E_{1/2}^r$</td>
<td>-2.000</td>
<td>-2.000</td>
<td>-2.000</td>
<td>-2.000</td>
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<tr>
<td>-30 ohm</td>
<td>$\Lambda$</td>
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<td>0.0687</td>
<td>0.136</td>
<td>0.137</td>
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<tr>
<td></td>
<td>$\alpha$</td>
<td>0.423</td>
<td>0.417</td>
<td>0.424</td>
<td>0.417</td>
</tr>
<tr>
<td></td>
<td>$d\alpha/dE$</td>
<td>-0.031</td>
<td>-0.054</td>
<td>-0.054</td>
<td>-0.054</td>
</tr>
<tr>
<td></td>
<td>$E_{1/2}^r$</td>
<td>-2.000</td>
<td>-2.000</td>
<td>-2.000</td>
<td>-2.000</td>
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<tr>
<td>-20 ohm</td>
<td>$\Lambda$</td>
<td>0.0695</td>
<td>0.0699</td>
<td>0.137</td>
<td>0.137</td>
</tr>
<tr>
<td></td>
<td>$\alpha$</td>
<td>0.424</td>
<td>0.418</td>
<td>0.425</td>
<td>0.420</td>
</tr>
<tr>
<td></td>
<td>$d\alpha/dE$</td>
<td>-0.028</td>
<td>-0.038</td>
<td>-0.038</td>
<td>-0.038</td>
</tr>
<tr>
<td></td>
<td>$E_{1/2}^r$</td>
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<td>-2.000</td>
<td>-2.000</td>
<td>-2.000</td>
</tr>
<tr>
<td>-10 ohm</td>
<td>$\Lambda$</td>
<td>0.0697</td>
<td>0.700</td>
<td>0.140</td>
<td>0.140</td>
</tr>
<tr>
<td></td>
<td>$\alpha$</td>
<td>0.425</td>
<td>0.421</td>
<td>0.425</td>
<td>0.420</td>
</tr>
<tr>
<td></td>
<td>$d\alpha/dE$</td>
<td>-0.018</td>
<td>-0.034</td>
<td>-0.034</td>
<td>-0.034</td>
</tr>
<tr>
<td></td>
<td>$E_{1/2}^r$</td>
<td>-2.000</td>
<td>-2.000</td>
<td>-2.000</td>
<td>-2.000</td>
</tr>
<tr>
<td>0 ohm</td>
<td>$\Lambda$</td>
<td>0.0698</td>
<td>0.0698</td>
<td>0.141</td>
<td>0.141</td>
</tr>
<tr>
<td></td>
<td>$\alpha$</td>
<td>0.425</td>
<td>0.425</td>
<td>0.424</td>
<td>0.424</td>
</tr>
<tr>
<td></td>
<td>$d\alpha/dE$</td>
<td>0.002</td>
<td>0.002</td>
<td>0.002</td>
<td>0.002</td>
</tr>
<tr>
<td></td>
<td>$E_{1/2}^r$</td>
<td>-2.000</td>
<td>-2.000</td>
<td>-2.000</td>
<td>-2.000</td>
</tr>
<tr>
<td>+10 ohm</td>
<td>$\Lambda$</td>
<td>0.0709</td>
<td>0.0709</td>
<td>0.141</td>
<td>0.141</td>
</tr>
<tr>
<td></td>
<td>$\alpha$</td>
<td>0.427</td>
<td>0.426</td>
<td>0.427</td>
<td>0.427</td>
</tr>
<tr>
<td></td>
<td>$d\alpha/dE$</td>
<td>0.000</td>
<td>0.004</td>
<td>0.004</td>
<td>0.004</td>
</tr>
<tr>
<td></td>
<td>$E_{1/2}^r$</td>
<td>-2.000</td>
<td>-2.000</td>
<td>-2.000</td>
<td>-2.000</td>
</tr>
<tr>
<td>+20 ohm</td>
<td>$\Lambda$</td>
<td>0.0709</td>
<td>0.0708</td>
<td>0.144</td>
<td>0.144</td>
</tr>
<tr>
<td></td>
<td>$\alpha$</td>
<td>0.428</td>
<td>0.430</td>
<td>0.427</td>
<td>0.428</td>
</tr>
<tr>
<td></td>
<td>$d\alpha/dE$</td>
<td>0.010</td>
<td>0.011</td>
<td>0.011</td>
<td>0.011</td>
</tr>
<tr>
<td></td>
<td>$E_{1/2}^r$</td>
<td>-2.000</td>
<td>-2.001</td>
<td>-2.001</td>
<td>-2.000</td>
</tr>
<tr>
<td>+30 ohm</td>
<td>$\Lambda$</td>
<td>0.0721</td>
<td>0.0718</td>
<td>0.145</td>
<td>0.144</td>
</tr>
<tr>
<td></td>
<td>$\alpha$</td>
<td>0.429</td>
<td>0.431</td>
<td>0.428</td>
<td>0.432</td>
</tr>
<tr>
<td></td>
<td>$d\alpha/dE$</td>
<td>0.015</td>
<td>0.031</td>
<td>0.031</td>
<td>0.031</td>
</tr>
<tr>
<td></td>
<td>$E_{1/2}^r$</td>
<td>-2.001</td>
<td>-2.000</td>
<td>-2.000</td>
<td>-2.000</td>
</tr>
<tr>
<td>+40 ohm</td>
<td>$\Lambda$</td>
<td>0.0721</td>
<td>0.0717</td>
<td>0.148</td>
<td>0.147</td>
</tr>
<tr>
<td></td>
<td>$\alpha$</td>
<td>0.430</td>
<td>0.435</td>
<td>0.428</td>
<td>0.432</td>
</tr>
<tr>
<td></td>
<td>$d\alpha/dE$</td>
<td>0.027</td>
<td>0.038</td>
<td>0.038</td>
<td>0.038</td>
</tr>
<tr>
<td></td>
<td>$E_{1/2}^r$</td>
<td>-2.000</td>
<td>-2.001</td>
<td>-2.000</td>
<td>-2.000</td>
</tr>
</tbody>
</table>

Simulation parameters $D = 3.33 \times 10^{-9}$ m$^2$ s$^{-1}$, $\alpha = 0.425$, $E_{1/2}^r = -2.000$ V, $T = 293$ K and electrode area = 0.019 cm$^2$. All potentials given as Volts and $d\alpha/dE$ given as V$^{-1}$. 
Thus, for an electrode of 0.039 cm radius, \( R_u \) would be 261 Ω in this solvent system. An error of ± 10 Ω would correspond to ± 3.8 % error in applying resistance compensation. Typically, an error of ± 5% is thought to be of an acceptable magnitude. Consequently, the values of \( R_u \) in Tables 4.4 and 4.5 which encompass the range ± 40 Ω are experimentally realistic. Residual uncompensated resistance (i.e. negative resistance errors), as expected, give rise to apparent kinetics that are slower than they should be with both methods of data analysis. With the Global Analysis method in the presence of uncompensated resistance, \( \alpha \) is underestimated for lower values of \( \Lambda \) in relation to the expected value of 0.425 but becomes overestimated with larger values of \( \Lambda \). In CPSV the estimation of \( \alpha \) suffers in a similar manner to Global Analysis although to a slightly lesser degree. With the Global Analysis method an apparently negative \( d\alpha /dE \) value is calculated for all resistance errors. The calculation of the apparent \( d\alpha /dE \) in the presence of resistive errors in CPSV produces different results to the Global Analysis with a negative dependency only being observed under conditions of residual uncompensated resistance. Overall, the presence of uncompensated resistance will cause an underestimation of \( d\alpha /dE \) and if overcompensation does occur only CPSV will produce a positive \( d\alpha /dE \) when \( \Lambda \) is maintained at the lower end of the range investigated here. The estimation of \( E_{1/2}^r \) is generally unaffected by the presence of any resistive error.

The consequence of incorrect charging current compensation is reported in Tables 4.6 and 4.7. Global Analysis consistently predicts a more accurate value of \( E_{1/2}^r \) than does CPSV as expected from previous discussions. From equations (4.4) and (4.6), which relate to CPSV, it can be seen that the accurate evaluation of \( E_{1/2}^r \) is a necessity if the 'kinetic correction' to \( \mu \) is to be assessed correctly. This then influences the calculation of \( k^o, \alpha \) and \( d\alpha /dE \). Whereas in Global Analysis the value of \( E_{1/2}^r \) is basically only necessary for an accurate determination of \( k^o \) and does not affect either \( \alpha \) or \( d\alpha /dE \). If \( E_{1/2}^r \) is known accurately, then in the presence of a
Table 4.6. Determination of electrode kinetic parameters by applying the Global Analysis method to digitally simulated data containing incomplete charging current correction

<table>
<thead>
<tr>
<th>Current Offset</th>
<th>Value</th>
<th>( \Lambda = 0.0700 )</th>
<th>( \Lambda = 0.140 )</th>
<th>( \Lambda = 0.700 )</th>
<th>( \Lambda = 1.40 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Linear</td>
<td>Quadratic</td>
<td>Linear</td>
<td>Quadratic</td>
</tr>
<tr>
<td>-4 %</td>
<td>( \Lambda )</td>
<td>0.0620</td>
<td>0.0790</td>
<td>0.149</td>
<td>0.152</td>
</tr>
<tr>
<td></td>
<td>( \alpha )</td>
<td>0.453</td>
<td>0.400</td>
<td>0.457</td>
<td>0.399</td>
</tr>
<tr>
<td></td>
<td>( da/dE )</td>
<td>-0.305</td>
<td>-0.494</td>
<td>-2.282</td>
<td>-5.349</td>
</tr>
<tr>
<td></td>
<td>( E_{1/2}^{r} )</td>
<td>-2.004</td>
<td>-2.002</td>
<td>-2.001</td>
<td>-2.001</td>
</tr>
<tr>
<td>-3 %</td>
<td>( \Lambda )</td>
<td>0.0731</td>
<td>0.0765</td>
<td>0.146</td>
<td>0.148</td>
</tr>
<tr>
<td></td>
<td>( \alpha )</td>
<td>0.447</td>
<td>0.406</td>
<td>0.451</td>
<td>0.405</td>
</tr>
<tr>
<td></td>
<td>( da/dE )</td>
<td>-0.228</td>
<td>-0.375</td>
<td>-1.687</td>
<td>-3.728</td>
</tr>
<tr>
<td></td>
<td>( E_{1/2}^{r} )</td>
<td>-2.003</td>
<td>-2.001</td>
<td>-2.001</td>
<td>-2.001</td>
</tr>
<tr>
<td>-2 %</td>
<td>( \Lambda )</td>
<td>0.0717</td>
<td>0.0741</td>
<td>0.143</td>
<td>0.145</td>
</tr>
<tr>
<td></td>
<td>( \alpha )</td>
<td>0.440</td>
<td>0.412</td>
<td>0.443</td>
<td>0.411</td>
</tr>
<tr>
<td></td>
<td>( da/dE )</td>
<td>-0.151</td>
<td>-0.253</td>
<td>-1.129</td>
<td>-2.372</td>
</tr>
<tr>
<td></td>
<td>( E_{1/2}^{r} )</td>
<td>-2.002</td>
<td>-2.001</td>
<td>-2.001</td>
<td>-2.001</td>
</tr>
<tr>
<td>-1 %</td>
<td>( \Lambda )</td>
<td>0.0704</td>
<td>0.0716</td>
<td>0.140</td>
<td>0.141</td>
</tr>
<tr>
<td></td>
<td>( \alpha )</td>
<td>0.432</td>
<td>0.418</td>
<td>0.435</td>
<td>0.418</td>
</tr>
<tr>
<td></td>
<td>( da/dE )</td>
<td>-0.074</td>
<td>-0.126</td>
<td>-0.587</td>
<td>-1.189</td>
</tr>
<tr>
<td></td>
<td>( E_{1/2}^{r} )</td>
<td>-2.001</td>
<td>-2.000</td>
<td>-2.000</td>
<td>-2.000</td>
</tr>
<tr>
<td>0 %</td>
<td>( \Lambda )</td>
<td>0.0692</td>
<td>0.0692</td>
<td>0.138</td>
<td>0.138</td>
</tr>
<tr>
<td></td>
<td>( \alpha )</td>
<td>0.425</td>
<td>0.425</td>
<td>0.425</td>
<td>0.426</td>
</tr>
<tr>
<td></td>
<td>( da/dE )</td>
<td>0.002</td>
<td>0.005</td>
<td>-0.003</td>
<td>-0.025</td>
</tr>
<tr>
<td></td>
<td>( E_{1/2}^{r} )</td>
<td>-1.999</td>
<td>-2.000</td>
<td>-2.000</td>
<td>2.000</td>
</tr>
<tr>
<td>+1 %</td>
<td>( \Lambda )</td>
<td>0.0681</td>
<td>0.0668</td>
<td>0.137</td>
<td>0.135</td>
</tr>
<tr>
<td></td>
<td>( \alpha )</td>
<td>0.418</td>
<td>0.432</td>
<td>0.415</td>
<td>0.434</td>
</tr>
<tr>
<td></td>
<td>( da/dE )</td>
<td>0.073</td>
<td>0.128</td>
<td>0.561</td>
<td>1.046</td>
</tr>
<tr>
<td></td>
<td>( E_{1/2}^{r} )</td>
<td>-1.998</td>
<td>-1.999</td>
<td>-1.999</td>
<td>-1.999</td>
</tr>
<tr>
<td>+2 %</td>
<td>( \Lambda )</td>
<td>0.0657</td>
<td>0.0644</td>
<td>0.136</td>
<td>0.132</td>
</tr>
<tr>
<td></td>
<td>( \alpha )</td>
<td>0.419</td>
<td>0.439</td>
<td>0.405</td>
<td>0.441</td>
</tr>
<tr>
<td></td>
<td>( da/dE )</td>
<td>0.139</td>
<td>0.241</td>
<td>0.953</td>
<td>1.597</td>
</tr>
<tr>
<td></td>
<td>( E_{1/2}^{r} )</td>
<td>-1.997</td>
<td>-1.998</td>
<td>-1.999</td>
<td>-1.999</td>
</tr>
<tr>
<td>+3 %</td>
<td>( \Lambda )</td>
<td>0.0659</td>
<td>0.0620</td>
<td>0.135</td>
<td>0.129</td>
</tr>
<tr>
<td></td>
<td>( \alpha )</td>
<td>0.417</td>
<td>0.445</td>
<td>0.395</td>
<td>0.448</td>
</tr>
<tr>
<td></td>
<td>( da/dE )</td>
<td>0.202</td>
<td>0.342</td>
<td>1.231</td>
<td>1.944</td>
</tr>
<tr>
<td></td>
<td>( E_{1/2}^{r} )</td>
<td>-1.996</td>
<td>-1.998</td>
<td>-1.999</td>
<td>-1.998</td>
</tr>
<tr>
<td>+4 %</td>
<td>( \Lambda )</td>
<td>0.0648</td>
<td>0.0597</td>
<td>0.134</td>
<td>0.126</td>
</tr>
<tr>
<td></td>
<td>( \alpha )</td>
<td>0.397</td>
<td>0.452</td>
<td>0.386</td>
<td>0.454</td>
</tr>
<tr>
<td></td>
<td>( da/dE )</td>
<td>0.261</td>
<td>0.433</td>
<td>1.442</td>
<td>2.196</td>
</tr>
<tr>
<td></td>
<td>( E_{1/2}^{r} )</td>
<td>-1.994</td>
<td>-1.997</td>
<td>-1.998</td>
<td>-1.998</td>
</tr>
</tbody>
</table>

Simulation parameters \( D = 3.33 \times 10^{-9} \) m² s⁻¹, \( \alpha = 0.425 \), \( E_{1/2}^{r} = -2.000 \) V, \( T = 293 \) K and electrode area = 0.019 cm². All potentials given as Volts and \( da/dE \) given as V⁻¹.
Table 4.7. Determination of electrode kinetic parameters by applying the CPSV method to digitally simulated data containing incomplete charging current correction with $E_{1/2}$ calculated from equation (4.5).

<table>
<thead>
<tr>
<th>Current Offset</th>
<th>Value</th>
<th>$\Lambda=0.0700$</th>
<th>$\Lambda=0.140$</th>
<th>$\Lambda=0.700$</th>
<th>$\Lambda=1.40$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Linear</td>
<td>Quadratic</td>
<td>Linear</td>
<td>Quadratic</td>
</tr>
<tr>
<td>-4 %</td>
<td>$\Lambda$</td>
<td>0.0963</td>
<td>0.0989</td>
<td>0.186</td>
<td>0.188</td>
</tr>
<tr>
<td></td>
<td>$\alpha$</td>
<td>0.412</td>
<td>0.383</td>
<td>0.400</td>
<td>0.360</td>
</tr>
<tr>
<td></td>
<td>$\text{d}a/d\text{E}$</td>
<td>-0.181</td>
<td>-0.346</td>
<td>-2.011</td>
<td>-2.009</td>
</tr>
<tr>
<td>-3 %</td>
<td>$\Lambda$</td>
<td>0.0879</td>
<td>0.0897</td>
<td>0.173</td>
<td>0.175</td>
</tr>
<tr>
<td></td>
<td>$\alpha$</td>
<td>0.417</td>
<td>0.397</td>
<td>0.407</td>
<td>0.380</td>
</tr>
<tr>
<td></td>
<td>$\text{d}a/d\text{E}$</td>
<td>-0.115</td>
<td>-0.231</td>
<td>-2.011</td>
<td>-2.008</td>
</tr>
<tr>
<td>-2 %</td>
<td>$\Lambda$</td>
<td>0.0818</td>
<td>0.0828</td>
<td>0.161</td>
<td>0.162</td>
</tr>
<tr>
<td></td>
<td>$\alpha$</td>
<td>0.420</td>
<td>0.407</td>
<td>0.413</td>
<td>0.396</td>
</tr>
<tr>
<td></td>
<td>$\text{d}a/d\text{E}$</td>
<td>-0.071</td>
<td>-0.142</td>
<td>-2.008</td>
<td>-2.005</td>
</tr>
<tr>
<td>-1 %</td>
<td>$\Lambda$</td>
<td>0.0749</td>
<td>0.0753</td>
<td>0.150</td>
<td>0.151</td>
</tr>
<tr>
<td></td>
<td>$\alpha$</td>
<td>0.423</td>
<td>0.418</td>
<td>0.419</td>
<td>0.411</td>
</tr>
<tr>
<td></td>
<td>$\text{d}a/d\text{E}$</td>
<td>-0.026</td>
<td>-0.064</td>
<td>-2.003</td>
<td>-2.005</td>
</tr>
<tr>
<td>0 %</td>
<td>$\Lambda$</td>
<td>0.0698</td>
<td>0.0698</td>
<td>0.141</td>
<td>0.141</td>
</tr>
<tr>
<td></td>
<td>$\alpha$</td>
<td>0.425</td>
<td>0.425</td>
<td>0.424</td>
<td>0.424</td>
</tr>
<tr>
<td></td>
<td>$\text{d}a/d\text{E}$</td>
<td>0.002</td>
<td>-0.002</td>
<td>-2.000</td>
<td>-2.000</td>
</tr>
<tr>
<td>+1 %</td>
<td>$\Lambda$</td>
<td>0.0652</td>
<td>0.0648</td>
<td>0.132</td>
<td>0.131</td>
</tr>
<tr>
<td></td>
<td>$\alpha$</td>
<td>0.427</td>
<td>0.432</td>
<td>0.429</td>
<td>0.435</td>
</tr>
<tr>
<td></td>
<td>$\text{d}a/d\text{E}$</td>
<td>0.025</td>
<td>0.046</td>
<td>-1.996</td>
<td>-1.997</td>
</tr>
<tr>
<td>+2 %</td>
<td>$\Lambda$</td>
<td>0.0609</td>
<td>0.0601</td>
<td>0.124</td>
<td>0.123</td>
</tr>
<tr>
<td></td>
<td>$\alpha$</td>
<td>0.428</td>
<td>0.437</td>
<td>0.433</td>
<td>0.445</td>
</tr>
<tr>
<td></td>
<td>$\text{d}a/d\text{E}$</td>
<td>0.043</td>
<td>0.085</td>
<td>-1.993</td>
<td>-1.994</td>
</tr>
<tr>
<td>+3 %</td>
<td>$\Lambda$</td>
<td>0.0557</td>
<td>0.0559</td>
<td>0.116</td>
<td>0.115</td>
</tr>
<tr>
<td></td>
<td>$\alpha$</td>
<td>0.430</td>
<td>0.442</td>
<td>0.437</td>
<td>0.453</td>
</tr>
<tr>
<td></td>
<td>$\text{d}a/d\text{E}$</td>
<td>0.059</td>
<td>0.118</td>
<td>-1.989</td>
<td>-1.992</td>
</tr>
<tr>
<td>+4 %</td>
<td>$\Lambda$</td>
<td>0.0532</td>
<td>0.0520</td>
<td>0.109</td>
<td>0.108</td>
</tr>
<tr>
<td></td>
<td>$\alpha$</td>
<td>0.431</td>
<td>0.446</td>
<td>0.440</td>
<td>0.461</td>
</tr>
<tr>
<td></td>
<td>$\text{d}a/d\text{E}$</td>
<td>0.072</td>
<td>0.146</td>
<td>-1.986</td>
<td>-1.989</td>
</tr>
</tbody>
</table>

* Errors too great to perform complete analysis.

Simulation parameters $D = 3.33 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, $\alpha = 0.425$, $E_{1/2} = -2.000 \text{ V}$, $T = 293 \text{ K}$ and electrode area = 0.019 cm$^2$. All potentials given as Volts and $\text{d}a/d\text{E}$ given as $V^{-1}$. 
charging current correction error, CPSV will of course be much more accurate than the Global Analysis method when the arbitrary zero current procedure is applied to the experimental data. In this sense CPSV could be envisaged to be superior to Global Analysis. Equations (3.29) and (3.30) show that the Global Analysis procedure relies on the difference between the forward and reverse sweep values of i and \( \mu \) to calculate the values of \( i^* \) and \( \mu^* \) at each potential. However, if a current offset is present then this will result in the erroneous estimation of \( i^* \) and \( \mu^* \). The results of this effect can be observed in Table 4.6 where, even for low values of \( \Lambda \) an apparently significant \( d\alpha/dE \) is introduced. However, the apparent value of \( d\alpha/dE \) is only positive if the voltammogram is overcorrected where this corresponds to an upward displacement on the current scale of the reverse sweep. Interestingly, as the current of the reverse sweep is displaced upwards (i.e. overcorrection), the value of \( \alpha \) decreases for the linear analysis but increases for the quadratic analysis, but as expected both methods give the same value when no charging current error is present. The value estimated for \( k^o \) is directly linked to the calculation of \( E^f_{1/2} \) and is therefore underestimated when the calculated potential is less than -2.000 V and overestimated when \( E^f_{1/2} \) is more negative than -2.000 V which occurs as a result of undercorrection. As usual, the results become less accurate as \( \Lambda \) approaches the reversible limit. Examination of Table 4.7 indicates that the errors in the determination of \( \alpha \) are greater for CPSV than for Global Analysis. Generally, the apparent \( \alpha \) value tends to increase as the reverse scan becomes further displaced negatively when using either linear and quadratic analysis, with the quadratic form of analysis being much more sensitive to such an effect. In summary, Global Analysis is more sensitive to the influence of a charging current correction error but is likely to produce a more accurate estimation of \( E^f_{1/2} \) than CPSV. Consequently, a comparison of results obtained for CPSV analysis using the values of \( E^f_{1/2} \) obtained from CPSV and Global Analysis will give a good indication as to the occurrence of a charging current correction error.
The analysis of the experimental data for the reduction of 2-methyl-2-nitropropane using the different methods of analysis are presented at six scan rates in Table 4.8. The four methods include the Global Analysis procedure and three CPSV analyses, each method contains both linear and quadratic weighted least squares regression analysis results. Global Analysis provides the most precise calculation in the sense that the standard deviation is the lowest for each calculated parameter. For all the data sets the α value calculated from the linear analysis was lower than found with the quadratic analysis, which is consistent with the behaviour observed in Table 4.1 when a potential dependent α was part of the simulation and the data was analysed in the same way as in Table 4.8. However, the potential dependent α determined by Global Analysis is lower than the value calculated by all the CPSV methods. The value of \( k^0 \) calculated by the Global Analysis is consistently lower for the quadratic analysis than the linear analysis, but this difference is only slight and again similar to the comparative results reported in Table 4.1. There is no obvious scan rate dependence on the calculated parameters suggesting that the data is free of any systematic error as a result of imperfect application of positive feedback to reduce the uncompensated resistance. Savéant and Tessier [52,54] have pointed out that a double layer correction is virtually unnecessary for this system because the potential of the plane of the reaction site, \( \phi \), has only a slight, but linear, dependency on the applied potential. Therefore, the intrinsic value of α is directly proportional to the apparent value of α. From equations (1.15) to (1.17), for an apparent rate constant of 3x10^{-4} m s^{-1} and an α of 0.45, the calculated value of \( \lambda/F \) is 1.00 V and therefore the predicted value of dα/dE is 0.25 V^{-1}. The result obtained by Global Analysis is approximately half the predicted value, but the consistency of the results of the quadratic analysis indicates that either the correct value has been obtained or that all the voltammograms are effected equally by a systematic error such as the under correction of the charging current (see Table 4.6).
<table>
<thead>
<tr>
<th>Scan Rate (V s⁻¹)</th>
<th>5</th>
<th>10</th>
<th>20</th>
<th>50</th>
<th>100</th>
<th>200</th>
<th>Ave. ± SD</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Δ</td>
<td>0.333</td>
<td>0.235</td>
<td>0.166</td>
<td>0.105</td>
<td>0.0774</td>
<td>0.0526</td>
<td></td>
</tr>
</tbody>
</table>

### Global Analysis

**Linear Analysis**

<table>
<thead>
<tr>
<th>k° (10⁴ m s⁻¹)</th>
<th>2.918</th>
<th>2.880</th>
<th>2.933</th>
<th>3.151</th>
<th>2.786</th>
<th>3.325</th>
<th>2.999 ± 0.200</th>
</tr>
</thead>
<tbody>
<tr>
<td>α</td>
<td>0.430</td>
<td>0.413</td>
<td>0.431</td>
<td>0.425</td>
<td>0.415</td>
<td>0.403</td>
<td>0.420 ± 0.011</td>
</tr>
<tr>
<td>DQ (10⁶ m² s⁻¹)</td>
<td>4.153</td>
<td>4.207</td>
<td>3.847</td>
<td>3.954</td>
<td>4.091</td>
<td>4.300</td>
<td>4.092 ± 0.167</td>
</tr>
<tr>
<td>E₁/₂ (V)</td>
<td>-1.994</td>
<td>-1.989</td>
<td>-1.993</td>
<td>-1.997</td>
<td>-1.987</td>
<td>-1.994</td>
<td>-1.992 ± 0.004</td>
</tr>
</tbody>
</table>

**Quadratic Analysis**

<table>
<thead>
<tr>
<th>k° (10⁴ m s⁻¹)</th>
<th>2.933</th>
<th>2.885</th>
<th>2.927</th>
<th>3.057</th>
<th>2.686</th>
<th>3.134</th>
<th>2.937 ± 0.154</th>
</tr>
</thead>
<tbody>
<tr>
<td>α</td>
<td>0.438</td>
<td>0.425</td>
<td>0.439</td>
<td>0.454</td>
<td>0.437</td>
<td>0.435</td>
<td>0.438 ± 0.009</td>
</tr>
<tr>
<td>dα/dE (V⁻¹)</td>
<td>0.123</td>
<td>0.128</td>
<td>0.069</td>
<td>0.176</td>
<td>0.099</td>
<td>0.134</td>
<td>0.121 ± 0.036</td>
</tr>
</tbody>
</table>

### CPSV Analysis (E₁/₂ from equation (4.5) with M = 5.99 x 10⁻⁶ C s⁻¹/² from equation (3.20) and Daverage from Global Analysis)

**Linear Analysis**

<table>
<thead>
<tr>
<th>k° (10⁴ m s⁻¹)</th>
<th>2.889</th>
<th>2.961</th>
<th>3.200</th>
<th>3.514</th>
<th>3.324</th>
<th>3.389</th>
<th>3.213 ± 0.246</th>
</tr>
</thead>
<tbody>
<tr>
<td>α</td>
<td>0.433</td>
<td>0.433</td>
<td>0.403</td>
<td>0.415</td>
<td>0.425</td>
<td>0.414</td>
<td>0.421 ± 0.012</td>
</tr>
<tr>
<td>E₁/₂ (V)</td>
<td>-1.993</td>
<td>-1.991</td>
<td>-1.996</td>
<td>-2.002</td>
<td>-1.999</td>
<td>-1.996</td>
<td>-1.996 ± 0.004</td>
</tr>
</tbody>
</table>

**Quadratic Analysis**

<table>
<thead>
<tr>
<th>k° (10⁴ m s⁻¹)</th>
<th>2.908</th>
<th>2.977</th>
<th>3.174</th>
<th>3.399</th>
<th>3.213</th>
<th>3.287</th>
<th>3.160 ± 0.186</th>
</tr>
</thead>
<tbody>
<tr>
<td>α</td>
<td>0.449</td>
<td>0.414</td>
<td>0.435</td>
<td>0.462</td>
<td>0.455</td>
<td>0.434</td>
<td>0.442 ± 0.017</td>
</tr>
<tr>
<td>dα/dE (V⁻¹)</td>
<td>0.246</td>
<td>-0.185</td>
<td>0.293</td>
<td>0.325</td>
<td>0.171</td>
<td>0.099</td>
<td>0.158 ± 0.187</td>
</tr>
</tbody>
</table>

### CPSV Analysis (E₁/₂ from equation (4.5) with M and Daverage from Global Analysis)

<table>
<thead>
<tr>
<th>M (10⁶ C s⁻¹/²)</th>
<th>6.00</th>
<th>6.20</th>
<th>5.80</th>
<th>5.90</th>
<th>6.00</th>
<th>6.15</th>
<th>6.01 ± 0.15</th>
</tr>
</thead>
</table>

**Linear Analysis**

<table>
<thead>
<tr>
<th>k° (10⁴ m s⁻¹)</th>
<th>2.894</th>
<th>3.100</th>
<th>3.098</th>
<th>3.439</th>
<th>3.330</th>
<th>3.524</th>
<th>3.231 ± 0.240</th>
</tr>
</thead>
<tbody>
<tr>
<td>α</td>
<td>0.431</td>
<td>0.401</td>
<td>0.428</td>
<td>0.427</td>
<td>0.425</td>
<td>0.399</td>
<td>0.419 ± 0.014</td>
</tr>
<tr>
<td>E₁/₂ (V)</td>
<td>-1.993</td>
<td>-1.994</td>
<td>-1.994</td>
<td>-2.001</td>
<td>-2.000</td>
<td>-1.998</td>
<td>-1.997 ± 0.003</td>
</tr>
</tbody>
</table>

**Quadratic Analysis**

<table>
<thead>
<tr>
<th>k° (10⁴ m s⁻¹)</th>
<th>2.913</th>
<th>3.124</th>
<th>3.086</th>
<th>3.358</th>
<th>3.215</th>
<th>3.278</th>
<th>3.162 ± 0.157</th>
</tr>
</thead>
<tbody>
<tr>
<td>α</td>
<td>0.448</td>
<td>0.400</td>
<td>0.442</td>
<td>0.461</td>
<td>0.455</td>
<td>0.446</td>
<td>0.442 ± 0.022</td>
</tr>
<tr>
<td>dα/dE (V⁻¹)</td>
<td>0.252</td>
<td>0.037</td>
<td>0.130</td>
<td>0.240</td>
<td>0.177</td>
<td>0.218</td>
<td>0.176 ± 0.081</td>
</tr>
</tbody>
</table>

### CPSV Analysis (E₁/₂, M and Daverage from Global Analysis)

<table>
<thead>
<tr>
<th>M (10⁶ C s⁻¹/²)</th>
<th>6.00</th>
<th>6.20</th>
<th>5.80</th>
<th>5.90</th>
<th>6.00</th>
<th>6.15</th>
<th>6.01 ± 0.15</th>
</tr>
</thead>
</table>

**Linear Analysis**

<table>
<thead>
<tr>
<th>k° (10⁴ m s⁻¹)</th>
<th>2.982</th>
<th>2.689</th>
<th>3.037</th>
<th>3.132</th>
<th>2.598</th>
<th>3.267</th>
<th>2.951 ± 0.259</th>
</tr>
</thead>
<tbody>
<tr>
<td>α</td>
<td>0.427</td>
<td>0.417</td>
<td>0.430</td>
<td>0.431</td>
<td>0.431</td>
<td>0.400</td>
<td>0.423 ± 0.012</td>
</tr>
<tr>
<td>E₁/₂ (V)</td>
<td>-1.994</td>
<td>-1.989</td>
<td>-1.993</td>
<td>-1.997</td>
<td>-1.987</td>
<td>-1.994</td>
<td>-1.992 ± 0.004</td>
</tr>
</tbody>
</table>

**Quadratic Analysis**

<table>
<thead>
<tr>
<th>k° (10⁴ m s⁻¹)</th>
<th>2.999</th>
<th>2.695</th>
<th>3.022</th>
<th>3.027</th>
<th>2.444</th>
<th>3.006</th>
<th>2.866 ± 0.243</th>
</tr>
</thead>
<tbody>
<tr>
<td>α</td>
<td>0.440</td>
<td>0.434</td>
<td>0.446</td>
<td>0.473</td>
<td>0.473</td>
<td>0.451</td>
<td>0.453 ± 0.017</td>
</tr>
<tr>
<td>dα/dE (V⁻¹)</td>
<td>0.209</td>
<td>0.197</td>
<td>0.148</td>
<td>0.280</td>
<td>0.215</td>
<td>0.228</td>
<td>0.213 ± 0.043</td>
</tr>
</tbody>
</table>
To analyse the data by the CPSV method and obtain a self-consistent data set over the entire scan rate range it was necessary to use the value of M estimated from the plot of $\mu^*$ versus E derived from Global Analysis. In the absence of this approach, small discrepancies in M cause large errors to be introduced into CPSV under quasi-reversible conditions as shown in Table 4.8. This problem can be understood from an examination of equations (4.4) and (4.6). The estimation of M from equation (3.20) based on the experimental conditions (i.e. concentration, electrode area and diffusion coefficient) proved to be generally correct but the slight variation between voltammograms at different scan rates renders this inadequate and individual M values must be estimated at each scan rate. This is readily achieved from the $\mu^*$ versus E plot from Global Analysis. Use of the more accurate $E_{1/2}$ value from Global Analysis gives a value of $d\alpha/dE$ of 0.213 V$^{-1}$ rather than 0.176 V$^{-1}$ using the estimate of $E_{1/2}$ from equation (4.5).

4.4. CONCLUSION.

An examination of the influence of the errors that may be present in a series of experiments to determine the electrode kinetics of a reaction demonstrates that reported results are likely to be dependent upon the method of calculation. Consequently, a comparison of results obtained by both Global Analysis and CPSV methods is extremely useful to ascertain whether any artifact is affecting the outcome of either or both methods. The incorporation of some parameters calculated by Global Analysis may actually improve the CPSV method.

The analysis of data for the reduction of 2-methyl-2-nitropropane show that a self-consistent set of data may be obtained over wide scan rate ranges using Global Analysis combined with CPSV. The analysis results obtained are consistent with previous kinetic investigations of this system.
CHAPTER FIVE

EVALUATION OF ELECTRODE KINETICS USING THE TECHNIQUES OF NORMALISED STEADY STATE VOLTAMMETRY AND DIGITAL SIMULATION OF THE MICRODISC ELECTRODE GEOMETRY WITH THE FAST QUASI-EXPLICIT FINITE DIFFERENCE METHOD.
5. INTRODUCTION.

The Global Analysis procedure which was the subject of Chapters 3 and 4 has the disadvantage that it is applied under conditions where errors, resulting from double layer capacitance and uncompensated resistance, may be introduced. This disadvantage is inherent in the measurement of transient voltammograms under predominantly planar diffusion conditions and therefore any post factum correction will only slightly improve the quality of the errant data. This implies that the experimental conditions need to be improved in order to eliminate these sources of error and steady-state measurements at microelectrodes offer such possibilities. As discussed in Section 1.1.5, steady-state voltammograms are almost unaffected by the presence of double layer capacitance and only minimal uncompensated resistance effects occur.

The microdisc electrode geometry is the most popular microelectrode design probably due to their ease of fabrication and commercial availability. However, theoretical treatments of the diffusion to this surface are very complex and no closed-form analytic solution relating the current and potential is presently available for the general case of slow electron transfer. Although, the limiting cases of fully reversible and fully irreversible electron transfer are tractable under steady state conditions [9]. An empirical current-potential relationship developed by Oldham et al [79] which describes the steady-state response at a microdisc electrode represents one of the more rigorous treatments of this problem. Subsequently, from this relationship a series of 'kinetic indicator diagrams' was produced from which kinetic parameters could be extracted after measuring the $E_{1/4}$, $E_{1/2}$ and $E_{3/4}$ potentials [31]. This method is akin to use of peak-to-peak separations in the tables produced by Nicholson [80] which were used widely in the early analysis of transient cyclic voltammetric data. More recently, development of procedures such as the Global Analysis have improved the
precision and scope of electrode kinetic analyses from transient cyclic voltammetry.

The ideal objective of achieving the total analysis of a steady-state voltammogram for the critical kinetic, thermodynamic and mass transport parameters has yet to be achieved using the kind of procedures developed for transient voltammetry. However, a method proposed by Parker and co-workers, for use with transient voltammetric data, has a conceptual basis that may be useful when used in conjunction with the empirical relationship of Oldham \textit{et al.} The technique of Normalised Potential Sweep Voltammetry [125-127] requires that the current scale is, as suggested by the name, normalised with respect to the peak current and compared with tabulated data over a defined potential range. In this chapter an analogous procedure, which is termed Normalised Steady State Voltammetry, has been formulated and tested using simulated steady-state voltammograms for an inlaid microdisc electrode geometry.

The numerical simulation of the complete steady state voltammogram at microdisc electrodes is also of interest and represents an important approach to solving voltammetric problems in the absence of a closed-form analytical solution. Many treatments of this problem have been produced for the steady state case and they include the Hopscotch algorithm with a uniform space grid [243] and a conformal map [103], theAlternating Direction Implicit method with a uniform space grid [244] and a two dimensional exponential space grid [105], a Galerkin method [27] and an orthogonal collocation procedure [245]. The Fast Quasi-Explicit Finite Difference (FQED) procedure, as developed by Feldberg [91], has been demonstrated to be very robust with respect to the presence of chemical kinetics and has been employed to solve the theory for transient voltammetry [92]. In this chapter, the computationally efficient FQED method will be introduced to steady state voltammetry at the microdisc electrode geometry by incorporating a two dimensional exponentially expanding space grid. The simulated voltammograms will then be evaluated using the
proposed Normalised Steady State Voltammetric method. This procedure will in fact validate the fidelity of the empirical Oldham-Zoski method, the Normalised Steady State Voltammetric method and the FQEFD method if internally consistent data sets are obtained.

5.1. THE THEORY OF NORMALISED STEADY STATE VOLTAMMETRY.

Oldham et al. have shown that the shape of a quasi-reversible steady state voltammogram is given by the following relationship [31]

\[ i = \frac{i_d}{\theta} \left[ 1 + \frac{\pi}{\kappa \theta} \left( \frac{2 \kappa \theta + 3 \pi}{4 \kappa \theta + 3 \pi^2} \right)^{-1} \right] \]  (5.1)

where \( \theta \) and \( \kappa \) are defined by the expressions

\[ \theta = 1 + (D_O/D_R) \exp[nF(E-E^0)/RT] \]  (5.2)

and

\[ \kappa = \kappa^o \exp[-\alpha nF(E-E^0)/RT] \]  (5.3)

respectively and \( \kappa^o \) is defined by equation (1.19). The diffusion limiting current, \( i_d \), is given as [164]

\[ i_d = 4nFDca \]  (5.4)

where \( c \) is the concentration of electroactive species in solution. Equation (5.1) can also be expressed as follows:

\[ \frac{1}{q \theta} - 1 = \frac{2(h + 1)}{3h(2h + \pi)} \]  (5.5)

where \( h \) is defined as

\[ h = \frac{2 \kappa \theta}{3 \pi} = \frac{2 \kappa^o}{3 \pi} \left[ 1 + \frac{D_O}{D_R} \exp \left[ \frac{nF}{RT} (E-E^0) \right] \right] \exp \left[ \frac{-\alpha nF}{RT} (E-E^0) \right] \]  (5.6)
and the normalised current, \( q \), is defined by

\[
q = \frac{i}{i_d} \tag{5.7}
\]

If it is assumed that the diffusion coefficients of the oxidised and reduced species are equivalent then equations (5.2) and (5.6) may be combined to produce the following result

\[
\frac{2\kappa_0^2}{3\pi h} = (\theta - 1)^\alpha \tag{5.8}
\]

If this equation is then expressed as follows

\[
\ln \left( \frac{2\theta}{3\pi h} \right) = \alpha \frac{n_F}{RT} (E - E^o) - \ln(\kappa^o) \tag{5.9}
\]

with a unique value of \( h \) being accessible at each potential from equation (5.5) by solving the following quadratic equation

\[
(6 / (q\theta) - 6)h^2 + [3\pi / (q\theta) - 3\pi - 2]h - 2 = 0 \tag{5.10}
\]

then it is obvious that regression analysis of \( \ln(2\theta/3\pi h) \) versus \((E-E^o)\) will result in an estimate of \( \alpha \) from the gradient and \( \kappa^o \), and therefore \( k^o \), from the intercept.

The potential dependence of \( \alpha \) is also calculable by this procedure, if \( \alpha \) is linearly dependent on potential as follows \([44,50,52-56,61,62,237,239,240]\)

\[
\alpha = \alpha_o + d\alpha/dE \ (E-E^o) \tag{5.11}
\]

where \( d\alpha/dE \) is the potential dependence of the charge transfer coefficient and \( \alpha_o \) is the value of \( \alpha \) at \( E^o \), then equation (5.9) can be recast as follows

\[
\ln \left( \frac{2\theta}{3\pi h} \right) = d\alpha/dE \frac{n_F}{RT} (E - E^o)^2 + \alpha_o \frac{n_F}{RT} (E - E^o) - \ln(\kappa^o) \tag{5.12}
\]

and quadratic regression analysis of \( \ln[2\theta / (3\pi h)] \) versus \((E-E^o)\) will produce
estimates of \(d\alpha/dE\), \(\alpha^0\), and \(\kappa^0\).

If \(\kappa^0\) approaches effective irreversibility, then \(\theta\) from equation (5.2) effectively becomes equal to unity in the region where an accurate measurement of \(q\) is accessible and therefore equation (5.1) simplifies to give

\[
q = \left[ 1 + \frac{\pi}{\kappa} \left( \frac{2\kappa + 3\pi}{4\kappa + 3\pi^2} \right) \right]^{-1}
\]  
(5.13)

This equation can be transformed to produce the following quadratic equation from which \(\kappa\) is readily solved at each potential

\[
4[(1/q)-1]\kappa^2 + [3\pi^2(1/q)-1] - 2\pi]\kappa - 3\pi^2 = 0
\]  
(5.14)

The linear regression analysis of equation (5.3) when converted to the following form

\[
\ln \kappa = -\alpha nF(\text{E-E}^0) / RT + \ln \kappa^0
\]

enables \(\alpha\) to be estimated from the gradient and \(\kappa^0\), therefore \(k^0\), from the intercept. The potential dependence of \(\alpha\) can also be investigated if equation (5.11) is substituted into equation (5.15) as follows

\[
\ln \kappa = -d\alpha/dE[nF / RT](\text{E-E}^0)^2 - \alpha_0 nF(\text{E-E}^0) / RT + \ln \kappa^0
\]  
(5.16)

and quadratic regression analysis is applied.

The analyses so far have all been dependent on the accurate estimate of \(E^0\), although it should be noted that both \(\alpha\) and \(d\alpha/dE\) can be measured under irreversible conditions in the absence of \(E^0\). An estimate of \(E^0\) is possible using equation (5.1) and the definition of \(\theta\) from equation (5.2) to produce the following equation

\[
\frac{1}{q} = \left[ 1 + \frac{\pi}{\kappa\theta} \left( \frac{2\kappa\theta + 3\pi}{4\kappa\theta + 3\pi^2} \right) \right] \exp[nFE/RT] + \left[ 1 + \frac{\pi}{\kappa\theta} \left( \frac{2\kappa\theta + 3\pi}{4\kappa\theta + 3\pi^2} \right) \right]
\]  
(5.17)

The application of linear regression analysis to \(1/q\) versus \(\exp[nFE/RT]\) will enable \(E^0\).
to be calculated as follows

$$E^0 = \frac{RT}{nF} \ln \left( \frac{\text{intercept}}{\text{gradient}} \right)$$

(5.18)

5.1.1. WEIGHTING PROCEDURES USED FOR NORMALISED STEADY STATE VOLTAMMETRY.

In any experiment there may be an inherently different reliability connected with each data point. The statistical analysis of large quantities of data requires that the inaccuracies connected with some of the data are not allowed to bias the remaining data and therefore the results obtained for such an analysis. Weighting of each datum has been advocated for the case of regression analysis [115,228,246]. The weighting selected for the regression analyses performed in this work is based on the weighting proposed for the log-plot analysis of polarographic data [228]. This weighting function is of the form

$$w = (1-q)^2 q^2$$

(5.19)

and the weighted linear and quadratic regression analyses were performed as outlined in Section 3.5. This method of weighting was used in conjunction with equations (5.9), (5.12), (5.14), (5.15) and (5.17).

The analysis for $E^0$ was performed somewhat differently to the weighted procedure just described. This was necessary because it was observed that the most accurate analysis occurred when the data within the vicinity of the actual $E^0$ was analysed. This will generally be the case for quasi-reversible conditions that are close to reversible, with the normalised current being most accurately defined in this region. When near the effectively irreversible regime, the current and therefore the normalised current will be virtually zero in the proximity of $E^0$ and it is under these conditions that an alternative method is required.
The procedure involves a series of iterations in which regression analysis is performed (without a weighting function) on a window of data (± 10 mV) centred initially around \( E_{1/2} \) and then centred on each successive estimate of \( E^o \) until the value of \( E^o \) calculated does not vary. This procedure ensures that the data closest to \( E^o \) is analysed, but there is the problem that eventually a point is reached where the normalised current becomes virtually zero and convergence will cause the estimate of \( E^o \) to fall short of the actual \( E^o \). When the voltammogram is close to reversible only a few iterations were necessary, but for the near irreversible case, in excess of twenty iterations were required.

A weighting function used exclusively for the analysis of \( E^o \) by equation (5.17) takes into account the exponential function which is applied to the independent potential data. Although the potential is usually considered the independent variable in voltammetry, the analysis required by equation (5.17) magnifies any error which can often be considered to be insignificant in most linear analysis systems. This is because the error associated with the exponential function is also exponential in nature. To overcome this situation, equation (5.19) was modified to incorporate an exponential component centred upon the easily determined value of \( E_{1/2} \) as follows

\[
w = (1-q)^2 \, q^2 \exp[-X_f (nF/RT) \left| (E-E_{1/2}) \right|] \tag{5.20}
\]

where \( X_f \) was empirically determined to have the form

\[
X_f = -32.0(E_{1/4} - E_{3/4}) + 3.8 \tag{5.21}
\]

and the minimum value of \( X_f \) applied was 0.05. The \( X_f \) factor is required in order to dilate the exponential function so that the response of the weighting function is in tune with the more dependable data. This data is centred about \( E_{1/2} \) and the potential window can best be described by a relationship based on the Tomes criterion of \( E_{1/4} - E_{3/4} \) [91].
5.2. FAST QUASI-EXPLICIT FINITE DIFFERENCE SIMULATION OF VOLTAMMOGRAMS AT AN INLAID MICRODISC ELECTRODE GEOMETRY.

The development of FQFED follows directly from explicit finite difference (EFD) procedures [91] and the DuFort-Frankel algorithm [247] with an essential component being the use of an exponentially expanding space grid [89,94]. If one considers the simple electron transfer

\[
    \begin{align*}
        F^0 \alpha & \rightarrow A_{\text{soln}}^+ \text{ ne}^- \rightarrow B_{\text{soln}}^-
    \end{align*}
\]

where equation (3.1) has been adapted for the present purpose to avoid confusion over the symbols. In later discussions, the symbols a and b with the appropriate superscripts and subscripts will correspond to the normalised concentrations of species A and B respectively and \( R_0 \) to the normalised electrode radius in the simulation.

Reference to the sphericity factor, \( \sigma \), as defined in equation (1.5) enables the predominant diffusion (spherical or planar) conditions to be defined from the criteria given by equation (1.6). Consequently, the value of \( \sigma \) can be used as an indicator for determining the required space grid geometry. Due to the constraints described below, it has been determined that \( D^* \), the dimensionless diffusion coefficient parameter in the simulation, should be maximised to ensure accuracy and stability. Empirically, \( D^* \) is given by equation (5.23)

\[
    D^* = 10^{-5} / (\nu \Delta t)^2
\]

where \( \Delta t \) is the simulation time increment. However, \( \nu \Delta t \) should not exceed 0.001V for the accurate simulation of voltammetric data. Therefore, from equations (1.5) and (5.23), and using the maximum allowable value of \( \nu \Delta t \), the value of \( R_0 \) can be found from equation (5.24).
\[ R_0 = \sqrt{\frac{10^{-5}RT}{Fo^2(u\Delta t)^3}} \]  

(5.24)

There is the additional constraint that \( R_0 \) should be greater than or equal to 25 to ensure that an adequate number of grid spaces are used to characterise the electrode surface. This will seldom be the case for a simulation of the steady state with \( \sigma > 40 \) and subsequently, the value of \( u\Delta t \) will need to be reduced so that it is less than 0.001\( V \). In this case, the value of \( R_0 \) is set at the minimum allowable level and \( u\Delta t \) is calculated as follows:

\[ u\Delta t = \left( \frac{10^{-5}RT}{FRo^2\sigma^2} \right)^{1/3} \]

(5.25)

and \( D^* \) is calculated on the basis of equation (5.23). Generally, the values of \( R_0, u\Delta t \) and \( D^* \) will have been optimised for use in the simulation by following this procedure.

5.2.1. THE TWO DIMENSIONAL EXPONENTIALLY EXPANDING SPACE GRID.

The two dimensions associated with the space grid are the direction normal to the electrode surface, denoted as the Y-axis, and the direction parallel to the electrode surface denoted as the R-axis. In terms of the exponentially expanding space grid for the Y-axis, there are two limiting cases for the calculation of the maximum number of space elements required for the simulation. The first, \( (i_{Ymax})_{\text{planar}} \), is for the case of planar diffusion (transient voltammetry) and the second, \( (i_{Ymax})_{\text{ss}} \), is for under steady-state conditions where the diffusion layer thickness is greater than for the planar diffusion situation. The maximum value derived from the following two equations is used to calculate the number of space elements required normal to the electrode surface.
\[(i_{Y_{\text{max}}})_{\text{planar}} = \frac{\ln(6(\exp[\beta] - 1))\sqrt{D^* m_{l_{\text{max}}}}}{} + 1}{\beta}\] (5.26)

where \(\beta\) characterises the degree of exponential expansion of the spatial grid [89], which was set equal to 0.5 and \((m_l)_{\text{max}}\) is the maximum number of iterations [89].

\[(i_{Y_{\text{max}}})_{\text{ss}} = \frac{\ln(1000(\exp[\beta] - 1))R_o + 1}{\beta}\] (5.27)

The factor of 1000 in equation (5.27) arises from the fact that under steady state conditions \(\sigma = 40\) and the minimum value of \(R_o\) is set at 25.

A related situation arises for the calculation of the maximum number of elements parallel to the electrode surface. However, in this case the exponentially expanding grid has two components which are defined with their origins at the edge of the microdisc electrode where the maximum current density and diffusive flux are known to occur [9,30]. This ensures that the spatial arrangement has the greatest density where the concentration changes are at a maximum. The number of elements representing the electrode surface is given by

\[i_{R_o} = 1 + \frac{\ln(R_o(\exp[\beta] - 1) + 1)}{\beta}\] (5.28)

and the total number of elements required is the maximum of the following two equations.

\[(i_{R_{\text{max}}})_{\text{planar}} = i_{R_o} + \frac{\ln(6(\exp[\beta] - 1))\sqrt{D^* m_{l_{\text{max}}}}}{} + 1}{\beta}\] (5.29)

\[(i_{R_{\text{max}}})_{\text{ss}} = i_{R_o} + \frac{\ln(1000(\exp[\beta] - 1))R_o + 1}{\beta}\] (5.30)

The geometry of the spatial grid is optimised by taking the above considerations into account.

The dimensionless diffusion parameters are calculated as follows: The
dimensionless diffusion parameter contains three subscripts, the first indicates the axis, the second denotes the boundary of the element (1 for inner and 2 for outer) and the third is the index with the Y or R denoting the axis of the index. In the $Y$-direction, the outer boundary of the $i_Y^{th}$ element is

$$D_{Y2i_Y}^* = D^* / \exp[2\beta(i_Y - 3/4)]$$  \hspace{1cm} (5.31)

and for the inner boundary of the $i_Y^{th}$ element

$$D_{Y1i_Y}^* = D^* / \exp[2\beta(i_Y - 5/4)] \hspace{1cm} i_Y \geq 2$$  \hspace{1cm} (5.32)

with a unique value required for the inner boundary of the first element.

$$D_{Y11}^* = \frac{D^*(\exp[\beta] - 1)}{\exp[1/2\beta] - 1}$$  \hspace{1cm} (5.33)

For the $R$-axis, it is necessary to consider two separate regions with the first being for $i_R > i_{Ro}$ (i.e. the region corresponding to the insulated plane of the electrode). This thickness of the $i_R^{th}$ element is

$$\Delta R_{i_R} = \exp[\beta(i_R - i_{Ro} - 1)]$$  \hspace{1cm} (5.34)

the spatial location of the outer boundary of the $i_R^{th}$ element is

$$R_{2i_R} = R_{o} + \frac{\exp[\beta(i_R - i_{Ro})] - 1}{\exp[\beta] - 1}$$  \hspace{1cm} (5.35)

and the inner boundary is

$$R_{1i_R} = R_{2i_R} - \Delta R_{i_R}$$  \hspace{1cm} (5.36)

The dimensionless diffusion parameters for the outer boundary of the $i_R^{th}$ element is

$$D_{R2i_R}^* = D^* / \{\Delta R_{2i_R}[\Delta R_{i_R}^{-1/2}(\Delta R_{i_R})^2 / R_{2i_R}]\}$$  \hspace{1cm} (5.37)
and the inner boundary is

\[
D^*_{RiR} = D^* / \left[ \Delta \tilde{R}_{iR} \left( \Delta R_{iR} + \frac{1}{2}(\Delta R_{iR})^2 / R_{iR} \right) \right]
\]  

(5.38)

where \( \Delta \tilde{R}_{iR} = \exp[\beta(i_R - i_{Ro} - 1/2)] \) and \( \Delta \tilde{R}_{2iR} = \exp[\beta(i_R - i_{Ro} - 3/2)] \). The inner boundary of the first element beyond \( i_{Ro} \) has a unique dimensionless diffusion parameter corresponding to

\[
D^*_{RiRo+1} = D^* / \left[ 2 \tilde{R}_{iRo+1} \left( \Delta R_{iRo+1} + \frac{1}{2}(\Delta R_{iRo+1})^2 / R_{o} \right) \right]
\]  

(5.39)

where \( \tilde{R}_{iR} \) is the spatial position in the element corresponding to the concentration assigned to the grid element and is given by

\[
\tilde{R}_{iR} = \frac{\exp[\beta(i_R - i_{Ro} - 1/2)] - 1}{\exp[\beta] - 1}
\]  

(5.40)

For \( i_R < i_{Ro} \) (i.e. the region corresponding to the electrode surface) a similar procedure is followed with the elements increasing in size when traversing from the perimeter to the centre of the electrode. This thickness of the \( i_R \)th element is

\[
\Delta R_{iR} = \exp[\beta(i_{Ro} - i_R)]
\]  

(5.41)

the spatial location of the outer boundary of the \( i_R \)th element is

\[
R_{2iR} = R_0 + \frac{\exp[\beta(i_{Ro} - i_R)] - 1}{\exp[\beta] - 1}
\]  

(5.42)

and the inner boundary is given by equation (5.36). The dimensionless diffusion parameters for the outer boundary of the \( i_R \)th element is the same as equation (5.37) and the inner boundary is given by equation (5.38) but the following changes are required with

\[
\Delta \tilde{R}_{2iR} = \exp[\beta(i_{Ro} - i_R - 1/2)]
\]  

(5.43)
\[ \Delta \bar{R}_{11} = \exp[\beta(i_{R_0} - i_R + 1/2)] \]  

(5.44)

The outer boundary of the element adjacent to \( i_{R_0} \) has a unique dimensionless diffusion parameter corresponding to

\[ D^*_{R2i_{R_0}} = D^* / \{ 2\bar{R}_{i_{R_0}} \Delta R_{i_{R_0}} - 1/2(\Delta R_{i_{R_0}})^2 / R_0 \} \]  

(5.45)

where \( \bar{R}_{i_{R}} \) is now given by

\[ \bar{R}_{i_{R}} = \frac{\exp[\beta(i_{R_0} - i_R + 1/2)] - 1}{\exp[\beta] - 1} \]  

(5.46)

The dimensionless diffusion parameter for the inner boundary of the second element is

\[ D^*_{R12} = D^* / \{ (R_0 - \bar{R}_2)(\Delta R_2 + 1/2(\Delta R_2)^2 / R_{12}) \} \]  

(5.47)

The value for the inner boundary of the first element equal to zero (i.e. \( D^*_{11} = 0 \)) with the value for the outer boundary as follows

\[ D^*_{R21} = D^* / \left\{ 1/2(R_0 - \bar{R}_2)^2 \left[ R_0 - \left( \frac{\exp[\beta(i_{R_0} - 1)] - 1}{\exp[\beta] - 1} \right) \right] \right\} \]  

(5.48)

Figure 5.1 depicts a subsection of the two-dimensional grid for steady state conditions with \( \sigma = 41.4 \) and shows that the smaller grid elements are grouped at the edge of the electrode and close to the electrode surface which are the regions where it is most critical to accurately represent the concentration profile. The whole grid has dimensions which extend approximately 640a (where a is the electrode radius) in both Y and R directions. Consequently, if the whole grid had been displayed, insufficient resolution would be available to observe the electrode or the smaller grid elements.
Figure 5.1. Schematic diagram of a segment of the two dimensional expanding grid where the grid lines represent the spatial centre of each array element.
5.2.2. THE ALGORITHM FOR THE SIMULATION.

It is essential that the initial conditions are correctly adjusted otherwise the simulation will initially oscillate and the accumulation of errors may create inaccuracy [91]. If $E_{\text{start}}$ is the initial potential, then the initial dimensionless concentrations of species $A$ and $B$ will be

$$a_{\text{start}} = \frac{w_e}{1 + w_e} \quad (5.49)$$

$$b_{\text{start}} = \frac{1}{1 + w_e} \quad (5.50)$$

where $w_e = \exp((nF/RT)(E_{\text{start}} - E^0))$. The initial concentrations of all the grid elements are initially set to be equal to these two starting concentrations

$$a^{iY,iR} = a^{iY,iR} = a_{\text{start}} \quad (5.51)$$

$$b^{iY,iR} = b^{iY,iR} = b_{\text{start}} \quad (5.52)$$

where the superscripts ('') and (') denote the extant and new concentrations separated by $\Delta t$ [91] and the subscripts indicate the indices relating to the $Y$ and $R$ co-ordinate system.

If Butler-Volmer kinetics are assumed, then the following equations will apply

$$k^*_{ef} = k^* \exp((\alpha nF/RT)(E - E^0)) \quad (5.53)$$

$$k^*_{eb} = k^* \exp((1 - \alpha)(nF/RT)(E - E^0)) \quad (5.54)$$

where $E$ is the potential and is incremented by $\pm \upsilon \Delta t$ during each cycle, where the sign of $\upsilon \Delta t$ designates the direction of the potential sweep. The parameter $k^*$ is the dimensionless heterogeneous rate constant and is calculated from the expression

$$k^* = \frac{ak^*D^*}{DR_0} \quad (5.55)$$
The FQED equations for the concentration change in the electroactive region of the electrode with $i_R \leq i_{R0}$ and $i_Y = 1$ are

$$\Delta a_{1,R} = (1/Q_a)\{D^*Y_{21}(a''_{2,R} - a'_{1,R}) + D^*R_{21i_R}(a''_{1,R}+1 - a'_{1,R})$$
$$+ D^*R_{11i_R}(a''_{1,R} - 1 - a'_{1,R}) + w_{ef}(b'_{1,i_R} + \Delta b_{1,i_R}) - w_{eb}a'_{1,i_R}\} \quad (5.56)$$

where

$$Q_a = 1 + w_{eb} + D^*Y_{21} + D^*R_{21i_R} + D^*R_{11i_R} \quad (5.57)$$

$$\Delta b_{1,i_R} = (1/Q_b)\{D^*Y_{21}(b''_{2,i_R} - b'_{1,i_R}) + D^*R_{21i_R}(b''_{1,i_R}+1 - b'_{1,i_R})$$
$$+ D^*R_{11i_R}(b''_{1,i_R} - 1 - b'_{1,i_R}) + w_{ef}(a'_{1,i_R} + \Delta a_{1,i_R}) - w_{eb}b'_{1,i_R}\} \quad (5.58)$$

where

$$Q_b = 1 + w_{ef} + D^*Y_{21} + D^*R_{21i_R} + D^*R_{11i_R} \quad (5.59)$$

The terms $w_{ef}$ and $w_{eb}$ are defined as

$$w_{ef} = k_{ef}^* / (1 + k_{ef}^*/D^*Y_{11} + k_{eb}^*/D^*Y_{11}) \quad (5.60)$$

$$w_{eb} = k_{eb}^* / (1 + k_{ef}^*/D^*Y_{11} + k_{eb}^*/D^*Y_{11}) \quad (5.61)$$

The simultaneous equations (5.56) and (5.57) are linear and readily solved algebraically to give the changes in concentration for each species at the electrode surface.

For the electroinactive region adjacent to the insulator surface, where $i_R > i_{R0}$ and $i_Y = 1$, the changes in concentration are calculated as follows

$$\Delta a_{1,R} = (1/Q)\{D^*Y_{21}(a''_{2,R} - a'_{1,R}) + D^*R_{21i_R}(a''_{1,R}+1 - a'_{1,R})$$
$$+ D^*R_{11i_R}(a''_{1,R} - 1 - a'_{1,R})\} \quad (5.62)$$

$$\Delta b_{1,i_R} = (1/Q)\{D^*Y_{21}(b''_{2,i_R} - b'_{1,i_R}) + D^*R_{21i_R}(b''_{1,i_R}+1 - b'_{1,i_R})$$
$$+ D^*R_{11i_R}(b''_{1,i_R} - 1 - b'_{1,i_R})\} \quad (5.63)$$

where

$$Q = 1 + D^*Y_{21} + D^*R_{21i_R} + D^*R_{11i_R} \quad (5.64)$$
The changes in concentrations for the remaining elements which represent the bulk solution are calculated from the following equations for $i_Y \geq 2$ and all $i_R$.

$$\Delta a_{i_Y,i_R} = (1/Q)\{D^*_Y 2i_Y (a''_{i_Y+1,i_R} - a'_{i_Y,i_R}) + D^* Y 1i_Y (a''_{i_Y-1,i_R} - a'_{i_Y,i_R}) \}
+ D^*_R 2i_R (a''_{i_Y,i_R+1} - a'_{i_Y,i_R}) + D^* R 1i_R (a''_{i_Y,i_R-1} - a'_{i_Y,i_R}) \} \quad (5.65)$$

$$\Delta b_{i_Y,i_R} = (1/Q)\{D^*_Y 2i_Y (b''_{i_Y+1,i_R} - b'_{i_Y,i_R}) + D^* Y 1i_Y (b''_{i_Y-1,i_R} - b'_{i_Y,i_R}) \}
+ D^*_R 2i_R (b''_{i_Y,i_R+1} - b'_{i_Y,i_R}) + D^* R 1i_R (b''_{i_Y,i_R-1} - b'_{i_Y,i_R}) \} \quad (5.66)$$

where $$Q = 1 + D^*_Y 2i_Y + D^* Y 1i_Y + D^*_R 2i_R + D^* R 1i_R \quad (5.67)$$

Upon the completion of one iterative cycle the concentrations of each grid element are updated using the following protocol for all $i_Y$ and all $i_R$

$$X_{temp} \leftarrow X'_{i_Y,i_R} + 2\Delta X_{i_Y,i_R}$$

$$X'_{i_Y,i_R} \leftarrow X''_{i_Y,i_R} \quad (5.68)$$

$$X''_{i_Y,i_R} \leftarrow X_{temp}$$

where $X$ is the generic symbol for $a$ and $b$. The procedure $p \leftarrow q$ means: Set the value of $p$ equal to the present value of $q$. The flux for each grid element at the electrode surface is given by

$$f_{i_R} = w_{ef}(a'_{1,i_R} + \Delta a_{1,i_R}) - w_{eb}(b'_{1,i_R} + \Delta b_{1,i_R}) \quad (5.69)$$

and the normalised current function for transient voltammetry equivalent to $\sqrt{\pi\chi(\sigma t)} [248]$ can be calculated as follows for each potential increment

$$f_{CV} = \frac{\sum f_{i_R}^* a_{i_R}}{\sqrt{\frac{nF D^*}{RT \omega \Delta t}}} \quad (5.70)$$
Also, the normalised current function under steady state conditions, which will be
designated \( q \), can be calculated

\[
q = \frac{\pi R_0 i_R}{4D^*} \sum_{1}^{f_{i_R} A_{i_R}}
\]  \hspace{1cm} (5.71)

In both equations (5.70) and (5.71), the symbol \( A_{i_R} \) is the area of the grid element in
the electroactive region of the grid and is calculated based on the microdisc geometry
of the electrode (i.e. each element is considered to be a concentric ring in the
cylindrical co-ordinate system and the area of the element is equal to the area of the
circle at the outer boundary minus the area of the circle at the inner boundary).

The simulation was programmed in compiled QUICK BASIC Version 4.0
using double precision and the CPU times (on a 25 MHz 80486 microprocessor with
built in math co-processor) varied between 3 and 30 minutes depending upon \( \sigma \). The
sphericity factor was varied between 41.4 and 160.3 but was mostly equal to 71.7 for
steady state simulations. The program "MICSIM.BAS" is listed in Appendix I

5.2.3. THE SIMULATION CONDITIONS.

The radius of the microdisc electrode assumed in the simulation was 1 \( \mu \text{m} \), the
electroreactant diffusion coefficient was \( 1 \times 10^{-9} \text{ m}^2 \text{s}^{-1} \) and the temperature was
298.15 K. The value of \( E^\circ \) for all the simulations was 0.000 V and the initial potential
was set at +0.200 V. The final potential was varied depending on the potential
window required to obtain a reasonable representation of the voltammogram.
However, under effectively irreversible conditions with \( \alpha \) equal to 0.1, the \( E_{1/2} \) and
Tomes criterion of \( E_{1/4} - E_{3/4} \) [78] could not be obtained because the wave was too
dilated and shifted too far from \( E^\circ \) on the potential scale but an analysis was possible
because the limiting current was known under reversible conditions.

As noted previously if \( \sigma \) is greater than 40 then it is considered that the steady
state has been attained [18]. Table 5.1 contains a comparison of the $E_{1/2}-E^o$ and Tornes criterion ($E_{1/4}-E_{3/4}$) results obtained for the three sphericity factors of 41.4, 71.7 and 160.3 and from an examination of the results it can be concluded that there is little difference between the values obtained from the simulated curves. There are slight differences between the simulated results and the values calculated from the curves given in reference 79, the consequence of these differences is intensively examined in section 5.3.

With the sphericity factor equal to 41.4, a slight peak was observed from an examination of the resultant simulated data under reversible conditions. Also, if the sphericity factor is set too high, the potential increments are substantially reduced and the accuracy is diminished due to an accumulation of errors. Therefore, a sphericity factor of 71.7 was used in the remaining analyses.

5.3. RESULTS AND DISCUSSION.

The validity of the empirical relationship between the current and the potential over a large range of values for the kinetic parameter, $\kappa^o$, was tested by applying the Normalised Steady State Voltammetric procedure to simulated steady state voltammograms and the results are listed in Table 5.2. The value of $E^o$ used in the analyses was 0.000 V and this was necessary in order to eliminate any inaccuracies bought about by an error in $E^o$ (this will be discussed later). The value of $\alpha$ was set at 0.500 and there was no deliberately added potential dependence in $\alpha$. The complete Normalised Steady State Voltammetric analysis is demonstrated in Figure 5.2(a,b,c,d) using a simulation curve where $\kappa^o = 1.000$, $\alpha = 0.500$ and $d\alpha/dE = 0$. From the data in Table 5.2, it is clear that the Normalised Steady State Voltammetric analysis procedure produces excellent results once the response is sufficiently removed from the reversible regime and the usable quasi-reversible range is entered (i.e. $\kappa^o < 20$).
Table 5.1. A comparison of $E_{1/2} - E^\circ$ and $E_{1/4} - E_{3/4}$ values measured from the simulated voltammograms with values estimated from reference 79.

<table>
<thead>
<tr>
<th>$x^\circ$</th>
<th>Reversible</th>
<th>$E_{1/2} - E^\circ$ Reference 79</th>
<th>$\sigma = 41.4$</th>
<th>$\sigma = 71.7$</th>
<th>$\sigma = 160.3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>$E_{1/2} - E^\circ$</td>
<td>0.0000</td>
<td>0.0004</td>
<td>0.0002</td>
<td>0.0001</td>
</tr>
<tr>
<td></td>
<td>$E_{1/4} - E_{3/4}$</td>
<td>0.0565</td>
<td>0.0562</td>
<td>0.0563</td>
<td>0.0564</td>
</tr>
</tbody>
</table>

| 10        | $E_{1/2} - E^\circ$ | # | -0.0003 | -0.0005 | -0.0006 |
|           | $E_{1/4} - E_{3/4}$ | # | 0.0570 | 0.0571 | 0.0572 |

| 5         | $E_{1/2} - E^\circ$ | -0.0036 | -0.0029 | -0.0031 | -0.0033 |
|           | $E_{1/4} - E_{3/4}$ | 0.0607 | 0.0601 | 0.0602 | 0.0603 |

| 1         | $E_{1/2} - E^\circ$ | -0.0068 | -0.0059 | -0.0061 | -0.0063 |
|           | $E_{1/4} - E_{3/4}$ | 0.0645 | 0.0636 | 0.0637 | 0.0638 |

| 0.5       | $E_{1/2} - E^\circ$ | -0.0277 | -0.0266 | -0.0268 | -0.0269 |
|           | $E_{1/4} - E_{3/4}$ | 0.0873 | 0.0856 | 0.0856 | 0.0857 |

| 0.1       | $E_{1/2} - E^\circ$ | -0.1221 | -0.1211 | -0.1211 | -0.1212 |
|           | $E_{1/4} - E_{3/4}$ | 0.1187 | 0.1168 | 0.1170 | 0.1172 |

| 0.05      | $E_{1/2} - E^\circ$ | # | -0.1563 | -0.1564 | -0.1564 |
|           | $E_{1/4} - E_{3/4}$ | # | 0.1179 | 0.1180 | 0.1182 |

| 0.01      | $E_{1/2} - E^\circ$ | -0.2402 | -0.2389 | -0.2389 | -0.2390 |
|           | $E_{1/4} - E_{3/4}$ | 0.1204 | 0.1182 | 0.1184 | 0.1186 |

# Unable to accurately determine these values from reference 79.

All potentials given as Volts.
Table 5.2. The effect of $\kappa^\circ$ on the analysis with $\sigma = 71.7$.

<table>
<thead>
<tr>
<th>Style of Analysis</th>
<th>$\kappa^\circ$</th>
<th>$\kappa^\circ=50.00$</th>
<th>$\kappa^\circ=10.00$</th>
<th>$\kappa^\circ=5.000$</th>
<th>$\kappa^\circ=1.000$</th>
<th>$\kappa^\circ=0.5000$</th>
<th>$\kappa^\circ=0.1000$</th>
<th>$\kappa^\circ=0.05000$</th>
<th>$\kappa^\circ=0.01000$</th>
</tr>
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<tr>
<td></td>
<td>$\chi^2$</td>
<td>QR</td>
<td>QR</td>
<td>QR</td>
<td>QR</td>
<td>QR</td>
<td>QR</td>
<td>QR</td>
<td>QR</td>
</tr>
<tr>
<td>Linear</td>
<td></td>
<td>83.76</td>
<td>11.86</td>
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<td>0.0993</td>
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<tr>
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<td>0.463</td>
<td>0.499</td>
<td>0.502</td>
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<td>0.509</td>
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<td>$\chi^2$</td>
<td>86.89</td>
<td>11.96</td>
<td>5.673</td>
<td>1.044</td>
<td>0.5121</td>
<td>0.1010</td>
<td>0.0917</td>
<td>0.05059</td>
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<tr>
<td></td>
<td>$\alpha$</td>
<td>0.466</td>
<td>0.503</td>
<td>0.504</td>
<td>0.505</td>
<td>0.505</td>
<td>0.500</td>
<td>0.527</td>
<td>0.497</td>
</tr>
<tr>
<td></td>
<td>$\frac{\Delta \alpha}{dE}$</td>
<td>1.078</td>
<td>0.238</td>
<td>0.072</td>
<td>-0.033</td>
<td>-0.033</td>
<td>-0.034</td>
<td>0.040</td>
<td>-0.034</td>
</tr>
</tbody>
</table>

$\frac{\Delta \alpha}{dE}$ given as $V^{-1}$.
Figure 5.2. (a) A simulated steady state voltammogram with $\sigma = 71.7$, $\kappa^c = 1.00$ and $\alpha = 0.500$. (b) The weighting function as given by equation (5.19).
Figure 5.2 (cont.). (c) A plot of equation (5.9) with the weighted least squares line of best fit. (d) A plot of equation (5.17) with the weighted least squares line of best fit.
Furthermore, Figure 5.2(b) calculated from equation (5.19) demonstrates that the weighting procedure effectively discriminates against errors which occur when weighting is absent when compared to Figure 5.2(c). A comparison of the results obtained in what is the effectively irreversible regime using both quasi-reversible (QR) and irreversible (IR) analysis indicates that \( \kappa^\circ \) should be less than or equal to 0.01 before the irreversible analysis procedure is invoked. The simulation assumes that \( \frac{d\alpha}{dE} = 0 \). However, the estimation of \( \frac{d\alpha}{dE} \) in this circumstance for \( \kappa^\circ < 5.000 \), resulted in a consistently small and negative value indicating that the procedure will be viable for experimental voltammograms, provided that the system is not too close to reversible.

The ability to accurately analyse voltammograms in both the quasi-reversible and the irreversible kinetic regimes was also examined with different values of \( \alpha \). Results are presented in Table 5.3 and the analysis is generally excellent with the only important inaccuracies occurring as \( \alpha \) approaches unity where the effective amount of data available for the analysis is substantially reduced. The origin of this problem is apparent from the use of the Toms criterion where for \( \alpha \) equal to 0.1, \( E_{1/4} - E_{3/4} \) is 330 mV but for \( \alpha \) equal to 0.9, \( E_{1/4} - E_{3/4} \) is only 61 mV. Again the apparent value of \( \frac{d\alpha}{dE} \) is small and negative whereas it should be zero, also the magnitude of \( \frac{d\alpha}{dE} \) increases as \( \alpha \) increases due to an effective decrease occurring in the amount of data used in the analysis. For the irreversible situation where \( \kappa^\circ = 0.01000 \), there is essentially no difference between the QR and IR analyses as expected based on the results of Table 5.2.

The analysis for the potential dependent \( \alpha \) using equations (5.12) and (5.16) was investigated using the three values of \( \frac{d\alpha}{dE} \) given in Table 5.4. The analysis can indeed determine \( \frac{d\alpha}{dE} \) with a reasonable degree of accuracy. As expected, the accuracy improves as \( \frac{d\alpha}{dE} \) increases and also as the degree of irreversibility increases. The linear analysis using equations (5.9) and (5.15) fails to maintain any
Table 5.3. The effect of $\alpha$ on the analysis with $\sigma = 71.7$.

<table>
<thead>
<tr>
<th>$\kappa=1.000$</th>
<th>$\alpha=0.100$</th>
<th>$\alpha=0.200$</th>
<th>$\alpha=0.300$</th>
<th>$\alpha=0.400$</th>
<th>$\alpha=0.500$</th>
<th>$\alpha=0.600$</th>
<th>$\alpha=0.700$</th>
<th>$\alpha=0.800$</th>
<th>$\alpha=0.900$</th>
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</thead>
<tbody>
<tr>
<td>$E_{1/2}$</td>
<td>-0.0527</td>
<td>-0.0398</td>
<td>-0.0339</td>
<td>-0.0299</td>
<td>-0.0268</td>
<td>-0.0244</td>
<td>-0.0230</td>
<td>-0.0215</td>
<td>-0.0200</td>
</tr>
<tr>
<td>$E_{1/4} - E_{3/4}$</td>
<td>0.3300</td>
<td>0.1729</td>
<td>0.1229</td>
<td>0.0996</td>
<td>0.0636</td>
<td>0.0768</td>
<td>0.0704</td>
<td>0.0654</td>
<td>0.0614</td>
</tr>
<tr>
<td>$QR$ Linear</td>
<td>$\kappa$</td>
<td>1.029</td>
<td>1.035</td>
<td>1.039</td>
<td>1.042</td>
<td>1.044</td>
<td>1.045</td>
<td>1.046</td>
<td>1.047</td>
</tr>
<tr>
<td></td>
<td>$\alpha$</td>
<td>0.102</td>
<td>0.203</td>
<td>0.305</td>
<td>0.406</td>
<td>0.508</td>
<td>0.611</td>
<td>0.714</td>
<td>0.817</td>
</tr>
<tr>
<td>$QR$ Quadratic</td>
<td>$\kappa$</td>
<td>1.034</td>
<td>1.041</td>
<td>1.042</td>
<td>1.043</td>
<td>1.044</td>
<td>1.044</td>
<td>1.045</td>
<td>1.045</td>
</tr>
<tr>
<td></td>
<td>$\alpha$</td>
<td>0.100</td>
<td>0.199</td>
<td>0.300</td>
<td>0.402</td>
<td>0.505</td>
<td>0.608</td>
<td>0.710</td>
<td>0.813</td>
</tr>
<tr>
<td>$do/dE$</td>
<td>-0.002</td>
<td>-0.015</td>
<td>-0.025</td>
<td>-0.032</td>
<td>-0.037</td>
<td>-0.047</td>
<td>-0.061</td>
<td>-0.079</td>
<td>-0.101</td>
</tr>
</tbody>
</table>

| $\kappa=0.01000$ | $E_{1/2}$     | -0.5973        | -0.3981        | -0.2985        | -0.2389        | -0.1994        | -0.1706        | -0.1493        | -0.1330        |
|                 | $E_{1/4} - E_{3/4}$ | -0.2973       | 0.1987         | 0.1482         | 0.1184         | 0.0991         | 0.0847         | 0.0738         | 0.0654         |
| $QR$ Linear     | $\kappa$      | 0.01010        | 0.00967        | 0.00961        | 0.00959        | 0.00957        | 0.00955        | 0.00953        | 0.00952        | 0.00950        |
|                 | $\alpha$      | 0.100          | 0.203          | 0.305          | 0.406          | 0.508          | 0.610          | 0.712          | 0.815          | 0.917          |
| $QR$ Quadratic  | $\kappa$      | 0.01010        | 0.01047        | 0.01024        | 0.01027        | 0.01029        | 0.01035        | 0.01036        | 0.01038        | 0.01040        |
|                 | $\alpha$      | 0.100          | 0.195          | 0.296          | 0.394          | 0.491          | 0.589          | 0.686          | 0.783          | 0.880          |
| $do/dE$         | 0.000          | -0.007         | -0.011         | -0.021         | -0.034         | -0.054         | -0.076         | -0.103         | -0.136         |
| $IR$ Linear     | $\kappa$      | 0.01007        | 0.00967        | 0.00961        | 0.00958        | 0.00955        | 0.00952        | 0.00948        | 0.00944        | 0.00940        |
|                 | $\alpha$      | 0.100          | 0.203          | 0.305          | 0.406          | 0.508          | 0.611          | 0.712          | 0.815          | 0.918          |
| $QR$ Quadratic  | $\kappa$      | 0.00993        | 0.01044        | 0.01022        | 0.01025        | 0.01029        | 0.01028        | 0.01027        | 0.01028        | 0.01029        |
|                 | $\alpha$      | 0.102          | 0.195          | 0.296          | 0.394          | 0.492          | 0.590          | 0.688          | 0.785          | 0.881          |
| $do/dE$         | 0.001          | -0.006         | -0.010         | -0.020         | -0.033         | -0.052         | -0.073         | -0.101         | -0.137         |

All potentials given as Volts and $do/dE$ given as V$^{-1}$. 146
<table>
<thead>
<tr>
<th>Potential Dependence of α</th>
<th>$\chi^2=50.00$</th>
<th>$\chi^2=10.00$</th>
<th>$\chi^2=5.000$</th>
<th>$\chi^2=1.000$</th>
<th>$\chi^2=0.5000$</th>
<th>$\chi^2=0.1000$</th>
<th>$\chi^2=0.05000$</th>
<th>$\chi^2=0.01000$</th>
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<tbody>
<tr>
<td>$\text{do/dE}=0.1$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E_{1/2}$</td>
<td>-0.0007</td>
<td>-0.0031</td>
<td>-0.0061</td>
<td>-0.0269</td>
<td>-0.0477</td>
<td>-0.1240</td>
<td>-0.1617</td>
<td>-0.2514</td>
</tr>
<tr>
<td>$E_{1/4} - E_{3/4}$</td>
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<td>0.0605</td>
<td>0.0639</td>
<td>0.0867</td>
<td>0.1026</td>
<td>0.1239</td>
<td>0.1269</td>
<td>0.1323</td>
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<td>Linear $\chi^2$</td>
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<td>1.044</td>
<td>0.5152</td>
<td>0.1054</td>
<td>0.0997</td>
<td>0.05438</td>
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<tr>
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<td>0.463</td>
<td>0.497</td>
<td>0.498</td>
<td>0.494</td>
<td>0.480</td>
<td>0.488</td>
<td>0.473</td>
<td>0.475</td>
</tr>
<tr>
<td>Quadratic $\chi^2$</td>
<td>86.79</td>
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<td>5.672</td>
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<td>0.5122</td>
<td>0.1008</td>
<td>0.0919</td>
<td>0.05045</td>
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<tr>
<td>$\alpha$</td>
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<td>0.503</td>
<td>0.504</td>
<td>0.504</td>
<td>0.501</td>
<td>0.526</td>
<td>0.499</td>
<td>0.508</td>
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<tr>
<td>$\text{do/dE}$</td>
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<td>0.168</td>
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<td>0.068</td>
<td>0.074</td>
<td>0.094</td>
<td>0.078</td>
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<tr>
<td>$E_{1/2}$</td>
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<td>-0.0031</td>
<td>-0.0061</td>
<td>-0.0269</td>
<td>-0.0482</td>
<td>-0.1315</td>
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<tr>
<td>$E_{1/4} - E_{3/4}$</td>
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<td>0.0605</td>
<td>0.0644</td>
<td>0.0882</td>
<td>0.1070</td>
<td>0.1407</td>
<td>0.1511</td>
<td>0.1848</td>
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<tr>
<td>Linear $\chi^2$</td>
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<td>11.72</td>
<td>5.593</td>
<td>1.050</td>
<td>0.5301</td>
<td>0.1432</td>
<td>0.1373</td>
<td>0.09835</td>
</tr>
<tr>
<td>$\alpha$</td>
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<td>0.492</td>
<td>0.489</td>
<td>0.473</td>
<td>0.459</td>
<td>0.387</td>
<td>0.392</td>
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<td>0.0992</td>
<td>0.0931</td>
<td>0.04904</td>
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<tr>
<td>$\alpha$</td>
<td>0.466</td>
<td>0.503</td>
<td>0.503</td>
<td>0.505</td>
<td>0.505</td>
<td>0.509</td>
<td>0.512</td>
<td>0.508</td>
</tr>
<tr>
<td>$\text{do/dE}$</td>
<td>1.408</td>
<td>0.505</td>
<td>0.358</td>
<td>0.273</td>
<td>0.278</td>
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<td>0.324</td>
<td>0.306</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E_{1/2}$</td>
<td>-0.0007</td>
<td>-0.0031</td>
<td>-0.0061</td>
<td>-0.0269</td>
<td>-0.0492</td>
<td>-0.1404</td>
<td>-0.1939</td>
<td>-0.3976</td>
</tr>
<tr>
<td>$E_{1/4} - E_{3/4}$</td>
<td>0.0575</td>
<td>0.0605</td>
<td>0.0649</td>
<td>0.0902</td>
<td>0.1120</td>
<td>0.1700</td>
<td>0.2081</td>
<td>-</td>
</tr>
<tr>
<td>Linear $\chi^2$</td>
<td>81.74</td>
<td>11.62</td>
<td>5.553</td>
<td>1.064</td>
<td>0.5574</td>
<td>1.259</td>
<td>1.239</td>
<td>1.255</td>
</tr>
<tr>
<td>$\alpha$</td>
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<td>0.485</td>
<td>0.476</td>
<td>0.442</td>
<td>0.412</td>
<td>0.024</td>
<td>0.025</td>
<td>0.014</td>
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<tr>
<td>Quadratic $\chi^2$</td>
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<td>11.92</td>
<td>5.664</td>
<td>1.044</td>
<td>0.5121</td>
<td>0.0987</td>
<td>0.0952</td>
<td>0.04904</td>
</tr>
<tr>
<td>$\alpha$</td>
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<td>0.502</td>
<td>0.503</td>
<td>0.505</td>
<td>0.505</td>
<td>0.510</td>
<td>0.514</td>
<td>0.508</td>
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<tr>
<td>$\text{do/dE}$</td>
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<td>0.486</td>
<td>0.510</td>
<td>0.514</td>
<td>0.509</td>
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</tbody>
</table>

All potentials given as Volts and $\text{do/dE}$ given as $V^{-1}$. 

17
accuracy for the estimation of \( \kappa^2 \) and \( \alpha \) as \( \frac{d\alpha}{dE} \) increases or \( \kappa^2 \) is reduced and this is expected due to the inappropriateness of the linear model in this situation. The advent of a potential dependent \( \alpha \) on steady state voltammograms serves to increase the difference between \( E^0 \) and \( E_{1/2} \) and decrease the slope which is apparent from the increase in \( E_{1/4}-E_{3/4} \).

The presence of a potential dependent \( \alpha \) in steady state voltammetry results in a current maxima when kinetic control of the current begins to predominate (irreversibility increases). The potential of the maxima, \( E_p \), can be calculated from equation (5.12) after it has been differentiated with respect to the potential and is then set equal to zero as follows

\[
2 \frac{d\alpha}{dE} \frac{nF}{RT} (E - E^0) + \alpha_0 \frac{nF}{RT} = 0
\]  

(5.72)

and therefore

\[
E_p = E^0 - \alpha_0 / (2 \frac{d\alpha}{dE})
\]  

(5.73)

This was observed in the simulated voltammograms and is demonstrated in Figures 5.3 and 5.4. Figure 5.3 shows the effect of decreasing \( \kappa^2 \) and the increase in prominence of the maxima. The shift in \( E_p \) is shown in Figure 5.4 for different values of \( \frac{d\alpha}{dE} \) with \( \alpha \) constant and equal to 0.500. It should be noted that because of the maxima, the diffusion limiting current will never be reached and therefore \( q \) will only be calculable through indirect methods such as measuring the limiting current under reversible conditions if possible, or by calculating \( i_d \) from equation (5.4) after determining each of the parameters required.

The small currents that are observed under steady state conditions can often contain a quantity of noise which impedes an accurate analysis of steady state data. Table 5.5 contains the analysis of voltammograms with a gaussian distributed noise component added (as described in Section 2.3), where the magnitude of the noise
Figure 5.3. Simulated voltammograms with dα/dE equal to 0.500, α equal to 0.500 and κ equal to (l to r) 10, 1.0, 0.10, 0.010.
Figure 5.4. Simulated voltammograms with $\kappa^*$ equal to 0.010, $\alpha$ equal to 0.500 and $\partial\alpha/\partial E$ equal to (in order) 0.10, 0.30, 0.50, 0.70.
Table 5.5. The effect of gaussian noise on the analysis with $\sigma = 71.7$.

<table>
<thead>
<tr>
<th>% Noise</th>
<th>$\chi^2=50.00$</th>
<th>$\chi^2=10.00$</th>
<th>$\chi^2=5.000$</th>
<th>$\chi^2=1.000$</th>
<th>$\chi^2=0.5000$</th>
<th>$\chi^2=0.1000$</th>
<th>$\chi^2=0.05000$</th>
<th>$\chi^2=0.01000$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>QR</td>
<td>QR</td>
<td>QR</td>
<td>QR</td>
<td>QR</td>
<td>QR</td>
<td>QR</td>
<td>QR</td>
</tr>
<tr>
<td>+1% of $i_d$</td>
<td>$E_{1/2}$</td>
<td>-0.0003</td>
<td>-0.0031</td>
<td>-0.0071</td>
<td>-0.0259</td>
<td>-0.0477</td>
<td>-0.1216</td>
<td>-0.1561</td>
</tr>
<tr>
<td></td>
<td>$E_{1/4} - E_{3/4}$</td>
<td>0.0572</td>
<td>0.0608</td>
<td>0.0646</td>
<td>0.0867</td>
<td>0.1061</td>
<td>0.1183</td>
<td>0.1190</td>
</tr>
<tr>
<td>Linear</td>
<td>$\kappa$</td>
<td>61.85</td>
<td>11.65</td>
<td>5.659</td>
<td>1.062</td>
<td>0.5333</td>
<td>0.1016</td>
<td>0.0957</td>
</tr>
<tr>
<td></td>
<td>$\alpha$</td>
<td>0.715</td>
<td>0.510</td>
<td>0.458</td>
<td>0.501</td>
<td>0.488</td>
<td>0.504</td>
<td>0.512</td>
</tr>
<tr>
<td>Quadratic</td>
<td>$\kappa$</td>
<td>70.15</td>
<td>11.98</td>
<td>5.705</td>
<td>1.062</td>
<td>0.5117</td>
<td>0.0991</td>
<td>0.0905</td>
</tr>
<tr>
<td></td>
<td>$\alpha$</td>
<td>0.762</td>
<td>0.535</td>
<td>0.472</td>
<td>0.490</td>
<td>0.541</td>
<td>0.516</td>
<td>0.540</td>
</tr>
<tr>
<td></td>
<td>$\text{d}\kappa/\text{d}E$</td>
<td>4.181</td>
<td>0.855</td>
<td>0.276</td>
<td>-0.114</td>
<td>0.331</td>
<td>0.046</td>
<td>0.106</td>
</tr>
<tr>
<td>+3% of $i_d$</td>
<td>$E_{1/2}$</td>
<td>-0.0004</td>
<td>-0.0036</td>
<td>-0.0061</td>
<td>-0.0273</td>
<td>-0.0485</td>
<td>-0.1206</td>
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</tr>
<tr>
<td></td>
<td>$E_{1/4} - E_{3/4}$</td>
<td>0.0549</td>
<td>0.0603</td>
<td>0.0655</td>
<td>0.0878</td>
<td>0.0965</td>
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<td>0.1213</td>
</tr>
<tr>
<td>Linear</td>
<td>$\kappa$</td>
<td>28.69</td>
<td>10.98</td>
<td>5.598</td>
<td>1.086</td>
<td>0.6784</td>
<td>0.1189</td>
<td>0.1142</td>
</tr>
<tr>
<td></td>
<td>$\alpha$</td>
<td>0.744</td>
<td>0.514</td>
<td>0.351</td>
<td>0.489</td>
<td>0.373</td>
<td>0.469</td>
<td>0.474</td>
</tr>
<tr>
<td>Quadratic</td>
<td>$\kappa$</td>
<td>33.72</td>
<td>11.74</td>
<td>5.854</td>
<td>1.084</td>
<td>0.5540</td>
<td>0.0950</td>
<td>0.0981</td>
</tr>
<tr>
<td></td>
<td>$\alpha$</td>
<td>0.863</td>
<td>0.718</td>
<td>0.457</td>
<td>0.499</td>
<td>0.539</td>
<td>0.569</td>
<td>0.546</td>
</tr>
<tr>
<td></td>
<td>$\text{d}\kappa/\text{d}E$</td>
<td>5.351</td>
<td>3.001</td>
<td>0.930</td>
<td>0.095</td>
<td>0.638</td>
<td>0.344</td>
<td>0.261</td>
</tr>
<tr>
<td>+5% of $i_d$</td>
<td>$E_{1/2}$</td>
<td>-0.0019</td>
<td>-0.0064</td>
<td>-0.0064</td>
<td>-0.0286</td>
<td>-0.0471</td>
<td>-0.1180</td>
<td>-0.1562</td>
</tr>
<tr>
<td></td>
<td>$E_{1/4} - E_{3/4}$</td>
<td>0.0552</td>
<td>0.0616</td>
<td>0.0739</td>
<td>0.0884</td>
<td>0.0952</td>
<td>0.1252</td>
<td>0.1229</td>
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<tr>
<td>Linear</td>
<td>$\kappa$</td>
<td>19.21</td>
<td>10.38</td>
<td>4.868</td>
<td>1.164</td>
<td>0.8263</td>
<td>0.1509</td>
<td>0.1472</td>
</tr>
<tr>
<td></td>
<td>$\alpha$</td>
<td>0.641</td>
<td>0.325</td>
<td>0.277</td>
<td>0.455</td>
<td>0.281</td>
<td>0.417</td>
<td>0.419</td>
</tr>
<tr>
<td>Quadratic</td>
<td>$\kappa$</td>
<td>22.30</td>
<td>10.75</td>
<td>4.644</td>
<td>1.163</td>
<td>0.5986</td>
<td>0.1022</td>
<td>0.1222</td>
</tr>
<tr>
<td></td>
<td>$\alpha$</td>
<td>0.841</td>
<td>0.620</td>
<td>0.466</td>
<td>0.459</td>
<td>0.508</td>
<td>0.576</td>
<td>0.506</td>
</tr>
<tr>
<td></td>
<td>$\text{d}\kappa/\text{d}E$</td>
<td>5.196</td>
<td>2.797</td>
<td>1.139</td>
<td>0.041</td>
<td>0.691</td>
<td>0.488</td>
<td>0.296</td>
</tr>
</tbody>
</table>

All potentials given as Volts and $\text{d}\kappa/\text{d}E$ given as $\text{V}^{-1}$. 
corresponds to 1, 3 and 5% of \( i_d \). Comparison with Table 5.2 indicates that, as expected, the errors introduced by the noise increase with an increase in the magnitude of the introduced noise. Significantly, the calculation of \( \kappa^e \) is virtually unaffected by the noise and the accuracy improves as the value of \( \kappa^e \) is decreased. The value calculated for \( \alpha \) is more affected by the noise, but this also improves as \( \kappa^e \) decreases which is due to the effective increase in data used for the analysis. The calculation of \( d\alpha/dE \) appears to be the most affected by the noise and the data in Table 5.5 indicates that this effect can be quite random, particularly in the near-reversible regime. The subtlety of a potential dependent \( \alpha \) may be obscured in the presence of substantial noise, but the calculation of \( \kappa^e \) and \( \alpha \) will still be possible in most cases. If the noise is maintained at a reasonable level, then accurate estimates of \( \kappa^e \), \( \alpha \) and \( d\alpha/dE \) will be possible provided that the system is not too close to reversible.

Since the accurate estimation of \( E^o \) is critical to the success of the Normalised Steady State Voltammetry procedure, four different approaches for the estimation of this parameter were investigated. Additionally, as observed in Figure 5.2(d), the exponential components of the regression analysis of equation (5.17) magnify any errors present, and the importance of this problem needs to be assessed. The iterative method is by far the most accurate method for all values of the kinetic parameter. The weaknesses of this procedure are that it is necessary to select the size of the data window to be used and the presence of noise creates problems because the data that is used on each successive iteration will have a relatively greater error due to the decrease in magnitude of the normalised current. The latter problem arises because in each iteration the window of data shifts towards \( E^o \) and for the more irreversible regime the voltammetric wave may be sufficiently dilated and shifted along the potential axis such that \( E^o \) will be at the foot of the wave where problems with the noise will become more important.

The weighting method described by equation (5.19), will be less likely to be
affected by noise but unfortunately it is particularly inaccurate as \( k^0 \) approaches the reversible limit because in this kinetic regime, the method is unable to discriminate against the errors introduced as \( q \) approaches zero. The significant deviation from the weighted line of best fit in Figure 5.2(d) demonstrates this problem. If the weighting function is further modified so that only the potential range where the normalised current is between 1% and 99% of the limiting current is used in the analysis, then the problem with the weighting method is alleviated for large values of \( k^0 \). However, this modification shifts the problem area to the near irreversible and irreversible kinetic regimes as seen in the data presented in Table 5.6. The voltammetric response for a microdisc electrode is asymmetric about \( E_{1/2} \) unlike the case with a microhemisphere \([9,30]\). This means that the normalised current slowly approaches unity over an increasingly larger range of potentials as the irreversibility of the process increases and this results in a bias for data further and further away from \( E^0 \), which includes most of the region where the normalised current will be below the 99% limit that has been imposed. If no limit is imposed on the weighting method a better balance is achieved between points either side of the potential where the weighting maxima occurred. However, even in this case the data at the potentials more negative than \( E_{1/2} \) exert a greater influence on the final calculated result and leads to the difference between \( E_{1/2} \) and \( E^0 \) being underestimated but not as severely as when the 1% to 99% limit is applied. Varying the limits for the weighted method to other ranges does not improve the analysis for the irreversible case as there is a reduction in the amount of data analysed, and in any case the data remains centred at \( E_{1/2} \) which is greatly removed from \( E^0 \).

The final procedure examined was based on the exponential weighting function described by equation (5.20) and incorporates the benefits of the two weighted procedures discussed above. Consequently, it has a broad range of applicability in contrast to the other two weighted methods which were only useful under either near-
reversible or near-irreversible conditions. However, this method is still not as generally accurate as the iterative method.

The presence of a potential dependent $\alpha$ has little effect on the calculation of $E^\circ$ for the quasi-reversible kinetic region. However, as irreversibility is attained, which corresponds to the regime where the kinetics dominate, then a further degradation in the analysis of $E^\circ$ occurs for the three weighted methods. The problems with these procedures is again related to the asymmetry of the steady state voltammetric response at a microdisc. The approach of the normalised steady state current to unity will be retarded in the presence of a potential dependent $\alpha$ because the forward rate of electron transfer at potentials more negative than $E^\circ$ is lower in comparison to the case where $d\alpha/dE$ is zero.

Data giving the influence of $\alpha$ on the estimation of $E^\circ$ by the different procedures is summarised in Table 5.7. The iterative procedure for the analysis of $E^\circ$ was the least accurate method for all values of $\alpha$ except for values very close to 0.5. The three weighted methods based on equations (5.19) and (5.20) produced relatively similar results with all methods exhibiting a trend in which the calculated $E^\circ$ value becomes slightly more negative as $\alpha$ is increased. This is most likely linked to the decrease in the effective amount of data that is used in the analysis as $\alpha$ increases.

Data in Table 5.6 shows that the error in the estimation of $E^\circ$ is less than $\pm 5 \text{ mV}$ for $\kappa^\circ \geq 0.05$. The presence of an error of this magnitude or less in the calculation of $E^\circ$ was tested with respect to how the error influences the determination of $\kappa^\circ$, $\alpha$ and $d\alpha/dE$ and the results are listed in Table 5.8. As expected, if the error in the determination of $E^\circ$ is a large fraction of the difference between $E^\circ$ and $E_{1/2}$ then the results become nonsensical. This is the case for $\kappa^\circ = 10.00$ where the true value of $E^\circ - E_{1/2}$ is 2.8 mV and an error of $\pm 1 \text{ mV}$ in $E^\circ$ cannot be tolerated. From the data contained in Table 5.8 it can be seen that if the calculated $E^\circ - E_{1/2}$ is greater than the true difference, then $\kappa^\circ$ is underestimated, $\alpha$ is overestimated and $d\alpha/dE$ increases in
Table 5.7. The effect of α on the calculation of $E^\circ$ with $\sigma = 71.7$.

<table>
<thead>
<tr>
<th>x/0=1.000</th>
<th>α=0.100</th>
<th>α=0.200</th>
<th>α=0.300</th>
<th>α=0.400</th>
<th>α=0.500</th>
<th>α=0.600</th>
<th>α=0.700</th>
<th>α=0.800</th>
<th>α=0.900</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{1/2}$</td>
<td>-0.0527</td>
<td>-0.0398</td>
<td>-0.0339</td>
<td>-0.0299</td>
<td>-0.0268</td>
<td>-0.0244</td>
<td>-0.0230</td>
<td>-0.0215</td>
<td>-0.0200</td>
</tr>
<tr>
<td>$E_{1/4} - E_{3/4}$</td>
<td>0.3300</td>
<td>0.1729</td>
<td>0.1229</td>
<td>0.0996</td>
<td>0.0856</td>
<td>0.0768</td>
<td>0.0704</td>
<td>0.0654</td>
<td>0.0614</td>
</tr>
<tr>
<td>$E_{\text{iterative}}$</td>
<td>0.0159</td>
<td>0.0133</td>
<td>0.0096</td>
<td>0.0054</td>
<td>0.0005</td>
<td>-0.0045</td>
<td>-0.0091</td>
<td>-0.0127</td>
<td>-0.0156</td>
</tr>
<tr>
<td>$E_{\text{weighted}}$</td>
<td>0.0066</td>
<td>0.0061</td>
<td>0.0056</td>
<td>0.0048</td>
<td>0.0035</td>
<td>0.0015</td>
<td>-0.0017</td>
<td>-0.0065</td>
<td>-0.0141</td>
</tr>
<tr>
<td>$E_{r1%=q&lt;99%}$</td>
<td>0.0085</td>
<td>0.0082</td>
<td>0.0076</td>
<td>0.0065</td>
<td>0.0049</td>
<td>0.0025</td>
<td>-0.0008</td>
<td>-0.0052</td>
<td>-0.0110</td>
</tr>
<tr>
<td>$E_{\text{exp weight}}$</td>
<td>0.0081</td>
<td>0.0070</td>
<td>0.0061</td>
<td>0.0055</td>
<td>0.0009</td>
<td>-0.0034</td>
<td>-0.0072</td>
<td>-0.0108</td>
<td>-0.0143</td>
</tr>
</tbody>
</table>

All potentials given as Volts.
Table 5.8. The effect of an errant estimation of $E^0$ on the analysis with $\sigma=71.7$

<table>
<thead>
<tr>
<th>$E^0_{\text{app}}$</th>
<th>$\chi^2=10.00$</th>
<th>$\chi^2=1.000$</th>
<th>$\chi^2=0.1000$</th>
<th>$\chi^2=0.01000$</th>
</tr>
</thead>
<tbody>
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<td></td>
<td>QR</td>
<td>QD</td>
<td>IR</td>
<td>QR</td>
</tr>
<tr>
<td>$E^0=+0.010V$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Linear</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\alpha$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quadratic</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\chi^0$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\alpha$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>dq/dE</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E^0=+0.005V$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Linear</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\alpha$</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Quadratic</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\chi^0$</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>$\alpha$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>dq/dE</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E^0=+0.001V$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Linear</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\alpha$</td>
<td></td>
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</tr>
<tr>
<td>Quadratic</td>
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</tr>
<tr>
<td>$\chi^0$</td>
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<tr>
<td>$\alpha$</td>
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</tr>
<tr>
<td>dq/dE</td>
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</tr>
<tr>
<td>$E^0=0.000V$</td>
<td></td>
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<tr>
<td>Linear</td>
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<tr>
<td>$\alpha$</td>
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<tr>
<td>Quadratic</td>
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<tr>
<td>$\chi^0$</td>
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<tr>
<td>$\alpha$</td>
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<td></td>
</tr>
<tr>
<td>dq/dE</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E^0=0.001V$</td>
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</tr>
<tr>
<td>Linear</td>
<td></td>
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</tr>
<tr>
<td>$\alpha$</td>
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<tr>
<td>Quadratic</td>
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<tr>
<td>$\chi^0$</td>
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</tr>
<tr>
<td>$\alpha$</td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>dq/dE</td>
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<td></td>
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<tr>
<td>Linear</td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>$\alpha$</td>
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</tr>
<tr>
<td>Quadratic</td>
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<td></td>
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<tr>
<td>$\chi^0$</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>$\alpha$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>dq/dE</td>
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<td></td>
<td></td>
</tr>
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<td>$E^0=0.010V$</td>
<td></td>
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</tr>
<tr>
<td>Linear</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\alpha$</td>
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<tr>
<td>Quadratic</td>
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<td></td>
</tr>
<tr>
<td>$\chi^0$</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>$\alpha$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>dq/dE</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

All potentials given as Volts and dq/dE given as $V^{-1}$. 
magnitude and becomes more positive. Also, it may be noted that the errors are slightly lower in magnitude when $E^o - E_{1/2}$ is overestimated than when $E^o - E_{1/2}$ is underestimated.

5.4. CONCLUSION.

The validity of a procedure based on the complete analysis of a steady state voltammogram obtained from a microdisc electrode has been demonstrated by analyzing data obtained by digital simulation. The procedure enables calculation of $E^o$, $k^o$, $\alpha$, $d\alpha/dE$ and $D$ which are the parameters which describe the electron transfer process at the electrode-solution interface. The existence of a peak in the steady state current when $d\alpha/dE$ is appreciable was also demonstrated and an equation giving the potential where the current maxima occurs was obtained.

The internal consistency of the simulation method and the normalised steady state method also confirm the validity of the simulation method based on a quasi-explicit finite difference procedure. Since the origins of the simulation procedure and the empirical equations from which the normalised method was derived are completely different it may be concluded, in fact, that the fidelity of both approaches has been confirmed in this comparative study.
CHAPTER SIX

THE VOLTAMMETRIC INVESTIGATION OF THE UNUSUAL ISOMERIC LABILITY IN BOTH OXIDATION STATES FOR THE REDOX SYSTEMS $\text{Fac/mer-[M(CO)}_3(\eta^3 - P_2P')]+/M(CO)_3(\eta^3 - P_2P')$ 

$(M = \text{Cr, Mo, W})$

$(P_2P' = \text{Bis(2-Diphenylphosphinoethyl)phenylphosphine})$.
6. INTRODUCTION.

The use of microelectrodes has extended the useful time domains under which electrode and chemical kinetics may be investigated by fast scan rate cyclic voltammetry and scan rates in excess of 1 million Volts per second are now available. This is a result of the lower $R_uC_d$ time constant and the decreased (ohmic) $iR_u$ drop associated with these electrodes (see references [81,82,175,177,180,184,249-251] for example). Additionally, the range of solvents which may be used for voltammetric studies has been extended [252]. However, in highly resistive media such as aromatic and chlorinated hydrocarbons, there are still substantial problems in using very fast scan rate cyclic voltammetry even with microelectrodes. Therefore, steady state measurements with minimal $iR_u$ drop and background current may be inherently more attractive under conditions of high resistance if high precision is required [162,163,168,253-255].

In practice, it is intuitively obvious that a sensible approach with microelectrodes would involve a judicious choice of both the steady state (slow scan rate) and transient (fast scan rate) responses, although because of instrumental and theoretical restrictions this concept has yet to be widely adopted.

The dominant mode of diffusion at a microdisc electrode is dependent upon the dimensionless parameter, $\sigma$, given in equation (1.6). At smaller values of $\sigma$, linear diffusion predominates ($\sigma < 1/17$ as given by equation (1.7)) and it is under these conditions that the maximum amount of qualitative mechanistic information can be obtained for reactions where rate constants are very high. Most fast scan rate studies reported to date have, in fact, utilised data obtained exclusively in the experimental regime where radial diffusion may be neglected. However, to obtain experimentally acceptable data in high resistance solvents which can be used for quantitative calculations, it is necessary to decrease the scan rate and reduce the electrode radius in
order to lower the current and therefore minimise ohmic distortion [252]. As a result of these constraints, radial diffusion will become important, the theory becomes more complex and the mechanistic information is reduced because the products of the electrochemical reaction (and the subsequent chemical reaction products) rapidly diffuse away from the electrode [256]. The minimum $iR_o$ drop actually is achieved at steady state [162,163] where the response is time (scan rate) independent but under these conditions no information on products can be obtained by direct observation of their electrochemistry. Nonetheless, steady state voltammetry is a powerful method for studying fast electrode processes because the accuracy of the measurements is considerably greater than when linear diffusion is present and when the $iR_o$ drop is high, as is the case in resistive media.

Therefore, under high resistance conditions it can be argued that it is sensible to obtain certain quantitative data accurately from studies at steady state, and near steady state, as well as from fast scan rate experiments. This of course implies that a theory needs to be available that incorporates both the linear and radial diffusion components and that suitable instrumentation is available to cope with the problems inherent with both steady state and fast scan rate measurements.

Many studies on the rates and mechanisms of substitution reactions have been undertaken for 18- and 17-electron metal carbonyl complexes [257]. Specifically, isotopic substitution studies of carbonyl exchange reactions have been widely reported and generally show considerable enhancement of lability for the 17-electron systems. For example, the rate of CO substitution of $V(CO)_6$ (17-electron system) is $10^{10}$ times faster than the corresponding reaction for the isostructural and also neutral 18-electron Cr(CO)$_6$ [258]. Extensive studies by Brown [259,260] and other workers [257] on a wide range of 17-electron systems have led to the general conclusion that 17-electron systems react much faster than the corresponding 18-electron systems. However, this conclusion is conditional upon the absence of over-riding steric and electronic
complications [261-263], since Basolo and coworkers have pointed out [257] that in
certain cases, where steric terms are operative, the 17- and 18-electron compounds
may react at similar rates [264].

Another kind of reaction which has been studied in both 17- and 18-electron
metal carbonyl systems is isomerisation [156]. Both cis→trans and fac→mer
isomerisations are invariably much faster in 17-electron compounds than in the 18-
electron analogs and in the 17-electron case are generally unidirectional (see for example references 138 and 265). Mingos [266] has shown that the electronic
preference for a particular isomer switches from cis (or fac) to trans (or mer) in the 18-
and 17-electron species respectively. Thus in the 17-electron systems both steric and
electronic factors favour trans (or mer) compared with the usually competing
influences of steric and electronic factors in the 18-electron systems. As a
consequence, in electrochemical terms the oxidation of a facial 18-electron compound
usually occurs as in equation (6.1)

\[
\begin{align*}
\text{fac}^0 &\begin{array}{c}
\Longleftrightarrow \\
\text{fac}^+ \\
\Longleftrightarrow
\end{array} \quad +e^- &\text{k}_{\text{fac}^+\text{→mer}^+} &\text{mer}^+ \\
\text{fac}^+ &\begin{array}{c}
\Longleftrightarrow \\
\text{mer}^+ \\
\Longleftrightarrow
\end{array} \quad +e^- \\
\text{mer}^+ &\begin{array}{c}
\Longleftrightarrow \\
\text{mer}^0 \\
\Longleftrightarrow
\end{array} &\text{k}_{\text{mer}^+\text{→mer}^0} &\text{mer}^0
\end{align*}
\]

with the isomerisation step following electron transfer normally being irreversible and
the equilibrium for the \text{fac}^+ \rightleftharpoons \text{mer}^+ reaction heavily favouring the \text{mer}^+ isomer.
Furthermore, \text{k}_{\text{fac}^+\text{→mer}^+} is usually much faster than the corresponding step
\text{k}_{\text{fac}^0\text{→mer}^0} in an 18-electron system.

As in the case of the substitution reactions, it is possible that steric effects may, in
certain circumstances, affect the rates of isomerisation in electrochemical studies of
metal carbonyl systems and modify the general conclusions reached in earlier studies.

In this chapter an electrochemical study is undertaken for the sterically
constrained facial and meridional \([M(CO)\beta(\eta^3 - P_2P')]^+ / M(CO)\beta(\eta^3 - P_2P')\) redox couples (where \(M = Cr, Mo, W; P_2P' = Ph_2PCH_2CH_2P(Ph)CH_2CH_2PPh_2\)) which display unusual isomeric lability in both oxidation states, and as a result do not conform to equations (6.1) and (6.2) under conventional electrochemical conditions. In addition, the necessity of employing both steady state and transient voltammetric procedures to determine the kinetics and mechanisms of reactions in highly resistive media, rather than solely steady state or fast scan rate transient methods alone, will be emphasised.

6.1. EXPERIMENTAL.

Conventional staircase cyclic voltammograms were recorded in dichloromethane (0.1 M \(Bu_4NBF_4\)) using a BAS 100A Electrochemical Analyzer and under the conditions employed, the differences between the staircase waveform and a linear ramp can be considered to be minimal due to the small steps employed (i.e. 1 mV per step) when incrementing the potential. A three electrode system was used with a platinum disc working electrode (radius 0.5 mm) and a platinum wire auxiliary electrode. The reference electrode was as described in Section 2.2 for dichloromethane. For variable temperature cyclic voltammetry, the temperature was regulated over the range -65°C to 25°C by using a dry ice/acetone bath and was monitored using an alcohol thermometer. All microelectrode experiments were performed in dichloromethane (0.5 M \(Bu_4NBF_4\)) with a two-electrode cell arrangement as described in Section 2.1.4.1. A platinum wire pseudo-reference electrode was used for both steady state and fast scan experiments at microelectrodes. The reversible redox couple \(Fe^{+}/Fe\) (\(Fe =\) ferrocene) was frequently measured to check the stability of the reference electrode and all results are quoted against this reference.

The experimental fast scan rate transient voltammograms were corrected for the
charging current and ohmic $iR_u$ drop by methods which were described in Section 2.1.4.1. The uncompensated cell resistance in dichloromethane (0.5 M Bu$_4$NBF$_4$) was measured using an a.c. impedance bridge at a frequency of 10 kHz on a solution of supporting electrolyte [16]. The measured resistance (22000 ohm) compared favourably with the calculated value of 23100 ohm obtained from the table of specific resistivities from reference 267 and applying the following equation [165]

$$R_u = \rho / 4a$$ (6.3)

where, $\rho$, is the specific resistivity. The anion in our experiments was BF$_4^-$, whereas in reference 267 it was ClO$_4^-$. However, from the results, the nature of the anion does not appear to be significant with respect to the uncompensated resistance. The double layer capacitance was also measured using the impedance bridge, and found to be 180 pF which is comparable with the value of 185 pF determined from the capacitive current, $i_c$, from equation (1.25) at the 25 µm radius platinum working electrode.

6.2. THE THEORY OF THE SQUARE SCHEME AND THE FQEFD SIMULATION FOR A MICRODISC ELECTRODE GEOMETRY.

6.2.1. GENERAL THEORY OF THE SQUARE SCHEME.

The square scheme may be represented via the following scheme

$$\begin{align*}
A + e^- & \rightleftharpoons B \\
\text{k}_{D \rightarrow A} & \parallel \text{k}_{A \rightarrow D} \\
\text{k}_{C \rightarrow B} & \parallel \text{k}_{B \rightarrow C} \\
D + e^- & \rightleftharpoons C
\end{align*}$$ (6.4)

When all rate constants are infinitely fast on the time scale of the voltammetric experiment, then the system is in apparent equilibrium with an equilibrium potential, $E_K$, dependent upon the equilibrium constants [147] as follows:
\[ K_{BC} = \frac{[B]([C])}{(6.5)} \]

\[ K_{AD} = \frac{[A][D]}{(6.6)} \]

\[ E_K = E^{o}_{AB} + \frac{RT}{F} \ln \left[ \frac{1+1/K_{BC}}{1+1/K_{AD}} \right] \]

\[ E_K = E^{o}_{DC} - \frac{RT}{F} \ln \left[ \frac{1 + K_{AD}}{1 + K_{BC}} \right] \]

As the scan rate increases (transient voltammetry) or the electrode size becomes sufficiently small (steady state voltammetry) the isomerisation kinetics may be 'outrun' and the reversible potential of the system will shift to the potential of the A/B couple i.e. \( E^{o}_{AB} \). Between these limits, and under fast scan rate conditions where linear diffusion terms are present, so that information on the products of the reaction become available, it may be possible to identify all four species if the equilibrium constants are favourable and at this stage it may be possible to estimate \( E^{o}_{DC} \) [147].

6.2.2. FQEF D SIMULATION OF THE SQUARE SCHEME AT A MICROMICRODISC ELECTRODE.

One of the advantages of the FQED simulation method is that complex mechanisms such as the square scheme may be readily encoded but more importantly, the robust nature of the method enables a wide range of kinetic regimes to be investigated without the need for further computational complexity. The equations for the simulation of the square scheme have been presented in the literature for the FQED technique [91,92] but the microdisc geometry has yet to be considered. Therefore, the equations will be given due to this unique electrode geometry and because encoding is relatively more complicated compared with the previous electron transfer example in section 5.2.

The considerations connected with the two dimensional grid are very similar to
those presented in section 5.1.1, except that the initial optimisation takes into account the fastest normalised chemical rate constant. The chemical rate constant has the general designation in equation (6.3) as \( k_{X \rightarrow Y} \) and this symbolises the chemical conversion of species \( X \) into species \( Y \). The general normalised chemical rate constant is calculated as follows

\[
k_{X \rightarrow Y}^* = \frac{a^2}{D} k_{X \rightarrow Y} \tag{6.9}
\]

where \( a \) is the electrode radius and an initial \( R_0 \) is calculated as \( \sqrt{50} k_{X \rightarrow Y}^{(\text{max})} \), the optimisation is then undertaken as before. The initial concentrations of species \( A, B, C \) and \( D \) are calculated from equations (6.5) - (6.8) after taking into account the simulation parameters of \( E_{AB}^0, E_{DC}^0, K_{AD}, K_{BC} \) and the initial potential.

The FQFED equations for the concentration change in the electroactive region of the electrode with \( i_R \leq i_{r_0} \) and \( i_Y = 1 \) are

\[
\Delta a_{1,i_R} = (1/Q_a)(D_{21}(a'_{2,i_R} - a'_{1,i_R}) + D_{R1,i_R}(a'_{1,i_R} + 1 - a'_{1,i_R}) + D_{R1,i_R}(a'_{1,i_R} + 1 - a'_{1,i_R}) + w_{fAB}(b'_{1,i_R} + \Delta b_{1,i_R}) \]

\[
\Delta a_{1,i_R} = (1/Q_a)(D_{21}(a'_{2,i_R} - a'_{1,i_R}) + D_{R1,i_R}(a'_{1,i_R} + 1 - a'_{1,i_R}) + w_{fAB}(b'_{1,i_R} + \Delta b_{1,i_R}) \]

\[
\Delta b_{1,i_R} = (1/Q_b)(D_{21}(b'_{2,i_R} - b'_{1,i_R}) + D_{R2,i_R}(b'_{1,i_R} + 1 - b'_{1,i_R}) + D_{R2,i_R}(b'_{1,i_R} + 1 - b'_{1,i_R}) + w_{fAB}(a'_{1,i_R} + \Delta a_{1,i_R}) \]

\[
\Delta b_{1,i_R} = (1/Q_b)(D_{21}(b'_{2,i_R} - b'_{1,i_R}) + D_{R2,i_R}(b'_{1,i_R} + 1 - b'_{1,i_R}) + w_{fAB}(a'_{1,i_R} + \Delta a_{1,i_R}) \]

where

\[
Q_a = 1 + w_{fAB} + k_{A \rightarrow D} + k_{AC \rightarrow BD} c_{1,i_R} + D_{21} + D_{R2,i_R} + D_{R1,i_R} \tag{6.11}
\]

\[
Q_b = 1 + w_{fAB} + k_{B \rightarrow C} + k_{BD \rightarrow AC} d_{1,i_R} + D_{21} + D_{R2,i_R} + D_{R1,i_R} \tag{6.12}
\]
\[ Q_b = 1 + w_{bAB} + k^*_B \rightarrow C + k^*_B \rightarrow D \rightarrow A C d'_{1,i_R} + D^*_{r2i_R} + D^*_{R1i_R} \quad (6.13) \]

\[ \Delta c_{1,i_R} = \left( \frac{1}{Q_c} \right) \left[ D^*_{Y21} (c''_{2,i_R} - c'_{1,i_R}) + D^*_R 2i_R (c''_{1,i_R} + 1 - c'_{1,i_R}) + D^*_{R1i_R} (c''_{1,i_R} + 1 - c'_{1,i_R}) + \omega_{DC} (d'_{1,i_R} + \Delta d_{1,i_R}) - c'_{1,i_R} (w_{bDC} + k^*_B \rightarrow C + k^*_B \rightarrow D (b'_{1,i_R} + \Delta b_{1,i_R}) + k^*_B \rightarrow D \rightarrow A C b'_{1,i_R}) \right] \quad (6.14) \]

where

\[ Q_c = 1 + w_{bDC} + k^*_C \rightarrow B + k^*_A \rightarrow B \rightarrow D a'_{1,i_R} + D^*_{Y21} + D^*_R 2i_R + D^*_R 1i_R \quad (6.15) \]

\[ \Delta d_{1,i_R} = \left( \frac{1}{Q_d} \right) \left[ D^*_{Y21} (d''_{1,i_R} - d'_{1,i_R}) + D^*_R 2i_R (d''_{1,i_R} + 1 - d'_{1,i_R}) + D^*_{R1i_R} (d''_{1,i_R} + 1 - d'_{1,i_R}) + \omega_{DC} (c'_{1,i_R} + \Delta c_{1,i_R}) - d'_{1,i_R} (w_{bDC} + k^*_D \rightarrow A + k^*_B \rightarrow D \rightarrow A C (a'_{1,i_R} + \Delta a_{1,i_R}) + k^*_A \rightarrow D \rightarrow A B a'_{1,i_R}) \right] \quad (6.16) \]

where

\[ Q_d = 1 + w_{DC} + k^*_D \rightarrow A + k^*_B \rightarrow D \rightarrow A C b'_{1,i_R} + D^*_{Y21} + D^*_R 2i_R + D^*_R 1i_R \quad (6.17) \]

The terms \( w_{AB}, w_{bAB}, w_{DC} \) and \( w_{bDC} \) are defined as

\[ w_{AB} = k^*_f_{AB} / (1 + k^*_f_{AB} / D^*_{Y11} + k^*_b_{AB} / D^*_{Y11}) \quad (6.18) \]

\[ w_{bAB} = k^*_b_{AB} / (1 + k^*_f_{AB} / D^*_{Y11} + k^*_b_{AB} / D^*_{Y11}) \quad (6.19) \]

\[ w_{DC} = k^*_f_{DC} / (1 + k^*_f_{DC} / D^*_{Y11} + k^*_b_{DC} / D^*_{Y11}) \quad (6.20) \]

\[ w_{bDC} = k^*_b_{DC} / (1 + k^*_f_{DC} / D^*_{Y11} + k^*_b_{DC} / D^*_{Y11}) \quad (6.21) \]

and

\[ k^*_f_{AB} = k^*_AB \exp[(\alpha n/F)(E - E^0_{AB})] \quad (6.22) \]

\[ k^*_b_{AB} = k^*_AB \exp[(1-\alpha)(nF/RT)(E - E^0_{AB})] \quad (6.23) \]
\[ k^*_{\text{DC}} = k^*_{\text{DC}} \exp((\alpha nF/RT)(E - E^\circ_{\text{DC}})) \] (6.24)

\[ k^*_{b\text{DC}} = k^*_{\text{DC}} \exp((1-\alpha)(nF/RT)(E - E^\circ_{\text{DC}})) \] (6.25)

where \( k^*_{XY} \) is the normalised heterogeneous rate constant calculated from equation (5.34). The simultaneous equations (6.10), (6.12), (6.14) and (6.16) are linear [91] and readily solved by the method of determinants to give the changes in concentration for each species at the electrode surface.

For the electroinactive region adjacent to the insulator surface, where \( i_R > i_{R0} \) and \( i_V = 1 \), the changes in concentration are calculated as follows

\[ \Delta a_{1,i_R} = (1/Q_a)(D^* Y_{121}(a''_{2,i_R} - a'_{1,i_R}) + D^* R_{2i_R}(a''_{1,i_R} + 1 - a'_{1,i_R})) \] (6.26)

\[ + D^* R_{1i_R}(a''_{1,i_R} - 1 - a'_{1,i_R}) + (k^* D \rightarrow A + k^* BD \rightarrow AC b'_{1,i_R})(d'_{1,i_R} + \Delta d_{1,i_R}) \]

\[ + k^* BD \rightarrow AC d'_{1,i_R} \Delta b_{1,i_R} - a'_{1,i_R}(k^* A \rightarrow D + k^* AC \rightarrow BD(c'_{1,i_R} + \Delta c_{1,i_R})) \]

where \( Q_a = 1 + k^* A \rightarrow D + k^* AC \rightarrow BD c'_{1,i_R} + D^* Y_{21} + D^* R_{2i_R} + D^* R_{1i_R} \) (6.27)

\[ \Delta b_{1,i_R} = (1/Q_b)(D^* Y_{21}(b''_{2,i_R} - b'_{1,i_R}) + D^* R_{2i_R}(b''_{1,i_R} + 1 - b'_{1,i_R})) \] (6.28)

\[ + D^* R_{1i_R}(b''_{1,i_R} - b'_{1,i_R}) + (k^* C \rightarrow B + k^* AC \rightarrow BD a'_{1,i_R})(c'_{1,i_R} + \Delta c_{1,i_R}) \]

\[ + k^* AC \rightarrow BD c'_{1,i_R} \Delta a_{1,i_R} - b'_{1,i_R}(k^* B \rightarrow C + k^* BD \rightarrow AC(d'_{1,i_R} + \Delta d_{1,i_R})) \]

where \( Q_b = 1 + k^* B \rightarrow C + k^* BD \rightarrow AC d'_{1,i_R} + D^* Y_{21} + D^* R_{2i_R} + D^* R_{1i_R} \) (6.29)

\[ \Delta c_{1,i_R} = (1/Q_c)(D^* Y_{21}(c''_{2,i_R} - c'_{1,i_R}) + D^* R_{2i_R}(c''_{1,i_R} + 1 - c'_{1,i_R})) \] (6.30)

\[ + D^* R_{1i_R}(c''_{1,i_R} - c'_{1,i_R}) + (k^* C \rightarrow B + k^* BD \rightarrow AC d'_{1,i_R})(b'_{1,i_R} + \Delta b_{1,i_R}) \]

\[ + k^* BD \rightarrow AC b'_{1,i_R} \Delta d_{1,i_R} - c'_{1,i_R}(k^* C \rightarrow B + k^* AC \rightarrow BD(a'_{1,i_R} + \Delta a_{1,i_R})) \]

where \( Q_c = 1 + k^* C \rightarrow B + k^* AC \rightarrow BD a'_{1,i_R} + D^* Y_{21} + D^* R_{2i_R} + D^* R_{1i_R} \) (6.31)

\[ \Delta d_{1,i_R} = (1/Q_d)(D^* Y_{21}(d''_{2,i_R} - d'_{1,i_R}) + D^* R_{2i_R}(d''_{1,i_R} + 1 - d'_{1,i_R})) \] (6.32)

\[ + D^* R_{1i_R}(d''_{1,i_R} - d'_{1,i_R}) + (k^* A \rightarrow D + k^* AC \rightarrow BD c'_{1,i_R})(a'_{1,i_R} + \Delta a_{1,i_R}) \]

\[ + k^* AC \rightarrow BD a'_{1,i_R} \Delta c_{1,i_R} - d'_{1,i_R}(k^* D \rightarrow A + k^* BD \rightarrow AC(b'_{1,i_R} + \Delta b_{1,i_R})) \]
where \( Q_d = 1 + k^*_{D \rightarrow A} + k^*_{BD \rightarrow AC} b^*_{iY, iR} + D^* Y_{2iY} + D^* R_{2iR} + D^* R_{1iR} \) \quad (6.33)

The changes in concentrations for the remaining elements which represent the bulk solution are calculated from the following equations for \( i_Y \geq 2 \) and all \( i_R \).

\[
\begin{align*}
\Delta a_{iY, iR} &= (1/Q_a) [D^* Y_{2iY} (a^*_{iY+1, iR} - a^*_{iY, iR}) + D^* Y_{1iY} (a^*_{iY-1, iR} - a^*_{iY, iR})
+ D^* R_{2iR} (a^*_{iY, iR+1} - a^*_{iY, iR}) + D^* R_{1iR} (a^*_{iY, iR-1} - a^*_{iY, iR})
+ (k^*_{A \rightarrow D} + k^*_{AC \rightarrow BD} b^*_{iY, iR}) (d^*_{iY, iR} + \Delta d_{iY, iR}) + k^*_{BD \rightarrow AC} d^*_{iY, iR} \Delta b_{iY, iR}
- a^*_{iY, iR} (k^*_{A \rightarrow D} + k^*_{AC \rightarrow BD} (c^*_{iY, iR} + \Delta c_{iY, iR}))]
\end{align*}
\] \quad (6.34)

where

\[
Q_a = 1 + k^*_{A \rightarrow D} + k^*_{AC \rightarrow BD} c^*_{iY, iR} + D^* Y_{2iY} + D^* Y_{1iY} + D^* R_{2iR} + D^* R_{1iR}
\] \quad (6.35)

\[
\Delta b_{iY, iR} = (1/Q_b) [D^* Y_{2iY} (b^*_{iY+1, iR} - b^*_{iY, iR}) + D^* Y_{1iY} (b^*_{iY-1, iR} - b^*_{iY, iR})
+ D^* R_{2iR} (b^*_{iY, iR+1} - b^*_{iY, iR}) + D^* R_{1iR} (b^*_{iY, iR-1} - b^*_{iY, iR})
+ (k^*_{C \rightarrow B} + k^*_{AC \rightarrow BD} a^*_{iY, iR}) (c^*_{iY, iR} + \Delta c_{iY, iR}) + k^*_{AC \rightarrow BD} c^*_{iY, iR} \Delta a_{iY, iR}
- b^*_{iY, iR} (k^*_{B \rightarrow C} + k^*_{BD \rightarrow AC} (d^*_{iY, iR} + \Delta d_{iY, iR}))]
\] \quad (6.36)

where

\[
Q_b = 1 + k^*_{B \rightarrow C} + k^*_{BD \rightarrow AC} d^*_{iY, iR} + D^* Y_{2iY} + D^* Y_{1iY} + D^* R_{2iR} + D^* R_{1iR}
\] \quad (6.37)

\[
\Delta c_{iY, iR} = (1/Q_c) [D^* Y_{2iY} (c^*_{iY+1, iR} - c^*_{iY, iR}) + D^* Y_{1iY} (c^*_{iY-1, iR} - c^*_{iY, iR})
+ D^* R_{2iR} (c^*_{iY, iR+1} - c^*_{iY, iR}) + D^* R_{1iR} (c^*_{iY, iR-1} - c^*_{iY, iR})
+ (k^*_{B \rightarrow C} + k^*_{BD \rightarrow AC} d^*_{iY, iR}) (b^*_{iY, iR} + \Delta b_{iY, iR}) + k^*_{BD \rightarrow AC} b^*_{iY, iR} \Delta d_{iY, iR}
- c^*_{iY, iR} (k^*_{C \rightarrow B} + k^*_{AC \rightarrow BD} (a^*_{iY, iR} + \Delta a_{iY, iR}))]
\] \quad (6.38)

where

\[
Q_c = 1 + k^*_{C \rightarrow B} + k^*_{AC \rightarrow BD} a^*_{iY, iR} + D^* Y_{2iY} + D^* Y_{1iY} + D^* R_{2iR} + D^* R_{1iR}
\] \quad (6.39)
\[ \Delta d_{iY,iR} = (1/Qd) \{ D^* Y_{2iY}(d''_{iY,iR} + d'_{iY,iR}) + D^* Y_{1iY}(d''_{iY,iR} - d'_{iY,iR}) + D^* R_{2iR}(d''_{iY,iR} + d'_{iY,iR}) + D^* R_{1iR}(d''_{iY,iR} - d'_{iY,iR}) + \Delta \alpha_{iY,iR} + \Delta \alpha_{iY,iR} \Delta c_{iY,iR} \} \]

where

\[ Qd = 1 + k^* D \rightarrow A + k^* BD \rightarrow AC b'_{iY,iR} + D^* Y_{2iY} + D^* Y_{1iY} + D^* R_{2iR} + D^* R_{1iR} \]

The rest of the algorithm is as previously outlined in section 5.2.2.

### 6.3. RESULTS AND DISCUSSION.

The triteriary phosphine Ph₂PCH₂CH₂P(Ph)CH₂CH₂PPh₂ (P₂P') was first prepared by Chatt and Hart in 1960 [268]. The Group 6 metal tricarbonyl derivatives CO-M(CO)₃(η³ - P₂P') have previously been prepared and characterised, including infrared and phosphorus-31 NMR spectroscopic studies, by other workers [269-271] and the observed spectra agree with published data [272]. The structures of CO-M(CO)₃(η³ - P₂P') and CO-Mo(CO)₃(η³ - P₂P') have also been confirmed in the solid state by X-ray crystallography [273].

#### 6.3.1. CYCLIC VOLTAMMETRIC OXIDATION OF Cr(CO)₃(η³ - P₂P') AT PLATINUM ELECTRODES IN DICHLOROMETHANE.

Scan rates of up to 0.5 V s⁻¹ and disc electrodes of radius of the order of 1 mm are often considered to be conventional conditions for cyclic voltammetry. Under these circumstances the mass transport to the electrode occurs essentially by linear diffusion [9]. Almost all previously reported metal carbonyl electrochemistry has been
conducted under conventional conditions with the use of low temperature procedures to slow the rate of chemical reactions to those that are accessible to the conventional voltammetric time-scale.

Conditions resulting from the use of microelectrodes where the electrode radius is less than 50 μm enables a wide range of scan rates to be accessed without a great need to alter the chemical reaction rates through thermal techniques. Also, there is the possibility of accessing these time domains under steady state conditions by varying the size of the electrode. Both of these procedures will be discussed under the heading of microelectrodes where appropriate.

6.3.1.1. CONVENTIONAL CYCLIC VOLTAMMETRIC CONDITIONS.

Figure 6.1 shows a cyclic voltammogram for the oxidation of \( \text{fac-Cr(CO)}_3(\eta^3 - P_2P') \) at a scan rate of 0.1 V s\(^{-1}\) at 20°C. Under these conditions a single chemically reversible one-electron diffusion controlled redox process is observed at around -0.1 V vs Fe\(^{3+}/\text{Fe}\) (labelled process 1). There is also a second irreversible one-electron oxidation response at more positive potential (peak potential about +0.7 V vs Fe\(^{3+}/\text{Fe}\)). This second response remains irreversible under all conditions of temperature examined and at faster scan rates its potential becomes still more positive and eventually it merges with the solvent background. This process is assigned to a further oxidation resulting in a very unstable Cr(II) carbonyl species and will not be considered further.

Spectroscopic measurements (\(^{31}\)P NMR and IR) show that the compound exists in dichloromethane (0.1 M Bu\(_4\)NCIO\(_4\)) as the \( \text{fac}^0 \) isomer and therefore an obvious interpretation of the voltammogram would be that process 1 is due to the simple reversible oxidation of the \( \text{fac}^0 \) isomer to the \( \text{fac}^+ \) isomer as follows

\[
\text{fac}^-[\text{Cr(CO)}_3(\eta^3 - P_2P')]^+ + e^- \rightleftharpoons \text{fac-Cr(CO)}_3(\eta^3 - P_2P')
\] (6.42)
Figure 6.1. The oxidation of 1mM Cr(CO)$_3$(η$^3$-P$_2$P') with 0.1 M Bu$_4$NBF$_4$ in dichloromethane at a 0.5mm radius Pt electrode with a scan rate of 0.1 V s$^{-1}$ and a temperature of 20°C.
That is, a fac\(^+\) isomer which is stable on the voltammetric timescale at room temperature is formed without the occurrence of the more usual isomerisation depicted in equation (6.1). However, as the temperature is lowered (Figure 6.2) the electrochemistry becomes more complex. On the first oxidation scan a single response is observed and on the reverse reductive scan two waves are seen instead of only one. Moreover, on the second oxidation scan an additional response is seen and on all subsequent scans all four responses are observed. It is apparent that process 1 at room temperature has split into two reversible processes labelled 2,2' and 3' at -45°C. This type of behavior is highly unusual in metal carbonyl chemistry but there are precedents in organic electrochemistry which involve conformational processes undergoing rapid equilibria at room temperature that become slow on the electrochemical timescale at low temperature [157,158]. The temperature dependence suggests a new type of experimental observation for metal carbonyl complexes based upon the well known square reaction scheme [138,156,265] and is as follows

\[
\begin{align*}
\text{fac}^+ + e^- & \rightleftharpoons \text{fac}^0 \\
{\text{mer}^+} & \rightleftharpoons \text{mer}^0
\end{align*}
\]

\[
\begin{align*}
& k_{\text{fac}^0 \rightarrow \text{fac}^+} \quad k_{\text{fac}^+ \rightarrow \text{mer}^+} \quad k_{\text{mer}^0 \rightarrow \text{fac}^0} \quad k_{\text{fac}^0 \rightarrow \text{mer}^0} \\
& k_{\text{mer}^+ \rightarrow \text{fac}^+} \quad k_{\text{fac}^+ \rightarrow \text{mer}^+}
\end{align*}
\]

(6.43)

in which the fac\(^+\) ↔ mer\(^+\) isomerisation step is in rapid equilibrium under conventional conditions at room temperature, similar to the case of the cis/trans-[Cr(CO)\(_4\)(P(OMe)\(_3\))\(_2\)]\(^+/\)Cr(CO)\(_3\)(P(OMe)\(_3\))\(_2\) system [274]. At low temperatures the average of the peak potentials at which processes 2 and 2' are observed approximates the \(E^0_{\text{fac}^+/\text{fac}^0}\) value and the average of the peak potentials, at which processes 3 and 3' are observed, approximates the \(E^0_{\text{mer}^+/\text{mer}^0}\) value. However, at room temperature the 17-electron fac\(^+\) ↔ mer\(^+\) isomerisation equilibrium is established so rapidly that on the conventional voltammetric timescale that the effective \(E_K\) (approximated by an average of the peak potential for processes 1 and 1') is a
Figure 6.2. (a) As for Figure 6.1. (b) As for (a) with the temperature lowered to -45°C.
function of $E^{\circ}_{\text{fac}+/\text{fac}0}$, $E^{\circ}_{\text{mer}+/\text{mer}0}$, $K_{\text{fac}+/\text{mer}+}$ and $K_{\text{fac}0/\text{mer}0}$. That is, at room temperature the voltammetry may be explained by an equilibrium square scheme, the theory of which has been discussed in detail by Bond and Oldham [143,275]. A proven example of exchange averaging of electrochemical responses has been reported [274] in the Cr(CO)$_4$(P(OMe)$_3$)$_2$ system, but in that case the 17-electron equilibrium was still established rapidly on the voltammetric time scale at low temperatures, so that the individual trans$^+/\text{trans}^0$ and cis$^+/\text{cis}^0$ redox responses were not observed.

To further test the suggestion that equation (6.43) is operative, it is necessary to reduce the timescale of the electrochemical experiment in order to perturb the equilibria. Since dichloromethane is a high resistance solvent, microelectrodes and high electrolyte concentrations are used to minimise the ohmic $iR_u$ drop [9].

6.3.1.2. VOLTAMMETRY AT MICRODISC ELECTRODES.

The transient voltammetric situation will be presented initially. Figure 6.3 shows oxidative cyclic voltammograms at 20°C for a solution of fac-Cr(CO)$_3$(η$^3$-P$_2$P') over the potential range -0.5 to +0.2 V vs Fc$^+/\text{Fc}$ at a platinum microelectrode (radius 25 μm) as a function of scan rate. Under these conditions a peak shaped voltammetric curve is obtained with mass transport predominantly by linear diffusion [9]. At low scan rates with the 25 μm radius electrode a single response (process 1) is observed, at intermediate scan rates two well defined chemically reversible redox processes are observed (processes 2,2' and 3,3'). These two stages are analogous to the room temperature and low temperature behavior shown in Figure 6.1. However, at very fast scan rates (>1000 V s$^{-1}$) the response is a single chemically reversible couple (process 2,2'). Thus, by increasing the scan rate, the observed response varies from one couple (slow scan rates) to two reversible couples (intermediate scan rates) and finally back to one reversible couple (very fast scan rates). In the previously
Figure 6.3. The oxidation of 2mM Cr(CO)$_3$(η$^3$ - P$_2$P') with 0.5 M Bu$_4$NB$F_4$ in dichloromethane at a 25 μm radius Pt electrode at a temperature of 20°C. Scan rates (a) 200 mV s$^{-1}$, (b) 200 V s$^{-1}$ and (c) 2000 V s$^{-1}$. 
described variable temperature experiments at conventional electrodes and conventional scan rates, the return to a single reversible response was not observed presumably because a sufficiently low temperature could not be achieved.

The data obtained with variable scan rates at the 25 µm radius platinum disc microelectrode can be interpreted as follows. At very slow scan rates (Figure 6.3a) equilibria are maintained for the fac⁰/mer⁰ and fac⁺/mer⁺ reactions and a single E_K is observed. At intermediate scan rates (Figure 6.3b), where processes 2,2' and 3,3' are observable, approximate E⁰_{fac⁺/fac⁰} and E⁰_{mer⁺/mer⁰} values can be obtained. At very fast scan rates the time scale of the electrochemical experiment outruns the various kinetic steps in the square reaction scheme (equation (6.43)) so that the system simplifies to the true fac⁺/fac⁰ couple whose E⁰_{fac⁺/fac⁰} value can be measured directly from the voltammogram (Figure 6.3c). The postulate of isomerisation occurring after electron transfer is based on analogy with many previously studied systems. It is supported by the fact that the separation of E⁰_{fac⁺/fac⁰} and E⁰_{mer⁺/mer⁰} is as expected [154,156,265].

In order to completely characterise the Cr(CO)₃(η³ - P₂P') system it is necessary to determine the standard potentials and the heterogeneous charge transfer rate constants of both the fac⁺/fac⁰ and the mer⁺/mer⁰ redox couples as well as the chemical kinetics and thermodynamics of the isomerisation steps fac⁺ ⇌ mer⁺ and fac⁰ ⇌ mer⁰. For this particular mechanism and under the transient experimental conditions, digital simulation procedures as outlined in Section 6.2.2. are the most useful theoretical tool. In principle the cross reaction fac⁺ + mer⁰ ⇌ fac⁰ + mer⁺ should also be included in the analysis, but this reaction has been shown to be unimportant on the voltammetric time scale [92] and digital simulation investigations based on the parameters estimated for the Cr(CO)₃(η³ - P₂P') system indicate this to be true.

The use of fast scan rates effects linear diffusion conditions; when kRT/F₀ is
small enough the scan rate competes with the kinetic process and the electrochemical properties of the reaction product may be directly observed. In this case knowledge is gained concerning the $mer^+/mer^0$ couple and the $fac^0 \rightleftharpoons mer^0$ isomerisation. It is then only necessary, from the simulation-experiment comparison used to calculate the kinetics, to estimate the forward rate constants as the reverse rate constants are fixed due to the equilibrium constants which in turn are dependent upon the formal potential of each couple and the equilibrium potential through the use of equations (6.5) - (6.8). The estimation of $E^0_{mer^+/mer^0}$ and $k_{fac^0\rightarrow mer^0}$ requires that a second cycle of the voltammogram is obtained. The various limiting stages of the mechanism as experimentally measured and theoretically simulated using parameters contained in Table 6.1 are illustrated at four different scan rates in Figure 6.4(a,b,c,d). Figure 6.4(a) shows the equilibrium situation at a scan rate of 200 mV s$^{-1}$ with some radial diffusion still evident. At a scan rate of 50 V s$^{-1}$ (Figure 6.4(b)), distinctly different responses for the isomeric pairs are observed and reduction of $fac^+$ is observed. In Figure 6.4(c) at a scan rate of 200 V s$^{-1}$ the reduction of $mer^+$ becomes diminished due to the dominance of the $fac^+$ process and finally only the $fac^+/fac^0$ couple is shown in Figure 6.4(d) at a scan rate of 2000 V s$^{-1}$.

However, at a scan rate of 2000 V s$^{-1}$ the comparison of experiment and theory is not as good as at lower scan rates. The heterogeneous charge transfer rate constants are large and the charge transfer coefficients are considerably less than 0.5 as given in Table 6.1. If the electrode kinetics are ignored and the charge transfer processes are assumed to be Nernstian, the correlation between simulations and experimental curves is further diminished. Although it is conceivable that quasi-reversible behavior may be exhibited by the $\text{Cr(CO)}_3(\eta^3 - \text{P}_2\text{P})$ system, it is obvious that other factors are influencing the shape of these voltammograms, presumably this is because of imperfections in the correction procedure or the use of an inappropriate diffusion model and this will be discussed further in Chapter Seven.
Figure 6.4. The oxidation of 2mM Cr(CO)$_3$(η$^3$ - P$_2$P') with 0.5 M Bu$_4$NBF$_4$ in dichloromethane at a 25 μm radius Pt electrode at a temperature of 20°C. Scan rates (a) 200 mV s$^{-1}$ and (b) 50 V s$^{-1}$. 
Figure 6.4 (cont.). The oxidation of $2 \text{mM Cr(CO)}_3(\eta^3 - P_2P')$ with $0.5 \text{ M Bu}_4\text{NBF}_4$ in dichloromethane at a 25 \(\mu\)m radius Pt electrode at a temperature of 20°C. Scan rates (c) 200 V s\(^{-1}\) and (d) 2000 V s\(^{-1}\).
Table 6.1. Thermodynamic and kinetic data for the redox systems $[\text{Cr(CO)}_3(\eta^3-$
P_2P')]^{+/0}$, $[\text{Cr(CO)}_3(\text{P}('\text{OME})_3)_3]^{+/0}$ and $[\text{Mo(CO)}_3(\eta^3-$
P_2P')]^{+/0}$ in dichloromethane.

| Parameter                   | $\text{Cr(CO)}_3(\eta^3-$
P_2P') | $\text{Cr(CO)}_3(\text{P}('\text{OME})_3)_3$ | $\text{Mo(CO)}_3(\eta^3-$
P_2P') |
<table>
<thead>
<tr>
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<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$E^0_{\text{fac}^+/\text{fac}^0}$ (V vs Fc$^+/\text{Fc}$)</td>
<td>-0.085</td>
<td>0.000</td>
<td>0.145</td>
</tr>
<tr>
<td>$E^0_{\text{mer}^+/\text{mer}^0}$ (V vs Fc$^+/\text{Fc}$)</td>
<td>-0.310</td>
<td>-0.13</td>
<td>-0.090</td>
</tr>
<tr>
<td>$E^0_K$ (V vs Fc$^+/\text{Fc}$)</td>
<td>-0.122</td>
<td>-</td>
<td>0.125</td>
</tr>
<tr>
<td>$K_{\text{fac}^0/\text{mer}^0}$</td>
<td>1540</td>
<td>0.25</td>
<td>10000</td>
</tr>
<tr>
<td>$K_{\text{fac}^+/\text{mer}^+}$</td>
<td>0.31</td>
<td>0.0016</td>
<td>0.91</td>
</tr>
<tr>
<td>$k_{\text{fac}^+\rightarrow\text{mer}^+}$ (s$^{-1}$)</td>
<td>500</td>
<td>0.11</td>
<td>1200</td>
</tr>
<tr>
<td>$k_{\text{mer}^+\rightarrow\text{fac}^+}$ (s$^{-1}$)</td>
<td>155</td>
<td>0.00017</td>
<td>1100</td>
</tr>
<tr>
<td>$k_{\text{fac}^0\rightarrow\text{mer}^0}$ (s$^{-1}$)</td>
<td>0.05</td>
<td>0.00018</td>
<td>0.1</td>
</tr>
<tr>
<td>$k_{\text{mer}^0\rightarrow\text{fac}^0}$ (s$^{-1}$)</td>
<td>77</td>
<td>0.000045</td>
<td>1000</td>
</tr>
<tr>
<td>$k^{\circ}_{\text{fac}^+\rightarrow\text{fac}^0}$ (10$^2$ m s$^{-1}$)</td>
<td>0.20</td>
<td>-</td>
<td>0.15</td>
</tr>
<tr>
<td>$\alpha_{\text{fac}^+\rightarrow\text{fac}^0}$</td>
<td>0.35</td>
<td>-</td>
<td>0.40</td>
</tr>
<tr>
<td>$k^{\circ}_{\text{mer}^+\rightarrow\text{mer}^0}$ (10$^2$ m s$^{-1}$)</td>
<td>0.30</td>
<td>-</td>
<td>0.12</td>
</tr>
<tr>
<td>$\alpha_{\text{mer}^+\rightarrow\text{mer}^0}$</td>
<td>0.45</td>
<td>-</td>
<td>0.45</td>
</tr>
</tbody>
</table>

$\text{Cr(CO)}_3(\text{P}('\text{OME})_3)_3^{+/0}$ data from reference 153.
Table 6.1 summarises the equilibrium and rate constants calculated from the comparison of simulated and experimental data for the \([\text{Cr}(\text{CO})_3(\eta^3 - P_2P')]^+/\text{Cr}(\text{CO})_3(\eta^3 - P_2P')\) redox system square reaction scheme shown in equation (6.43) together with electrode kinetic data. The values obtained for the thermodynamic parameters via the simulations conform closely to the values obtained by the calculation based on the limiting situations where chemically reversible data are obtained. For comparison purposes Table 6.1 also includes data for the \(\text{Cr}(\text{CO})_3(\text{P}[\text{OMe}]_3)_3\) system [153] which exhibits typical behavior in the context of the relative stability of the various isomers in the square reaction scheme. The equilibrium constant \(K_{\text{fac}^+\text{mer}^+}\) for \(\text{Cr}(\text{CO})_3(\eta^3 - P_2P')\) only slightly favours the \(\text{mer}^+\) isomer, \((K_{\text{fac}^+\text{mer}^+} = 0.31)\), whereas in previously studied systems the \(\text{mer}^+\) isomer is strongly favoured [138,156,265]. Additionally the back reaction \(\text{mer}^+ \rightarrow \text{fac}^+\) \((k_{\text{mer}^+ \rightarrow \text{fac}^+} = 1600)\) is many orders of magnitude faster than usual (Table 6.1). In the \(\text{fac}^0/\text{mer}^0\) pair of isomers the equilibrium constant heavily favours the \(\text{fac}^0\) isomer, but the unusual feature is that the rates of both the forward and reverse isomerisation reactions are sufficiently fast to influence the cyclic voltammograms obtained at conventional scan rates.

To determine the kinetics of all steps and to calculate the thermodynamics of the processes, it becomes necessary to perturb the equilibrium observed with conventionally sized electrodes and low scan rates. With the use of microelectrodes, as noted in the introduction, the simplest way to minimise problems associated with background current and \(iR_o\) drop, and to enter the kinetic regime, is to use the radial diffusive properties of these electrodes found at the steady state or more correctly, near-steady state regime observed at low scan rates. Under these conditions, the influence of the reaction products and the \(\text{fac}^+ \rightleftharpoons \text{mer}^+\) reaction following electron transfer is a function of the parameter \(ka^2/D\) (where \(k\) is a first-order homogeneous chemical rate constant): when this parameter is small (small \(k\) and/or small \(a\)) the
reaction layer will be larger than the diffusion layer and the kinetics will have a diminished effect; when the parameter is large (large k and/or large a) the reaction layer will be smaller than the diffusion layer and the kinetics will play a significant role. Figure 6.5 shows experimental data obtained at electrodes of variable radii under steady state conditions for the Cr(CO)\(_3\)(η\(^3\)-P\(_2\)P) oxidation process at a concentration of 5x10\(^{-4}\) M. Both the background current and iR\(_0\) drop are relatively unimportant in these experiments and this is in contrast to the case with transient experiments. It can be seen that the isomerisation step becomes less important, the smaller the electrode radius becomes, as concluded by noting that a decrease in the electrode radius causes a shift in E\(_{1/2}\) towards E\(^0\)\(_{\text{fac}^+/\text{fac}^0}\) under steady state conditions. This expected shift is demonstrated theoretically in Figure 6.6 and Table 6.2, from the results of digital simulations using parameters which include the experimental results reported earlier from fast scan rate data obtained under predominantly linear diffusion conditions.

Steady state voltammograms are also very sensitive to electron transfer kinetics when the electrode is very small and the advent of non-reversible electron transfer kinetics may cause a shift in E\(_{1/2}\) to a value well removed from the actual E\(^0\) value of the fac+/fac\(^0\) couple as can be seen in Table 6.2. Measurement of the Tomes criterion of E\(_{3/4}\)-E\(_{1/4}\) indicates the onset of quasi-reversible or irreversible electron transfer and is useful in estimating the shift in potential due to the electrode kinetics. The position of E\(_{1/2}\) is dependent on the sum of the shift due to the contribution of the square scheme and also the shift due to the electrode kinetics. It is possible to estimate the reversible half-wave potential, E\(^f\)\(_{1/2}\), in the presence of quasi-reversible electrode behaviour, but in the absence of chemical reactions coupled to electron transfer from the working curves from Figures 2 and 3 of the paper by Oldham et al [79]. Using the difference of E\(_{3/4}\)-E\(_{1/4}\) and knowing the charge transfer coefficient, \(\alpha\), the estimation of E\(^f\)\(_{1/2}\) - E\(_{1/2}\) is readily found. The data obtain in this work under steady state conditions lead to the conclusion that the electrode kinetics are fast.
Figure 6.5. The steady state oxidation of $0.5 \text{ mM Cr(CO)}_3(\eta^3 - \text{P}_2\text{P'})$ with $0.5 \text{ M Bu}_4\text{NBF}_4$ in dichloromethane with a scan rate of $10 \text{ mV s}^{-1}$ and a temperature of $20^\circ\text{C}$.

Microdisc Radii (a) 0.3, (b) 0.5, (c) 1.0, (d) 2.5 and (e) 5.0 $\mu\text{m}$. 
Figure 6.6. The simulation of the steady state oxidation of Cr(CO)$_3$(η$^3$ - P$_2$P') with the parameters as given in Table 6.1. Microdisc Radii (1 to r) 0.3, 0.5, 1.0, 2.5 and 5.0 μm.
Table 6.2. Theoretical results from the steady state simulation (scan rate 10 mV s\(^{-1}\)) of the square scheme using parameters \(E^{0}_{AB} = -0.085\) V, \(E^{0}_{DC} = -0.310\) V and \(E_{K} = -0.122\) V, other parameters as given in Table 6.1 with \(k^{\circ} = k^{\circ}_{AB} = k^{\circ}_{DC}\) and \\
\(\alpha_{AB} = \alpha_{DC} = 0.5.\\n\\n| Disc Radius (\mu m) | \(k^{\circ}\rightarrow\) (cm s\(^{-1}\)) | \(k^{\circ}=10\) (cm s\(^{-1}\)) | \(k^{\circ}=1\) (cm s\(^{-1}\)) | \(k^{\circ}=0.1\) (cm s\(^{-1}\)) | \(k^{\circ}=0.01\) (cm s\(^{-1}\)) |
<table>
<thead>
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<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3 E(_{1/2})</td>
<td>-0.088</td>
<td>-0.087</td>
<td>-0.080</td>
<td>-0.029</td>
<td>0.081</td>
</tr>
<tr>
<td>E(<em>{3/4})-E(</em>{1/4})</td>
<td>0.056</td>
<td>0.057</td>
<td>0.066</td>
<td>0.105</td>
<td>0.118</td>
</tr>
<tr>
<td>0.5 E(_{1/2})</td>
<td>-0.090</td>
<td>-0.090</td>
<td>-0.085</td>
<td>-0.049</td>
<td>0.056</td>
</tr>
<tr>
<td>E(<em>{3/4})-E(</em>{1/4})</td>
<td>0.056</td>
<td>0.057</td>
<td>0.063</td>
<td>0.097</td>
<td>0.117</td>
</tr>
<tr>
<td>1.0 E(_{1/2})</td>
<td>-0.093</td>
<td>-0.094</td>
<td>-0.091</td>
<td>-0.069</td>
<td>0.021</td>
</tr>
<tr>
<td>E(<em>{3/4})-E(</em>{1/4})</td>
<td>0.056</td>
<td>0.057</td>
<td>0.060</td>
<td>0.084</td>
<td>0.116</td>
</tr>
<tr>
<td>2.5 E(_{1/2})</td>
<td>-0.103</td>
<td>-0.103</td>
<td>-0.101</td>
<td>-0.090</td>
<td>-0.023</td>
</tr>
<tr>
<td>E(<em>{3/4})-E(</em>{1/4})</td>
<td>0.055</td>
<td>0.056</td>
<td>0.057</td>
<td>0.070</td>
<td>0.111</td>
</tr>
<tr>
<td>5.0 E(_{1/2})</td>
<td>-0.110</td>
<td>-0.111</td>
<td>-0.109</td>
<td>-0.103</td>
<td>-0.056</td>
</tr>
<tr>
<td>E(<em>{3/4})-E(</em>{1/4})</td>
<td>0.054</td>
<td>0.054</td>
<td>0.055</td>
<td>0.062</td>
<td>0.101</td>
</tr>
</tbody>
</table>

All potentials are given as Volts.
The problem with using slow scan rates to obtain steady state conditions at a solid microelectrode is that the electrode surface state may vary during the course of the experiment, leading to a dependence on electrode pre-treatment and lower reproducibility. Experimental data obtained over the concentration range of $5 \times 10^{-4}$ to $2 \times 10^{-3}$ M as a function of radius are given in Table 6.3 and the errors reflect this problem. Thus, a decrease in the expected reproducibility of $\pm 1$ mV for data obtained when iR drop and background current are negligible is found. The dependence on the electrode pre-treatment and conditions mean that typical errors of $\pm 3$ mV in $E_{1/2}$ and $\pm 5$ mV in $E_{3/4}-E_{1/4}$ were found for the steady state measurements.

Despite some limitations with respect to reproducibility, experimentally the data obtained with very small electrodes of radius $< 1 \mu$m indicates that this is an excellent method for characterising the

$$k^\circ, \alpha$$

$$fac^0 \rightleftharpoons fac^+ + e^-$$

(6.44)

reaction. The $E_{3/4}-E_{1/4}$ values, despite some irreproducibility due to the sloping background which is particularly obvious at lower concentrations, indicate that the value of $k^\circ$ is fast and greater than $0.005$ m s$^{-1}$ and the $E^\circ_{fac^+/fac^0}$ (V vs Fe$^{3+}$/Fe$^{2+}$) is estimated to be $-0.082 \pm 0.003$ V which is in excellent agreement with the value obtained at fast scan rates. The charge transfer coefficient, $\alpha$, could not be determined reliably because the process is too close to reversible under steady state conditions. When the $E^\circ_{fac^+/fac^0}$ is used in conjunction with the value of $E_K^\circ$, which is $-0.122$ V, and equation (6.7) a value for $K_{fac^+/mer^+}$ can be calculated if it is assumed that $1/ K_{fac^0/mer^0} << 1$ as is the case here. The value of $K_{fac^+/mer^+}$ was found to be $0.26$ which again is in excellent agreement with the result obtained using fast scan rate transient experiments. Additionally, the steady state measurements enable the
Table 6.3. Experimental steady state results for the oxidation of Cr(CO)₃(η³-P₂P') in dichloromethane (0.5M Bu₄NBF₄) at 20°C as a function of electrode radius at a platinum disc microelectrode.\(^a\)

<table>
<thead>
<tr>
<th>Disc Radius (μm)</th>
<th>E₁/₂ (V vs Fe⁺⁺/Fe)</th>
<th>E₃/₄ - E₁/₄ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>-0.083</td>
<td>0.073</td>
</tr>
<tr>
<td>0.5</td>
<td>-0.080</td>
<td>0.066</td>
</tr>
<tr>
<td>1.0</td>
<td>-0.093</td>
<td>0.070</td>
</tr>
<tr>
<td>2.5</td>
<td>-0.106</td>
<td>0.068</td>
</tr>
<tr>
<td>5.0</td>
<td>-0.117</td>
<td>0.066</td>
</tr>
<tr>
<td>50.0</td>
<td>-0.122(^b)</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Scan rate used with all electrodes was 10 mV s\(^{-1}\) except for the 50.0 μm electrode where it was 100 mV s\(^{-1}\). Concentration of Cr(CO)₃(η³-P₂P') was varied over the range 5×10\(^{-4}\) to 2×10\(^{-3}\) M.

\(^b\) This potential was calculated from the average of the peak potentials of the voltammogram obtained under conditions where linear diffusion is dominant.
diffusion coefficient of \( \text{fac-Cr(CO)}_3(\eta^3\text{-P}_2\text{P'}) \) to be directly estimated from equation (5.4) and was found to be \((6.0 \pm 0.2) \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}\) and this was assumed to be the diffusion coefficient of all species in solution.

6.3.2. CYCLIC VOLTAMMETRIC OXIDATION OF Mo(CO)_3(\eta^3\text{- P}_2\text{P'}).

6.3.2.1. CONVENTIONAL CYCLIC VOLTAMMETRIC CONDITIONS.

At conventional scan rates and electrode sizes the molybdenum complex gives an initial two-electron irreversible oxidation process at a potential of about +0.1 V vs \( \text{Fe}^+/\text{Fe} \), which remains chemically irreversible regardless of the switching potential, at temperatures down to -65°C. This is followed at more positive potentials and also on the reverse scan by a series of processes which are not relevant to an investigation of the applicability of the square reaction scheme for this compound. The electrochemical reversibility of the first electron transfer step, which is of interest in the present study, is implied in the shape of the voltammogram. The observation of the chemically irreversible two-electron process implies the existence of a chemical step (non-isomerisation) following the initial electron transfer. This non-isomerisation chemical step produces electroactive species and occurs in competition with the isomerisation reaction.

6.3.2.2. VOLTAMMETRY AT MICROSIC ELECTRODES.

Figure 6.7 shows cyclic voltammograms for Mo(CO)_3(\eta^3\text{- P}_2\text{P'}) at scan rates of 5, 200 and 2000 V s\(^{-1}\) at a platinum microdisc electrode of radius 25 \( \mu \text{m}\). At scan rates greater than 5 V s\(^{-1}\) the influence of the chemical reaction (not isomerisation) following the first electron transfer step is minimised at the short timescale of this experiment and the process reverts to an overall one-electron rather than a two-electron
Figure 6.7. The oxidation of 2mM Mo(CO)$_3$(η$^3$ - P$_2$P') with 0.5 M Bu$_4$NBF$_4$ in dichloromethane at a 25 μm radius Pt electrode at a temperature of 20°C. Scan rates (a) 5 V s$^{-1}$, (b) 200 V s$^{-1}$ and (c) 2000V s$^{-1}$.
process.

At a scan rate of 5 V s\(^{-1}\) (Figure 6.7(a)) the redox process now appears to be a chemically reversible one-electron step, process 1,1', (equation (6.45)) analogous to that observed for Cr(CO)\(_3\)(\(\eta^3\)-P\(_2\)P') at a scan rate of 0.2 V s\(^{-1}\) (Figure 6.2(a)).

\[
[\text{Mo(CO)}_3(\eta^3\text{-}P_2\text{P'})]^+ + e^- \rightleftharpoons \text{Mo(CO)}_3(\eta^3\text{-}P_2\text{P'})
\] (6.45)

As the scan rate is increased to 200 V s\(^{-1}\), the apparently simple one-electron process is split into processes 2,2' and 3,3' (Figure 6.7(b)) corresponding to the presence of the square reaction scheme (equation (6.43)). At very fast scan rates (\(\geq 2000\) V s\(^{-1}\)) a single one-electron response, process 2,2', corresponding to fac\(^+\)/fac\(^0\) couple for the oxidation of fac-Mo(CO)\(_3\)(\(\eta^3\)-P\(_2\)P') is observed (Figure 6.7(c)). That is, once a sufficiently short timescale is achieved to avoid the influence of the non-isomerisation chemical step, then the system is similar to that of its chromium analog. However, for molybdenum much faster scan rates are required to achieve the chemically reversible fac\(^+\)/fac\(^0\) redox couple (compare Figures 6.2 and 6.7).

Results of calculations based on the limiting cases of chemically reversible data obtained at fast and slow scan rates and digital simulations of the electrochemistry for the molybdenum system are contained in Table 6.1. All the rate constants are much faster than for chromium. The mer\(^+\)/mer\(^0\) response (Figure 6.7(b)) is not as well pronounced as in the chromium case (Figures 6.2 and 6.4) so that the values for \(E^\circ_{\text{mer}^+\text{/mer}^0}\), \(K_{\text{fac}^0\text{/mer}^0}\), \(k_{\text{fac}^0\rightarrow\text{mer}^0}\) and \(k_{\text{mer}^0\rightarrow\text{fac}^0}\) are relatively imprecise.

However, it is still possible to calculate \(K_{\text{fac}^+\text{/mer}^+}\) accurately because its value is derived from \(E_K\) and \(E^\circ_{\text{fac}^+\text{/fac}^0}\) both of which can be precisely determined. The value of \(K_{\text{fac}^+\text{/mer}^+}\) is 0.91 which indicates that the mer\(^+\) isomer is the slightly thermodynamically favoured isomer. The value of 0.91 is consistent with the difficulty in observing a well defined mer\(^+\) + e\(^-\) \rightleftharpoons mer\(^0\) response under any conditions of scan rate since the concentration of mer\(^+\) at the electrode surface can never be high.
6.3.3. CYCLIC VOLTAMMETRIC OXIDATION OF W(CO)$_3$(η$^3$ - P$_2$P$^\prime$).

6.3.3.1. CONVENTIONAL CYCLIC VOLTAMMETRIC CONDITIONS.

Under conventional conditions W(CO)$_3$(η$^3$ - P$_2$P$^\prime$) displays a chemically irreversible oxidation response at about +0.09 V vs Fe$^{+}$/Fe with additional small responses at more positive potentials and also on the reverse scan similar to those observed for Mo(CO)$_3$(η$^3$ - P$_2$P$^\prime$).

6.3.3.2. VOLTAMMETRY AT MICRODISC ELECTRODES.

As with the molybdenum complex, by using a microelectrode and fast scan rates, the influence of non-isomerisation chemical reaction following electron transfer can be minimised. The voltammetry at fast scan rates in the tungsten system is similar to that in the molybdenum case although conditions could not be achieved when the mer$^+$/mer$^0$ couple can be clearly observed above background using scan rates up to 8000 V s$^{-1}$, this is shown in Figure 6.8. With the sparingly soluble fac-W(CO)$_3$(η$^3$ - P$_2$P$^\prime$) (s.a.d. soln.< 1x10$^{-3}$ M) it is not at present possible in dichloromethane to use higher scan rates with adequate charging current and ohmic iR$_{w}$ drop corrections. However it could be shown that the tungsten system provides the first case where the fac$^+$ isomer is the thermodynamically preferred isomer in a seventeen electron metal carbonyl system. That is, the value of K$_{fac^+/mer^+}$ is greater than 1, but because of experimental and theoretical limitations for this system neither this nor other thermodynamic parameters can be determined accurately. This is demonstrated in Figure 6.9 for a variety of values of K$_{fac^+/mer^+}$ based on the parameters determined for Cr(CO)$_3$(η$^3$ - P$_2$P$^\prime$). It is indicated that if the equilibrium constant is greater than three then the square scheme essentially reduces to a reversible fac$^+$ + e$^-$ $\rightleftharpoons$ fac$^0$ redox.
Figure 6.8. The oxidation of 2mM W(CO)$_3$(η$^3$ - P$_2$P) with 0.5 M Bu$_4$NBF$_4$ in dichloromethane at a 25 μm radius Pt electrode at a temperature of 20°C.
Scan rate = 200 V s$^{-1}$. 

Figure 6.9. A simulation for the oxidation of W(CO)$_3$(η$^3$ - P$_2$P') based on parameters from Table 6.1 for Cr(CO)$_3$(η$^3$ - P$_2$P'). $K_{f+a+/m+}$ (I) 0.33, (II) 0.50 and (III) 1.0. Scan rate equals 50 V s$^{-1}$. 
Figure 6.9 (cont). A simulation for the oxidation of W(CO)₃(η⁻³ - P₂P') based on parameters from Table 6.1 for Cr(CO)₃(η⁻³ - P₂P'). K_{fac+mer+} (IV) 2.0, (V) 3.0 and (VI) 4.0. Scan rate equals 50 V s⁻¹.
process.

6.4. GENERAL DISCUSSION OF THE STRUCTURAL EFFECTS FOR M(CO)$_3$(η$^3$ - P$_2$P$'$).

The thermodynamics of these M(CO)$_3$(η$^3$ - P$_2$P$'$) systems are not unusual in the sense that the $E^0$ values of the two isomeric redox couples and their difference in potential are typical for Group 6 metal tricarbonyl complexes. The unusual feature of these systems is that all the rate constants are much greater than is usual for other tricarbonyl systems. In particular the mer$^+\rightarrow$fac$^+$ isomerisation, which normally does not influence electrochemical measurements, is much faster than usual and is significant on the voltammetric timescale in the [M(CO)$_3$(η$^3$ - P$_2$P$'$)]$^+$/M(CO)$_3$(η$^3$ - P$_2$P$'$) systems. Additionally, the equilibrium constant $K_{\text{fac}^+$/mer$^+$ which usually heavily favours the mer$^+$ isomer ($K_{\text{fac}^+$/mer$^+$ << 1) is now delicately balanced around the value $K_{\text{fac}^+$/mer$^+$ = 1 and actually favours the fac$^+$ isomer for tungsten ($K_{\text{fac}^+$/mer$^+$ > 1). Although the tungsten case provides the first example where the fac$^+$ isomer is preferred in the seventeen electron cation, the values of $K_{\text{fac}^+$/mer$^+$ are in fact quite similar in all three cases but with a definite trend in the sequence from chromium to molybdenum to tungsten. While the data appears to be unique with respect to metal tricarbonyl chemistry, an analogous situation may apply to cis$^+/\text{trans}^+$ isomerisation in the [Mo(CO)$_4$(carbene)$_2$]$^+$ system where the unusual situation of the cis$^+$ isomer being favoured over the trans$^+$ isomer has been reported [276]. It can be concluded that in the case of the M(CO)$_3$(η$^3$ - P$_2$P$'$) complexes, but not in previously studied tricarbonyl systems, there are significant steric pressures in both the facial and meridional isomers which are delicately balanced with the well known electronic preferences for particular isomers in each oxidation state [266]. Molecular models based on the known crystal structures [273] of both fac-Cr(CO)$_3$(η$^3$ - P$_2$P$'$) and fac-
Mo(CO)₃(η³ - P₂P') indicate that in the facial geometry there is a substantial interaction between a phenyl group of each of the two terminal diphenylphosphino groups unless the phenyl rings are parallel. This steric interaction was discussed in the crystallographic paper [273]. In the solid state these phenyl rings are indeed roughly parallel thereby minimizing this interaction, but in solution the phenyl rings would normally rotate and this leads to even greater interaction. Using the same bond distances for the mer isomer as those found for the facial isomer, molecular models show that this particular steric effect is completely absent in the meridional isomer, but instead there is considerable strain in the formation of the two five membered chelate rings which originates in the unfavourable angles at the central phosphorus atom. The complexes are therefore subject to strain in both configurations and are not completely stable in either isomeric form for either the 18- or 17-electron configurations. For the present complexes in the 17-electron state these influences reveal themselves in both kinetic and thermodynamic effects and they rapidly interconvert between the two highly strained isomeric structures. The effect of replacing three monodentate ligands with the tridentate P₂P' ligand is to increase the value of \( K_{fac+\text{mer}+} \) by several orders of magnitude (Table 6.1). However, the variation in \( K_{fac+\text{mer}+} \) upon changing the metal is relatively small.

6.5. CONCLUSION.

Oxidative cyclic voltammetric experiments have been carried out in dichloromethane solution on the sterically strained eighteen electron M(CO)₃(η³ - P₂P') complexes (M = Cr, Mo, W; P₂P' = Ph₂PCH₂CH₂P(Ph)CH₂CH₂PPPh₂). A wide range of scan rates (0.01 V s⁻¹ to 8000 V s⁻¹) and temperatures (20°C to -60°C) have been used at both conventional and micro platinum disc electrodes to establish the mechanism of the one-electron oxidation process to form a seventeen electron cation.
At room temperature \( \text{fac}^- \cdot \text{Cr(CO)}_3(\eta^3 - \text{P}_2\text{P}) \) gives a single chemically reversible one-electron oxidation response, but as the temperature is lowered (conventional electrodes) or the scan rate increased (microelectrodes) the process splits into two responses. At still faster scan rates (microelectrodes) only one reversible response is observed. These observations are consistent with the square reaction scheme

\[
\begin{align*}
\text{fac}^+ + e^- & \rightleftharpoons \text{fac}^0 \\
\text{k}_{\text{mer}^+ \rightarrow \text{fac}^+} & \rightleftharpoons \text{k}_{\text{fac}^+ \rightarrow \text{mer}^+} \\
\text{k}_{\text{mer}^0 \rightarrow \text{fac}^0} & \rightleftharpoons \text{k}_{\text{fac}^0 \rightarrow \text{mer}^0} \\
\text{mer}^+ + e^- & \rightleftharpoons \text{mer}^0
\end{align*}
\]

but the kinetics of the isomerisation steps are faster than in all other similar metal carbonyl systems previously studied. At room temperature the potential of the observed response is a function of \( E^{\circ}_{\text{fac}^+ / \text{fac}^0}, E^{\circ}_{\text{mer}^+ / \text{mer}^0}, K_{\text{fac}^+ / \text{mer}^+}, \) and \( K_{\text{fac}^0 / \text{mer}^0}. \)

At low temperatures (conventional electrodes) or high scan rates (microelectrodes) the individual redox couples are observed. At the fastest scan rates and under steady state conditions the electrochemical experiment outruns the timescale of the \( \text{fac}^+ \rightarrow \text{mer}^+ \) isomerisation so that only the \( \text{fac}^+ / \text{fac}^0 \) couple is observed. Digital simulation of the voltammograms has allowed the determination of all the equilibrium and rate constants in the square scheme for the chromium and molybdenum compounds. Of particular interest is the fact that the equilibrium constant \( K_{\text{fac}^+ / \text{mer}^+} \) only weakly favours \( \text{mer}^+ \) for chromium, is close to unity for molybdenum and weakly favours \( \text{fac}^+ \) for tungsten. Normally the \( \text{mer}^+ \) isomer is heavily favoured.

Additionally, the kinetics of all the isomerisation steps are much faster than for all the other Group 6 metal carbonyl derivatives previously studied. The voltammetric oxidations of \( \text{Mo(CO)}_3(\eta^3 - \text{P}_2\text{P}) \) and \( \text{W(CO)}_3(\eta^3 - \text{P}_2\text{P}) \) at room temperature and slow scan rates are complicated by an additional non-isomerisation chemical step after electron transfer. However, at faster scan rates (\( > 5 \text{ V s}^{-1} \)) the influence of the kinetics of this additional reaction are minimised and the systems then show behavior
analogous to that of Cr(CO)\textsubscript{3}(\eta^{3} - P_{2}P')}, although all rate constants for all isomerisation steps are even greater than for chromium. The unusual position of equilibria and the fast kinetics of the isomerisation steps in these compounds are attributed to steric strains within the tridentate ligand in both isomeric forms of the complexes which lead to a delicate structural energy balance being achieved in both oxidation states.

It has also been demonstrated that a balanced approach to a complex mechanism will enable elucidation of the mechanism and subsequent quantitation. The strength of this procedure is that the individual advantages inherent in steady state and transient voltammetry can be used in a complementary manner even in such a highly resistive solvent as dichloromethane. The example presented showed excellent correlation between both diffusional regimes, except for the very fast scan rate cyclic voltammetry where there is a discrepancy observed between experiments and theoretical simulations.
CHAPTER SEVEN

EFFECTS OBSERVED IN MICROELECTRODE VOLTAMMETRY AT HIGH CURRENT DENSITIES IN LOW DIELECTRIC SOLVENTS SUCH AS DICHLOROMETHANE.
7. INTRODUCTION.

The relatively poor correlation between experiment and theoretically based simulation observed in Chapter Six under fast scan rate conditions for the substituted metal carbonyl systems in dichloromethane could be interpreted as an instrumental artifact (i.e. incomplete correction of the uncompensated resistance and/or charging current) or indicate the presence of a competing process not accounted for in the mechanism and simulation. The benefits of dichloromethane as an electrochemical solvent include inertness in both the chemical and electrochemical senses, particularly under anodic conditions [277-278], and the improved solubility of many non-polar organic and organometallic species in this low dielectric constant solvent (\(\varepsilon = 8.93\), where \(\varepsilon\) is the dielectric constant of dichloromethane [279]). The poor solubility of the substituted metal carbonyl compounds of Chapter Six in the more electrochemically preferable solvent of acetonitrile was, in fact, the reason why the voltammetry was performed in dichloromethane. However, the low dielectric constant of dichloromethane has the disadvantage that dissolution of ionic solutes (i.e. supporting electrolytes) is hindered which results in a higher solution resistance in comparison to solvents with high dielectric constants [278].

Apart from the problems of uncompensated resistance, a chemical consideration is that significant changes in solvation may result from the formation of ion-pairs when a change in oxidation state occurs in a solvent such as dichloromethane. Ion-pair formation causes a decrease in the effective localised charge as a result of the interaction between the positively and negatively charged species. The influence of ion-pairing is demonstrated in Figure 7.1 for the electrolyte tetra n-butylammonium perchlorate using data from reference 267 where it can be seen that because of significant ion-pairing the specific conductance, which is a measure of the ionic activity in solution, differs markedly at higher concentrations in comparison to
Figure 7.1. (a) Plot of the Specific Conductance of Bu₄NClO₄ in dichloromethane versus concentration. (b) Expected conductance based on the extrapolation from dilute solutions.
the predicted specific conductance extrapolated from the conductance at lower concentrations. However, sufficient electrolyte is dissociated in dichloromethane to support the transport of charge through the solution and ion migration may still be assumed to be insignificant based on the arguments presented in Section 1.1.1. The analyte concentration in conventional cyclic and linear sweep voltammetric experiments is usually less than millimolar. However, in many fast scan voltammetric experiments at microelectrodes much higher concentrations are used and in the presence of electrolyte the likelihood of significant ion-pairing will be substantial. Consequently, the effect of ion-pairing may need to be considered in a solvent such as dichloromethane when high concentrations of analyte are used.

The condition of the electrode surface has always been a major consideration in electrochemistry [66,280,281] and at high analyte concentrations, the electrode surface condition may be modified by the adsorption or precipitation of the reactant or product at the electrode surface. Surface blocking due to film formation, adsorption or precipitation is likely to inhibit the electrode performance in most circumstances. There are three possible limiting cases which describe the influence of electrode blocking [282,283]. (a) If the initial conditions are consistent with planar diffusion (i.e. the geometric electrode radius and scan rate ensure $\sigma < \frac{1}{17}$) then the diffusion layer, $\delta$, defined as

$$\delta = \sqrt{\frac{RTD}{nF\upsilon}}$$

(7.1)

for cyclic and linear sweep voltammetry [282], is considerably greater than the mean radius of the active and inactive sites on the electrode surface (i.e. $\bar{a}_a$ and $\bar{a}_i << \delta$) and a transient voltammogram will result with an observed rate constant given by [283]

$$k^o_{obs} = \theta_a k^o_a + \theta_i k^o_i$$

(7.2)

In equation (7.2), the fraction of the electrode area that is active is given as $\theta_a$, the
fraction that is inactive is \( \theta_i \) and \( k^o a \) and \( k^o i \) are the standard heterogeneous rate constants for the active and the inactive sites respectively. However, commonly \( k^o i \) is zero for the inactive sites due to the complete blocking of these sites. (b) The second case arises when \( \bar{a}_a < \delta < \bar{a}_i \) in which case, the active sites will act as an array of microelectrodes to produce steady state conditions. (c) The third case is for \( \bar{a}_a \) and \( \bar{a}_i \gg \delta \), in which case the observed behaviour will resemble a transient voltammetric response because diffusional decoupling of all the active sites occurs. However, all these cases are relative in the sense that an increase in scan rate from the conditions of the first case will lead to behaviour due to the second case as observed at microelectrode ensembles with a equal to 0.1 - 0.5 \( \mu m \) [284,285] and a further increase in scan rate will produce the third case.

In view of the above discussion, problems in dichloromethane are likely to arise at high current densities. The use of high analyte concentrations in fast scan rate methods gives rise to problems with resistance and adsorption which interfere more at high current densities. When a blocking film forms at the electrode surface as a result of electrolysis, the rate of film production is proportional to the concentration of the reacting species which in turn, is commonly proportional to the current density [1] and is therefore amplified at high current densities. The current density is the ratio of the current and the electrode area and is given the symbol \( j \) [1]. The experimental use of microelectrodes creates two distinctly different possibilities where relatively high current density regimes may be encountered, particularly when coupled with high concentrations of electroactive species. The first case refers to steady state conditions where the current density is inversely proportional to the electrode radius and is maximal at very small electrode dimensions, and the second case is achieved under transient conditions at fast scan rates.

In the following discussion, the approximation that a shrouded hemisphere and a microdisc electrode may be treated in an equivalent fashion will be used and this has
been validated for a reversible process \([9,31]\). For a shrouded hemisphere electrode, the maximum faradaic current that can be obtained is given in equation 7.3 \([18]\).

\[
 i_{\text{max}} = i_d \left( 1 + 0.4463 \frac{r_0}{\sqrt{\frac{nFv}{RTD}}} \right) 
\]

This equation gives the maximum current under all conditions of scan rate and electrode radius. In the two limiting cases this equation reduces to either the steady state limiting current (in this case \(i_d = 2\pi nFDc_0\)) or the peak current under transient conditions. From equation (7.3) the relationship between the current density and the sphericity factor can be derived to give

\[
 i \frac{1}{nFc} = \frac{D}{r_0} \left( 1 + \frac{0.4463}{\sigma} \right) 
\]

Figure 7.2 (curve 1) is a general plot of \(j/nFc\) versus \(\sigma\) for values of \(r_0 = 25 \mu m\) and \(D = 1x10^{-9} \text{ m}^2 \text{ s}^{-1}\) which shows that the current density function increases with a decrease in the sphericity factor. Curve 2 of Figure 7.2 represents the steady state case for a scan rate of 0.010 \text{ V s}^{-1} with the electrode radius being varied between 0.1 and 100 \(\mu m\). Under these conditions the current density function increases with an increase in the sphericity factor. Curve 3 of Figure 7.2 represents the situation for conventional voltammetric conditions (i.e. \(r_0 = 1 \text{ mm}\) with scan rates in the range 0.01 \(\leq v \leq 100 \text{ V s}^{-1}\)) and indicates that under conventional conditions the current density is low in comparison. The intercept of curve 1 and curve 2 corresponds to the minimum current density which occurs at a scan rate of 25 \text{ V s}^{-1} for \(r_0 = 25 \mu m\). It may be no coincidence that the best correlation between experiment and simulation observed in Chapter Six is observed in this scan rate region.

Interestingly, under steady state conditions at a microdisc electrode, there is a non-linear current distribution across the electrode surface. A normalised current density function to describe this electrode geometry can be written in terms of the
Figure 7.2. Plot of the current density function versus the sphericity factor from equation (7.4). The conditions for curves 1 to 3 are given in the main text.
radial distance, \( r \) \([9,30]\).

\[
\frac{n}{2nF \Delta c} = \frac{1}{\sqrt{a^2 - r^2}}
\]  

(7.5)

This function is plotted in Figure 7.3. A line representing the average current density also is included in Figure 7.3 and indicates that the average current density is double the current density at the centre of the disk \([9,30]\). However, at the edge of the microdisc, the current density is substantially greater than the average value and approaches infinity at the very edge of the electrode, so that very high current densities may be achieved at some part of the electrode surface.

In this chapter, the behaviour observed for the substituted metal carbonyl systems in Chapter Six will be compared with that of the model compounds of ferrocene, cobaltocenium hexafluorophosphate, ruthenium(II)-tris-(2,2'-bipyridine) perchlorate. These organometallic model compounds have charges of 0, +1 and +2 respectively, if dissociated in solution, and enable the effect of charge to be investigated with respect to the change in charge occurring during electron transfer.

7.1. EXPERIMENTAL.

The very fast scan rate experiments were achieved with the experimental procedures and instrumentation described in Chapter Six. Other experiments at scan rates up to 1 V s\(^{-1}\) were conducted with a BAS 100A Electrochemical Analyzer. The waveform in the latter instrument is actually a staircase rather than a linear ramp. However, because of the small potential step size (i.e. 1 mV per step), the waveform was assumed to be equivalent to a linear ramp.
Figure 7.3. (---) Steady state current distribution across the surface of a microdisc electrode based on equation (7.5). (---) Average current density.
7.2. THE VOLTAMMETRY OF FERROCENE IN DICHLOROMETHANE.

The oxidation of ferrocene (equation (7.6)) [63, 67, 172, 267], as is the case with the substituted metal carbonyl compounds investigated in Chapter Six, corresponds to the oxidation of a neutral molecule to give a species with a charge of +1.

\[ \text{Fc}^+ + e^- \rightleftharpoons \text{Fc}^0 \] (7.6)

Furthermore, the almost equivalent reversible potentials ensures that a meaningful comparison is possible. The heterogeneous rate constant for the oxidation of ferrocene is greater than 5x10^{-2} m s^{-1} in acetonitrile [172]. Assuming a similar situation applies in dichloromethane then reversible or near reversible behaviour will be evident under most conditions.

Figure 7.4 contains simulation-experiment (background corrected) comparisons for 2 mM Fc and 0.5 M Bu4NBF4 in dichloromethane at the three scan rates of 20, 200 and 2000 V s^{-1} using simulated data from the program "MICSIM.BAS". With this relatively high ferrocene concentration a reasonable correlation between experiment and simulation is obtained with a scan rate of 20 V s^{-1} (Figure 7.4(a)) at most potentials. However, the peak current on the reverse (reduction) scan direction is greater than the peak current calculated from the simulation. With a scan rate of 200 V s^{-1} (Figure 7.4 (b)), a significant difference between the simulated voltammogram and the experiment is observed at all potentials beyond the the oxidation peak, and at a scan rate of 2000 V s^{-1}, discrepancies between the experiment and simulation are more pronounced. The charging current has been subtracted with an accuracy of better than 2%, so that this is not the source of the problem most evident in Figure 7.4(c).

The behaviour of ferrocene parallels the observations for the substituted metal
Figure 7.4. Simulation-experiment comparison for 2 mM Fc and 0.5 M Bu4NBF4 in dichloromethane. (a) Scan rate = 20 V s⁻¹ with simulation parameters \( k^0 = 1.0 \times 10^{-2} \) m s⁻¹ and \( \alpha = 0.5 \). (b) 200 V s⁻¹ with \( k^0 = 1.5 \times 10^{-2} \) m s⁻¹ and \( \alpha = 0.5 \).
Figure 7.4 (cont.). Simulation-experiment comparison for 2 mM Fc and 0.5 M Bu$_4$NBF$_4$ in dichloromethane. (c) Scan rate = 2000 V s$^{-1}$ with simulation parameters $k^o = 1.7 \times 10^{-2}$ m s$^{-1}$ and $\alpha = 0.5$. 
carbonyl compounds studied in Chapter Six. Examples of fast scan rate ferrocene voltammograms from the literature [252,256] (Figure 7.5) also exhibit discrepancies from theory in various solvents, although this has rarely been connected. A study involving the voltammetry of ferrocene in heptane and toluene, which are solvents with a lower dielectric constant than dichloromethane, at a microelectrode under steady state conditions [286] indicated that a film containing an ion pair of Fe⁺ and the anion from the supporting electrolyte may be accumulated at the electrode surface and give rise to behaviour consistent with an adsorption process during the reductive cycle. A further study [287] of ferrocene (0.2 M) in acetonitrile using a Pt wire working electrode (area = 0.01 cm²) where the current density function j/nFc of equation (7.4) and Figure 7.2 is equal to 0.32 also supports the hypothesis of adsorption or film formation. At this high concentration and high current density, a green film was formed on the electrode surface.

The current density is directly proportional to the concentration of the electroactive species as well as to the electrode area and the scan rate, so that high values could be achieved by the suitable alteration of all three variables. However, the option of achieving high current densities via the use of high concentrations enables less demanding experimental conditions to be used to observe these anomalies since an excellent faradaic to charging current ratio is achieved at the same time. Figure 7.6 shows the effect of increasing the concentration of ferrocene on the voltammetry with 0.1 M Bu₄NPF₆ as the electrolyte. At millimolar concentrations or less, the response is indistinguishable from the theoretically predicted reversible behaviour when the scan rate is 1 V s⁻¹. However, as the concentration of ferrocene is increased the reductive process splits into two peaks, with the second peak having a potential more negative than the peak that is observed at lower current densities.

Repetitive cycling with a 47.8 mM ferrocene solution (Figure 7.7(a)) reveals that the familiar peak shaped transient response is transformed into a sigmoidal steady
Figure 7.5. Literature example from reference 256 showing the much broader oxidation response compared to the reductive peak shape for conditions of 4 mM Fe with 0.6 M Bu$_4$NClO$_4$ in acetonitrile at a 0.95 μm radius Pt electrode.
Figure 7.6. The concentration dependence of Fc with 0.5 M Bu₄NPF₆ in dichloromethane at a scan rate of 1 V s⁻¹. (a) 25.8 mM Fc. (b) 36.8 mM Fc.
Figure 7.6 (cont.). The concentration dependence of Fc with 0.5 M Bu4NPF6 in dichloromethane at a scan rate of 1 V s⁻¹. (c) 44.2 mM Fc, (d) 48.7 mM Fc.
Figure 7.7. (a) The effect of repetitive cycling for 48.7 mM Fc with 0.5 M Bu₄NPF₆ in dichloromethane at a scan rate of 1 V s⁻¹. (b) Recorded 5 minutes after (a).
Figure 7.7. (c) Recorded 25 minutes after (a).
state response on the oxidative cycle, presumably due to a blocking mechanism [282-285,288-290]. Concomitantly, the second peak becomes dominant during the reductive cycles. The stability of the blocking film is demonstrated in Figures 7.7(b) and (c) where the voltammograms were obtained 5 and 25 minutes after the voltammogram in Figure 7.7(a) was recorded.

Figure 7.8(a) is a voltammogram obtained at high concentrations with a scan rate of 10 mV s\(^{-1}\) after the electrode has been physically polished. At mM and lower concentrations, a steady state response is observed. However, there is a significant separation between the forward and reverse sweeps at potentials more positive than the \(E_{1/2}\) of \(\text{Fe}^+/\text{Fe}\) and other evidence for the existence of an accumulated surface film as observed at high concentrations in acetonitrile in reference 287. The stability of the film formed in this slow scan rate experiment is demonstrated in Figures 7.8(b) and (c) where voltammograms were recorded after 15 and 25 minutes respectively and reverting to a scan rate of 1 V s\(^{-1}\).

The concentration dependence for the oxidation of ferrocene confirms the behaviour apparent at fast scan rates where high current densities are also achieved. The implications arising from these observations for investigations under fast scan rate conditions or in the steady state using small electrodes are that the surface condition of the electrode may be substantially changing during the course of each experiment.

7.3. VOLTAMMERTY OF COBALTOCENIUM HEXAFLUOROPHOSPHATE IN DICHLOROMETHANE.

The reduction of cobaltocenium ion (\(\text{Cc}^+\)) has been advocated for use as a reference process in cases where ferrocene is not suitable [291,292]. \(\text{Cc}^+\) is readily reduced to give the neutral cobaltocene as in equation (7.7).

\[
\text{Cc}^+ + \text{e}^- \rightleftharpoons \text{Cc}^0
\]  
(7.7)
Figure 7.8. (a) The effect of a steady state experiment for 48.7 mM Fe with 0.5 M Bu$_4$NPF$_6$ in dichloromethane at a scan rate of 10 mV s$^{-1}$. (b) Recorded 15 minutes after (a) with a scan rate of 1 V s$^{-1}$. 
Figure 7.8. (c) Recorded 25 minutes after (a) with a scan rate of 1 V s\(^{-1}\) and repetitive cycling.
The fast scan rate, background corrected, experimental voltammograms and the simulated voltammograms are shown in Figure 7.9 for scan rates of 20, 200 and 2000 V s⁻¹. At scan rates less than 1 V s⁻¹, theory and experiment are indistinguishable. However, at fast scan rates, differences do exist. The comparison of the simulation and experiment in Figure 7.9(a) at 20 V s⁻¹ shows some discrepancies and with increasing scan rate (Figure 7.9(b) and (c)), the peak shape for the oxidative sweep broadens and begins to resemble the shape observed for the oxidation of ferrocene.

The parallel behaviour of Cc⁺ after reduction and ferrocene suggests a common mechanism may be operative. For solvents with dielectric constants less than the range of 10-15, there are relatively few free ions in solution although the exact situation is dependent upon the ion size, charge distribution, hydrogen-bonded ion pairs and specific ion solvation [278,279]. This implies that the initially dissolved cobaltocenium hexafluorophosphate exists as ion associated pairs or even aggregates whereas the Cc⁺ that is produced as a result of the oxidation of Cc⁰ exists in a free ion state and accumulates at the electrode surface until ion association and dissolution occurs. The mechanism for the cyclic voltammetry of Cc⁺ could be envisaged as

\[
\text{Forward scan.} \quad E^{o}_{1}, k_{1}^{1} \quad \quad (Cc^{+}SE^{-})_{\text{solv}} + e^{-} \xrightleftharpoons[k_{2}]{k_{1}} (Cc^{0}SE^{-})_{\text{solv}} \xrightarrow{k_{3}} (Cc^{0})_{\text{solv}} + (SE^{-})_{\text{frec}}
\]

\[
\text{Reverse scan.} \quad E^{o}_{2}, k_{2}^{2} \quad \quad (Cc^{0})_{\text{solv}} - e^{-} \xrightarrow{k_{2}} (Cc^{+})_{\text{frec}} + (SE^{-})_{\text{frec}} \xrightarrow[k_{3}]{k_{2}} (Cc^{+}SE^{-})_{\text{film}} \xrightarrow{k_{3}} (Cc^{+}SE^{-})_{\text{solv}}
\]

where SE⁻ is the anion of the supporting electrolyte. The values of \(E^{o}_{1}\) and \(E^{o}_{2}\) would be expected to be slightly different due to the energy of solvation. The poorer solvation of SE⁻ in dipolar aprotic solvents [279], such as dichloromethane, compared to protic solvents is a result of the absence of hydrogen bonding interactions. Therefore, the ion size and charge distribution characteristics of the supporting
Figure 7.9. Simulation-experiment comparison for 1.92 mM CcPF₆ and 0.5 M Bu₄NBF₄ in dichloromethane. (a) Scan rate = 20 V s⁻¹ with simulation parameters $k^o = 1.0\times10^{-3}$ m s⁻¹ and $\alpha = 0.5$. (b) 200 V s⁻¹ with $k^o = 4.0\times10^{-3}$ m s⁻¹ and $\alpha = 0.5$. 
Figure 7.9 (cont.). Simulation-experiment comparison for 1.92 mM \( \text{CcPF}_6 \) and 0.5 M \( \text{Bu}_4\text{BF}_4 \) in dichloromethane. (c) Scan rate = 2000 V s\(^{-1}\) with simulation parameters \( k^o = 5.0 \times 10^{-3} \text{ m s}^{-1} \) and \( \alpha = 0.5 \).
electrolyte anion will be important to the above mechanism.

A similar mechanism could be proposed for ferrocene.

\[
\begin{align*}
\text{Forward scan.} & \quad E^0_3, k^0_3 \\
(\text{SE}^-)_{\text{free}} + (\text{Fc}^0)_{\text{solv}} - e^- & \overset{k_5}{\underset{k_6}{\rightleftharpoons}} (\text{Fc}^+)_\text{free} + (\text{SE}^-)_{\text{free}} \\
& \overset{k_7}{\underset{k_8}{\rightleftharpoons}} (\text{Fc}^+\text{SE}^-)_{\text{film}} \\
\text{Reverse scan.} & \quad E^0_3, k^0_3 \\
(\text{Fc}^+)_\text{free} + e^- & \overset{k_9}{\underset{k_{10}}{\rightleftharpoons}} (\text{Fc}^0)_{\text{solv}} \\
\text{and} & \quad E^0_4, k^0_4 \\
(\text{Fc}^+\text{SE}^-)_{\text{film}} + e^- & \overset{k_7}{\underset{k_8}{\rightleftharpoons}} (\text{Fc}^0\text{SE}^-)_{\text{film}} \\
& \overset{k_4}{\underset{k_5}{\rightleftharpoons}} (\text{SE}^-)_{\text{free}} + (\text{Fc}^0)_{\text{solv}} \\
\end{align*}
\]

The process involving the reduction of \((\text{Fc}^+\text{PF}_6^-)_{\text{film}}\) has a more negative potential (i.e. \(E^0_4\)) due to stabilization as a result of film formation.

In summary, the \(\text{Fc}^+/\text{Fc}\) and \(\text{Cc}^+/\text{Cc}\) systems both appear to form passivating films on the electrode surface during the oxidative cycle of a cyclic voltammogram and this process is enhanced at high current densities. The same kind of behaviour is also found with the substituted metal carbonyl compounds examined in Chapter Six and is probably a common phenomenon in dichloromethane. The inability of dichloromethane to rapidly solvate the free cation, produced as a result of electrolysis, or the anion of the supporting electrolyte at high concentrations causes film formation and literature examples including the solvents toluene, heptane, benzene, chlorobenzene and acetonitrile also exhibit similar behaviour.

7.4. VOLTAMMETRY OF RUTHENIUM(II)-TRIS-(2,2'-BIPYRIDINE) PERCHLORATE IN DICHLOROMETHANE.

Ruthenium(II)-tris-(2,2'-bipyridine) perchlorate (Ru(bipy)_3(ClO_4)_2) where bipy = 2,2'-bipyridine) is a compound which is often used in electrochemiluminescence experiments [293-298]. Electrochemically, there are three
well defined reductive responses in the range -1.2 to -1.8 V versus a Ag quasi-
reference electrode (Ag QRE) in acetonitrile corresponding to the reduction sequence
Ru(bipy)\(_{3}^{2+}\) → Ru(bipy)\(_{3}^{+}\) → Ru(bipy)\(_{3}^{0}\) → Ru(bipy)\(_{3}^{-}\) and one oxidative response
in the range +1.0 to +1.2 V versus Ag QRE corresponding to Ru(bipy)\(_{3}^{2+}\) → 
Ru(bipy)\(_{3}^{3+}\) [295,298]. The greater range of charges for Ru(bipy)\(_{3}(ClO_4)_{2}\) enables the effect of charge to be further examined.

The reductive voltammetry of Ru(bipy)\(_{3}^{2+}\) is shown in Figures 7.10(a), (b)
and (c). At fast scan rates, there are two well defined responses at -1.90 and -2.15 V
versus Fc\(^+\)//Fc and a third less well defined response near the solvent limit at -2.45 V
versus Fc\(^+\)//Fc when the scan rate is 5 V s\(^{-1}\) (Figure 7.10(a)). The processes
correspond to equations (7.10) to (7.12)

\[
\begin{align*}
-1.90 \text{ V vs Fc}^{+}/\text{Fc} & \quad \text{Ru(bipy)}_{3}^{2+} + e^{-} \quad \text{Ru(bipy)}_{3}^{+} & (7.10) \\
-2.15 \text{ V vs Fc}^{+}/\text{Fc} & \quad \text{Ru(bipy)}_{3}^{+} + e^{-} \quad \text{Ru(bipy)}_{3}^{0} & (7.11) \\
-2.45 \text{ V vs Fc}^{+}/\text{Fc} & \quad \text{Ru(bipy)}_{3}^{0} + e^{-} \quad \text{Ru(bipy)}_{3}^{-} & (7.12)
\end{align*}
\]

At a scan rate is 50 V s\(^{-1}\) (Figure 7.10(b)) it becomes noticeable that the oxidative
response due to Ru(bipy)\(_{3}^{+}\) → Ru(bipy)\(_{3}^{2+}\) at a potential of -1.90 V versus Fc\(^+\)//Fc is
appreciably smaller than any of the five other processes observed. When the scan rate
is further increased to 500 V s\(^{-1}\) (Figure 7.10(c)) this feature becomes even more
obvious. Again it appears that interaction with the anion of the supporting electrolyte
occurs and the effect becomes increasingly important as the charge on the ruthenium
increases.

If charge is important then anomalies should be even more apparent during the
oxidation of Ru(bipy)\(_{3}^{2+}\) → Ru(bipy)\(_{3}^{3+}\). Experimental results shown in Figures
7.11(a), (b), (c), (d) and (e) confirm this. The electrode process is

\[
\begin{align*}
+0.70 \text{ V vs Fc}^{+}/\text{Fc} & \quad \text{Ru(bipy)}_{3}^{3+} + e^{-} \quad \text{Ru(bipy)}_{3}^{2+} & (7.13)
\end{align*}
\]
Figure 7.10. Voltammograms for 2 mM Ru(bipy)$_3$(ClO$_4$)$_2$ and 0.5 M Bu$_4$NB$_4$F$_4$ in dichloromethane at a 25 μm radius Pt electrode. (a) Scan rate = 5 V s$^{-1}$. (b) 50 V s$^{-1}$. 
Figure 7.10 (cont.).Voltammograms for 2 mM Ru(bipy)$_3$ClO$_4$$_2$ and 0.5 M
Bu$_4$NBF$_4$ in dichloromethane at a 25 μm radius Pt electrode. (c) Scan rate = 500 V s$^{-1}$.
At the lowest scan rate of 50 mV s\(^{-1}\) on a 5 \(\mu\)m radius microdisc electrode (Figure 7.11(a)), behaviour consistent with a precipitation mechanism is observed [287]. This indicates that the behaviour observed in Figures 7.11(b) and (c) is due to an electrolyte interaction and eventually precipitation occurs when the charge becomes large enough and the time scale is sufficiently long so that nucleation can occur. The effect of increasing the scan rate is shown in Figures 7.11(b), (c), (d) and (e). At a scan rate of 2 V s\(^{-1}\) (Figure 7.11(b)), the time scale has been reduced and the nucleation that precedes the previously observed precipitation does not occur. However, evidence for adsorption [281,299] and accumulation of Ru(bipy)_3^{2+} on the electrode surface is observed as is the case with a scan rate of 20 V s\(^{-1}\) (Figure 7.10(c)). At scan rates of 200 and 2000 V s\(^{-1}\) (Figure 7.10(d) and (e) respectively) the ratio of \(i_{pc}\) to \(i_{pa}\) (1.2 at 200 V s\(^{-1}\) and 1.4 at 2000 V s\(^{-1}\)) is very similar to the behaviour observed for ferrocene with scan rates of 20 and 200 V s\(^{-1}\) (see Figure 7.4(a) and (b)).

Overall, the change in charge that accompanies the electrochemical processes of the three compounds examined has a significant effect upon the shapes of the voltammograms observed. Ru(bipy)_3^{2+} has a larger ionic radius than either Fe\(^{3+}\) or Cc\(^{+}\) and the effect does not become apparent until the Ru(bipy)_3 attains a larger positive charge. The data in Table 7.1 supports this observation, although comparatively the charge-volume ratio, which reflects the effective charge distribution for an ion, for Fe\(^{3+}\) is somewhat greater than the value calculated for Ru(bipy)_3^{2+}. The apparent effects observed increase with increasing positive charge and decreasing ionic radius in cases where charge is equivalent, they are consistent with an ion pairing-adsorption-precipitation mechanism due to the insolubility of the cations.
Figure 7.11. Voltammograms for 2 mM Ru(bipy)$_3$(ClO$_4$)$_2$ and 0.5 M Bu$_4$NBF$_4$ in dichloromethane at a 5 μm radius Pt electrode. (a) Scan rate = 50 mV s$^{-1}$. (b) Scan rate = 2 V s$^{-1}$. 
Figure 7.11 (cont.). Voltammograms for 2 mM Ru(bipy)$_3$(ClO$_4$)$_2$ and 0.5 M Bu$_4$NBF$_4$ in dichloromethane at a 5 μm radius Pt electrode. (c) Scan rate = 20 V s$^{-1}$. (d) Scan rate = 200 V s$^{-1}$. 
Figure 7.11 (cont.). Voltammograms for 2 mM Ru(bipy)$_3$(ClO$_4$)$_2$ and 0.5 M Bu$_4$NBF$_4$ in dichloromethane at a 5 μm radius Pt electrode. (e) Scan rate = 2000 V s$^{-1}$. 
Table 7.1. Ionic radii and effective charge-volume ratios for various anions and cations.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Ionic radius (Å)</th>
<th>Charge-volume ratio ((10^3 \text{ Å}^3))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru(bipy)_3^{3+}</td>
<td>7.8@</td>
<td>1.51</td>
<td>[300]</td>
</tr>
<tr>
<td>Ru(bipy)_2^{2+}</td>
<td>7.8@</td>
<td>1.01</td>
<td>[300]</td>
</tr>
<tr>
<td>Ru(bipy)_3^{3+}</td>
<td>7.8@</td>
<td>0.50</td>
<td>[300]</td>
</tr>
<tr>
<td>Ru(bipy)_3^{0}</td>
<td>7.8@</td>
<td>0</td>
<td>[300]</td>
</tr>
<tr>
<td>Ru(bipy)_3^-</td>
<td>7.8@</td>
<td>-0.50</td>
<td>[300]</td>
</tr>
<tr>
<td>Fc^+</td>
<td>2.03$</td>
<td>28.5</td>
<td>[67]</td>
</tr>
<tr>
<td>Cc^+</td>
<td>2.03</td>
<td>28.5</td>
<td>[67]</td>
</tr>
<tr>
<td>TBA^+</td>
<td>~5.4&amp;</td>
<td>~1.5</td>
<td>this work</td>
</tr>
<tr>
<td>B(Ph)$_4^+$</td>
<td>~5.6&amp;</td>
<td>~1.4</td>
<td>this work</td>
</tr>
<tr>
<td>BF$_4^-$</td>
<td>1.77#</td>
<td>-43.1</td>
<td>[301,302]</td>
</tr>
<tr>
<td>PF$_6^-$</td>
<td>1.92#</td>
<td>-33.7</td>
<td>[301,302]</td>
</tr>
<tr>
<td>ClO$_4^-$</td>
<td>1.82#</td>
<td>-39.6</td>
<td>[301,302]</td>
</tr>
</tbody>
</table>

@ Assumes that no volume change occurs with change in overall charge, although slight increases in radius have been observed as the charge becomes increasingly negative (see reference 67 for examples).

$ Assumes that Fc^+ is exactly iso-structural with Cc^+ based on the similarity between Co(Cp')$_2^{2+}$ and Fe(Cp')$_2^{2+}$ (where Cp' = pentamethylcyclopentadiene) in reference 67.

& Estimated using a minimised potential energy PC-Model gas phase calculation.

# Calculated from the core atom - outer atom bond length plus half the radius of the outer atom.
7.5. GENERAL IMPLICATIONS OF HIGH CURRENT DENSITIES AND ELECTROLYTE EFFECTS IN ORGANIC SOLVENTS.

A major advantage of microelectrodes includes the ability to probe very short time domains via either steady state or fast scan rate transient methods in high resistance, low dielectric constant solvents. Fast scan rate experiments generally require the use of relatively high concentrations of electrolytes in order to reduce the solution resistance. Additionally, high concentration of analyte also are often used to discriminate against charging current. However, the high current densities which are therefore present with fast scan rate experiments combined with high concentrations of supporting electrolyte lead to conditions where ion-pair formation, adsorption and film formation may lead to departures from the ideal diffusion controlled processes found at lower current densities.

Under steady state conditions, the problem of electrolyte interaction is probably reduced due to the rapid mass transport of molecules to and from the electrode surface relative to planar diffusion conditions experienced with faster scan rates. However, the slow scan rates associated with this type of experiment may allow stochastic nucleation processes sufficient time to occur as observed for the oxidation of Ru(bipy)$_3^{2+}$. An effective strategy to overcome the increase in current density as a result of decreasing the electrode radius should be to increase the scan rate so that the sphericity factor remains constant. Under steady state conditions the current density is independent of the scan rate. However, a decrease in electrode size increases the rate of electrolysis. Consequently, a reduction in the total electrolysis time should ensure an equivalent passage of charge across the electrode interface.
7.6. CONCLUSIONS.

Under conditions of high current density and high concentration of electrolyte ion pairing-adsorption-precipitation processes are likely in low dielectric constant solvents such as dichloromethane. The processes are associated with the charged species produced as a result of electrochemical reactions. Adsorption and electrode blocking mechanisms become dominant at fast scan rates due to the high current density and introduce a chemical limitation in addition to the usual instrumental limitations that occurs in experiments of this nature. The magnitude of the effect is dependent upon the relative charge and size of the participating ions. In the examples that were studied, it appears that the cations interact with the anion of the supporting electrolyte which are present in great excess. In dipolar aprotic solvents, such as dichloromethane, the solvation of anions is generally more difficult than cations and this is the opposite to the more commonly used protic solvents where substantial hydrogen bonding can occur. Therefore, alternative supporting electrolytes with different anions to the presently widely accepted perchlorate, tetrafluoroborate and hexafluorophosphate may be useful in circumstances where the relatively non-polar solvent becomes overburdened with the concentration of ions produced at the electrode surface. The major problem with the anions commonly used is their small size, the use of larger anions such as tetraphenylborates (see Table 7.1) will minimise the interaction of analyte and electrolyte due to the relative improvement in solvation which will accompany the use of such ions.
CHAPTER EIGHT

GENERAL CONCLUSIONS.
8. CONCLUSIONS.

The Global Analysis procedure has been shown represent a very powerful tool for the investigation of electron transfer kinetics. The modification achieved in this thesis to include electrodes of spherical geometry enables the application of Global Analysis to the widely used mercury sphere electrodes as well as planar disc electrodes.

The acknowledged advantages of the Global Analysis method are: (1) All the data from a single experiment are used which improves the accuracy and minimises noise effects; (2) All parameters are calculated from a single experiment so that irreproducibilities between experiments are avoided. As a consequence, the irreproducibilities from experiment to experiment are more readily detected; (3) The analysis is objective and, unlike simulation-curve-fitting methods, requires no recursive operations or subjective judgements; (4) The analysis provides an internal check on the validity of Butler-Volmer kinetics.

However, the Global Analysis retains the vulnerability towards interfering artifacts such as charging current and uncompensated resistance as is the case with other electrochemical techniques used for the determination of transport, kinetic and thermodynamic parameters. An analysis of the errors introduced as a result of incomplete compensation of these two factors indicates that Global Analysis can be particularly susceptible to residual charging current errors. The use of the Convolution Potential Sweep Voltammetry method along with a restriction of the voltammetric data to include only the forward sweep allows an analysis to be performed even though charging current errors may be present in the cyclic voltammogram. The use of a subset of parameters calculable from Global Analysis improves the application of CPSV in this circumstance.

The analysis of the experimental system of 2-methyl-2-nitropropane in
acetonitrile demonstrates that Global Analysis produces results which are consistent with alternative methods found in the literature. The potential dependence of the charge transfer coefficient can be calculated from the Global Analysis method when a quadratic regression analysis is incorporated and $d\alpha/dE$ was observed in this case. Although there is a reasonable body of literature data to support the theoretical assertion that a potential dependence of $\alpha$ exists, this question cannot be confirmed by the one example investigated in this study. Therefore the application of the Global Analysis method to further experimental systems is warranted in order to fully resolve this question. Additionally, the extension of the Global Analysis method to include the analysis of chemical steps would offer an extremely powerful and quantitative procedure to compliment the widely used technique of cyclic voltammetry.

The advantages of steady state techniques over transient methods enables discrimination against uncompensated resistance and charging current errors. However, the development of theory to describe the steady state response using microelectrodes is mathematically difficult especially for the more popular microdisc geometry. Two routes to evaluating electrode kinetics under steady state conditions were investigated. The comparison of the Oldham-Zoski empirical relationship for current and potential with a Fast Quasi-Explicit Finite Difference simulation of the microdisc electrode geometry showed an excellent correlation and a method described as Normalised Steady State Voltammetry was developed for the analysis of steady state voltammograms obtained with microdisc electrodes. A complete analysis, similar to Global Analysis, is possible using Normalised Steady State Voltammetry based on the analysis of simulated steady state data. The presence of a potential dependent $\alpha$ has a significant effect on the shape of steady state voltammograms under quasi-reversible conditions. A peak shaped appearance, as opposed to the usual sigmoidal shape, is apparent when the potential dependence of $\alpha$ is incorporated into the simulated data. This may offer an alternative experimental method for the investigation
of this phenomenon without the uncertainties introduced by uncompensated resistance and charging current which interfere during the application of transient techniques.

Oxidative cyclic voltammetric experiments were carried out in dichloromethane solution on the sterically strained eighteen electron $M$(CO)$_3$(η$^3$ - P$_2$P') complexes ($M$ = Cr, Mo, W; P$_2$P' = Ph$_2$PCH$_2$CH$_2$P(Ph)CH$_2$CH$_2$PPh$_2$). A wide range of scan rates (0.01 V s$^{-1}$ to 8000 V s$^{-1}$) and temperatures (20 °C to -60 °C) were used at both conventional and micro platinum disc electrodes to establish the mechanism of the one-electron oxidation process to form a seventeen electron cation. Digital simulation of the voltammograms has allowed the determination of all the equilibrium and rate constants in the observed square scheme for the chromium and molybdenum compounds. Of particular interest is the fact that the equilibrium constant ($K_{fac^+/mer^+}$) only weakly favors $mer^+$ for chromium, is close to unity for molybdenum and weakly favors $fac^+$ for tungsten. Normally the $mer^+$ isomer is heavily favored.

Additionally, the kinetics of all the isomerisation steps are much faster than for all the other Group 6 metal carbonyl derivatives previously studied. The unusual position of equilibria and the fast kinetics of the isomerisation steps in these compounds are attributed to steric strains within the tridentate ligand in both isomeric forms of the complexes which lead to a delicate structural energy balance being achieved in both oxidation states.

It was demonstrated that a balanced approach to a complex mechanism enables elucidation of the mechanism and subsequent quantitation. The strength of this procedure is that the individual advantages inherent in steady state and transient voltammetry can be used in a complementary manner even in such a highly resistive solvent as dichloromethane. The example presented showed excellent correlation between both diffusional regimes, except for the very fast scan rate cyclic voltammetry where there is a discrepancy observed between experiments and theoretical simulations.
The observed discrepancy between experiment and theory at fast scan rates for
the substituted metal carbonyl system was found to be related to the blocking of the
electrode surface by the formation of an insoluble salt containing the cationic product
of electrolysis and the anion of the supporting electrolyte. Similar phenomena was
observed for other organometallic compounds due to the change in the charge of a
species during electrolysis and as a result, the solvation requirements of a reactant and
product in a redox couple may be substantially different. This is particularly the case,
as observed in Chapters Six and Seven, for processes involving the oxidation of a
neutral species in a low dielectric constant solvent such as dichloromethane.

The high current densities and high analyte concentrations present with very
fast scan rate voltammetry enhances the problem of insoluble salt formation and
electrode blocking. Consequently, the surface condition of the electrode may change
during a voltammetric experiment which can introduce errors when comparing
experiments with theoretical models which do not include these additional processes.

The role of the supporting electrolyte anion does not receive very much
consideration in most voltammetric experiments due to the similarity of the most
popular anions of tetrafluoroborate, hexafluorophosphate and perchlorate. Also, in
applications where a supporting electrolyte has insufficient solubility in a non-aqueous
solvent, it is usually the cation which is varied and this is not surprising due to the
range of choice and flexibility that are available, particularly with the tetraalkyl-
ammonium cations. The development and use of alternative supporting electrolyte
anions is therefore proposed to be very important for voltammetry in non-aqueous
solvents.
APPENDIX I
DSO CONTROLLER PROGRAM

for use with the GOULD 4035 DSO

The following programs must also be resident on the disk for this program to function:

CONFIG.SYS
QIBB4.QBL
GRAPHICS.COM
GPIB.COM

Declarations for QuickBASIC 4.0/4.5 applications.

Common GPIB status variables

COMMON SHARED /NISTATBLK/ IBSTA%, IBERR%, IBCNT%

GPIB Subroutine Declarations

DECLARE SUB IBBNA (BD%, BDNAME$)
DECLARE SUB IBCAC (BD%, v%)
DECLARE SUB IBCLR (BD%)
DECLARE SUB IBCMD (BD%, CMD$)
DECLARE SUB IBCMDA (BD%, CMD$)
DECLARE SUB IBDMA (BD%, v%)
DECLARE SUB IBEOS (BD%, v%)
DECLARE SUB IBEOT (BD%, v%)
DECLARE SUB IBFIND (BDNAME$, BD%)
DECLARE SUB IBDTS (BD%, v%)
DECLARE SUB IBIST (BD%, v%)
DECLARE SUB IBLER (BD%)
DECLARE SUB IBONL (BD%, v%)
DECLARE SUB IBDAD (BD%, v%)
DECLARE SUB IBPCT (BD%)
DECLARE SUB IBPCC (BD%, v%)
DECLARE SUB IBRD (BD%, RDS$)
DECLARE SUB IBRDA (BD%, RDS$)
DECLARE SUB IBRDF (BD%, FLNAME$)
DECLARE SUB IBRD1 (BD%, IARR%(), cnt%)
DECLARE SUB IBRDA (BD%, IARR%(), cnt%)
DECLARE SUB IBRPP (BD%, PPR%)
DECLARE SUB IBRSC (BD%, v%)
DECLARE SUB IBRSP (BD%, spr%)
DECLARE SUB IBSV (BD%, v%)
DECLARE SUB IBSAD (BD%, v%)
DECLARE SUB IBSIC (BD%)
DECLARE SUB IBSRE (BD%, v%)
DECLARE SUB IBSTOP (BD%)
DECLARE SUB IBTMO (BD%, v%)
DECLARE SUB IBTRAP (MASK%, mode%)
DECLARE SUB IBTRG (BD%)
DECLARE SUB IBWAIT (BD%, MASK%)  
DECLARE SUB IBWRT (BD%, WRT$)  
DECLARE SUB IBWRTA (BD%, WRT$)  
DECLARE SUB IBWRTF (BD%, FLNAME$)  
DECLARE SUB IBWTI (BD%, IARR%(), cnt%)  
DECLARE SUB IBWTIA (BD%, IARR%(), cnt%)

' GPIB Function Declarations

DECLARE FUNCTION ILBNA% (BD%, BDNAMES$)  
DECLARE FUNCTION ILCAC% (BD%, v%)  
DECLARE FUNCTION ILCLR% (BD%)  
DECLARE FUNCTION ILCMD% (BD%, CMD$, cnt%)  
DECLARE FUNCTION ILCMDA% (BD%, CMD$, cnt%)  
DECLARE FUNCTION ILDMA% (BD%, v%)  
DECLARE FUNCTION ILEOS% (BD%, v%)  
DECLARE FUNCTION ILEOT% (BD%, v%)  
DECLARE FUNCTION ILFIND% (BDNAMES$)  
DECLARE FUNCTION ILGTS% (BD%, v%)  
DECLARE FUNCTION ILIST% (BD%, v%)  
DECLARE FUNCTION ILOC% (BD%)  
DECLARE FUNCTION ILONL% (BD%, v%)  
DECLARE FUNCTION ILPAD% (BD%, v%)  
DECLARE FUNCTION ILPCT% (BD%)  
DECLARE FUNCTION ILPPC% (BD%, v%)  
DECLARE FUNCTION ILRD% (BD%, RDS, cnt%)  
DECLARE FUNCTION ILRDA% (BD%, RDS, cnt%)  
DECLARE FUNCTION ILRDF% (BD%, FLNAME$)  
DECLARE FUNCTION ILRDI% (BD%, IARR%(), cnt%)  
DECLARE FUNCTION ILRDIA% (BD%, IARR%(), cnt%)  
DECLARE FUNCTION ILRPP% (BD%, PPR%)  
DECLARE FUNCTION ILRSC% (BD%, v%)  
DECLARE FUNCTION ILRSP% (BD%, spr%)  
DECLARE FUNCTION ILRSV% (BD%, v%)  
DECLARE FUNCTION ILSAD% (BD%, v%)  
DECLARE FUNCTION ILSIC% (BD%)  
DECLARE FUNCTION ILSRE% (BD%, v%)  
DECLARE FUNCTION ILSTOP% (BD%)  
DECLARE FUNCTION ILTMO% (BD%, v%)  
DECLARE FUNCTION ILTRAP% (MASK%, mode%)  
DECLARE FUNCTION ILTRG% (BD%)  
DECLARE FUNCTION ILWAIT% (BD%, MASK%)  
DECLARE FUNCTION ILWRT% (BD%, WRT$, cnt%)  
DECLARE FUNCTION ILWRTA% (BD%, WRT$, cnt%)  
DECLARE FUNCTION ILWRTF% (BD%, FLNAME$)  
DECLARE FUNCTION ILWRTI% (BD%, IARR%(), cnt%)  
DECLARE FUNCTION ILWRTIA% (BD%, IARR%(), cnt%)

DIM x%(1023), y%(1023), x1%(1023), y1%(1023), resu%(1023), rs%(1023)

x$ = "CRO"  
CALL IBFIND(x$, cro%)  
'assign device name cro  
IF cro% < 0 THEN PRINT "IBFIND ERROR"; STOP 'check for error  
CALL IBCLR(cro%)  
'clear interface  
GOSUB 14200  
'wait till cro ready  
5000 CLS
PRINT "Choose from one of the following:"
PRINT "1. Set up CRO"
PRINT "2. Run experiment from computer"
PRINT "3. Run experiment from cro"
PRINT "4. Subtract one curve from another"
PRINT "5. Print results/curves"
PRINT "6. Exit to DOS"
PRINT "7. Plot data on screen"
PRINT "8. Average scans"
PRINT "9. Smooth data"
PRINT "10. Display data pairs"
PRINT "11. Set data disk drive"
PRINT : PRINT
5500 INPUT "ENTER CHOICE (1,2,3,4,5,6,7,8,9,10 or 11) : " ; a%
IF a% < 1 OR a% > 11 THEN 5500
5800 ON a% GOSUB 14600, 6000, 24400, 11100, 7400, 5900, 25450, 30000, 40000, 50000, 5810
5810 CLS : INPUT " Input data disk drive to either a: or b: or c: "; disk$: GOTO 5000
5900 CALL IBCLR(cro%); CALL IBLOC(cro%); CLS : SYSTEM
6000 CLS
6100 CALL IBCLR(cro%); GOSUB 14200
6200 PRINT "Press any key to arm cro"
6300 xx$ = INPUT$(1)
6400 a$ = "ARM"
6500 CALL IBWR(cro%, a$)
6600 CLS
6700 PRINT "CRO armed." 
6800 txt$ = "TXT="ARMED": CALL IBWR(cro%, txt$)
6900 GOSUB 13700 'do a serial poll
7000 IF spr% <> 74 THEN 6900 'wait till scan acquired
7100 CLS
7200 GOSUB 20900
7300 GOTO 5000
7400 'PLOT CURVE ON XY RECORDER, THROUGH CRO.
7500 CLS
7600 PRINT "This routine will plot a curve on the XY recorder attached"
7700 PRINT "to the CRO. Both the CRO and XY recorder must be turned on."
7800 PRINT
7900 
8000 CALL IBCLR(cro%)
8100 lock$ = "LOCK=ON" 'lock display to enable safe data storage in cro
8200 CALL IBWR(cro%, lock$)
8300 PRINT
8400 INPUT "Enter name of potential file to plot : "; pfl$
8500 PRINT
8600 INPUT "Enter name of current file to plot : "; ifl$
8700 PRINT
8750 txt$ = "TXT="RECEIVING CH1": CALL IBWR(cro%, txt$)
8800 p1$ = "ST1=": p1$ = p1$ + CHR$(4) + CHR$(0): CALL IBWR(cro%, p1$)
9000 CALL IBWR(cro%, ifl$)
9100 GOSUB 13700; IF spr% <> 0 THEN 9100
9200 CLS : PRINT IBCNT%: " bytes of data written from "; ifl$, " to Ch1 of CRO"
9300 CALL IBCLR(cro%)
9350 txt$ = "TXT="RECEIVING CH2": CALL IBWR(cro%, txt$)
9400 p2$ = "ST2=": CALL IBWRT(cro%, p2$)
9600 CALL IBWRTF(cro%, pfl$)
9700 GOSUB 13700: IF spr% <> 0 THEN 9700
9800 PRINT: PRINT IBWRT1%; " bytes of data written from ": pfl$; " to Ch2 of CRO"
9900 rp$ = "RP=55E-1": CALL IBWRT(cro%, rp$)
10000 PRINT: PRINT: PRINT "hit any key to commence plot"
10100 xx$ = INPUT$(1): plt$ = "PLOT"
10200 txt$ = "TXT="PLOTTING": CALL IBWRT(cro%, txt$)
10300 CALL IBWRT(cro%, plt$): PRINT
10400 PRINT "Plotting..."
10500 GOSUB 13700: IF spr% <> 74 THEN 10500
10600 PRINT
10700 lock$ = "LOCK=OFF"
10800 CALL IBWRT(cro%, lock$)
10900 txt$ = "TXT": CALL IBWRT(cro%, txt$)
11000 GOTO 5000
11100 ' routine to subtract two curves
11200 CLS
11300 INPUT "Enter sample filename : "; samp$
11400 INPUT "Enter blank filename : "; blan$
11500 PRINT
11600 INPUT "Enter result filename : "; resu$
11700 OPEN "i", #1, disk$ + samp$
11750 FOR ii% = 0 TO 1023: INPUT #1, x%(ii%): NEXT
11775 CLOSE #1
11800 OPEN "i", #2, disk$ + blan$
11850 FOR ii% = 0 TO 1023: INPUT #2, x1%(ii%): NEXT
11875 CLOSE #2
11900 OPEN "o", #3, disk$ + resu$
12000 CLS
12100 PRINT "Calculating difference between "; samp$; " and "; blan$
12150 la% = 0: sm% = 0: larg% = 0: smal% = 0
12200 FOR ii% = 0 TO 1023
12250 resu%(ii%) = x%(ii%) - x1%(ii%)
12650 IF resu%(ii%) > larg% THEN larg% = resu%(ii%)
12660 IF resu%(ii%) < smal% THEN smal% = resu%(ii%)
12700 NEXT ii%
12750 IF larg% > 127 THEN la% = larg% - 127: GOTO 12770
12760 IF smal% < -128 THEN sm% = smal% + 128: GOTO 12785
12770 FOR hh% = 0 TO 1023
12775 PRINT #3, resu%(hh%); la%
12780 NEXT hh%
12782 GOTO 12800
12785 FOR gg% = 0 TO 1023
12790 PRINT #3, resu%(gg%); sm%
12795 NEXT gg%
12800 CLS
12900 PRINT ii%: " points transferred to "; resu$
13200 CLOSE #3
13300 PRINT: PRINT "Hit any key to continue"
13400 xx$ = INPUT$(1)
13500 GOTO 5000
13600 STOP
13700 ' serial poll
13800 CALL IBSP(cro%, spr%)
13900 RETURN
14000 PRINT "Error...."
14100 STOP
14200 ' subroutine to determine if cro is ready
14300 GOSUB 13700
14400 IF spr% <> 0 THEN 14300
14500 RETURN
14600 ' set up cro
14700 CLS
14800 PRINT "Front panel setting and default value."
14900 PRINT
15000 PRINT "    1. Pretrigger ="; pt$
15100 PRINT "    2. Storage mode ="; mode$
15200 PRINT "    3. Capture mode = Single"
15300 PRINT "    4. Timebase ="; tnb$
15400 PRINT "    5. Return to main menu"
15500 PRINT
15600 PRINT "To alter setting enter appropriate number (1,2,3,4, or 5)"
15700 PRINT
15800 INPUT "Enter choice : "; aa$
15900 IF aa% < 1 OR aa% > 5 THEN 15700
16000 ON aa% GOTO 16100, 17800, 19100, 19800, 5000
16100 'set pretrigger on cro
16200 CLS
16300 pta% = 0
16400 PRINT "Present value for pretrigger is "; pt$
16500 PRINT
16600 PRINT "    1. 0%"
16700 PRINT "    2. 25%"
16800 PRINT "    3. 75%"
16900 PRINT "    4. 100%"
17000 PRINT
17100 INPUT "Enter choice : "; pta$
17200 IF pta% < 1 OR pta% > 4 THEN 17100
17300 IF pta% = 1 THEN pt$ = "PT=0%": pt$ = "0%"
17400 IF pta% = 2 THEN pt$ = "PT=25%": pt$ = "25%"
17500 IF pta% = 3 THEN pt$ = "PT=75%": pt$ = "75%"
17600 IF pta% = 4 THEN pt$ = "PT=100%": pt$ = "100%"
17700 CALL IBWRT(cro%, pt$): GOTO 14700
17800 'set storage mode
17900 CLS
18000 PRINT "Present state for storage mode is "; mode$
18100 PRINT "- note, front panel switches must not be set on non-storage."
18200 PRINT
18300 PRINT "Choose either: 1. Refresh"
18400 PRINT "   or 2. Roll"
18500 PRINT
18600 INPUT "Enter choice : "; mode$
18700 IF mode% < 1 OR mode% > 2 THEN 18600
18800 IF mode% = 1 THEN mode$ = "MODE=REFR": mode$ = "REFRESH"
18900 IF mode% = 2 THEN mode$ = "MODE=ROLL": mode$ = "ROLL"
19000 CALL IBWRT(cro%, mode$): GOTO 14700
19100 'note on capture mode
19200 CLS
19300 PRINT "The only mode available is single capture "
19400 PRINT
19500 PRINT "Hit any key to continue"
19600 xx$ = INPUT$(1)
19700 GOTO 14700
19800 "set timebase
19900 CLS
20000 PRINT "Present timebase is "; tmb$; " secs."
20100 PRINT
20200 PRINT "Choose a value in the range 50 to 5E-6 (ie 50 sec.to 5 uscc/div.)."
20300 PRINT "in a 1, 2, 5 sequence. (ie only # starting with 1,2,or 5)."
20400 PRINT "The value MUST be in exponential format, also must not contain"
20500 PRINT "a decimal point. ": PRINT
20600 INPUT "Enter value : "; tmb$
20700 mb1$ = "HSA=" + tmb$: CALL IBWRT(cro%, tmb$
20800 GOTO 14700
20900 " subroutine to write to files
21000 CLS
21100 PRINT "Is current being measured on Ch1 & potential on Ch2 (Y or N) ";
21200 PRINT
21300 J1$ = INPUT$(1); IF J1$ = "Y" OR J1$ = "y" THEN j2 = 0: GOTO 21800
21400 IF J1$ = "N" OR J1$ = "n" THEN 21500 ELSE 21100
21500 PRINT
21600 PRINT "It will be assumed that Ch1 = potential & Ch2 = current "
21700 j2 = 1
21800 IF j2 = 0 THEN b1$ = "ST1": b2$ = "ST2"
21900 IF j2 = 1 THEN b1$ = "ST2": b2$ = "ST1"
22400 "now write data to the files
22500 txt$ = "TXT=SENDING DATA": CALL IBWRT(cro%, txt$)
22550 cnt$ = 5000: qq$ = "NB=BIN": CALL IBWRT(cro%, qq$): qq$ = "BL=0":
22600 CALL IBWRT(cro%, b1$)
22700 red$ = SPACE$(8)
22800 CALL IBRD(cro%, red$): PRINT red$
22900 GOSUB 14200: IF j2 = 0 THEN CALL IBRD1(cro%, y1%(), cnt$) ELSE CALL
23000 IBRD1(cro%, x1%(), cnt$)
23000 PRINT
23200 PRINT IBCNT%; "bytes of data transferred from Ch1"
23300 CALL IBWRT(cro%, b2$)
23400 red2$ = SPACE$(8)
23500 CALL IBRD(cro%, red2$): PRINT red2$
23600 GOSUB 14200: IF j2 = 0 THEN CALL IBRD1(cro%, x1%(), cnt$) ELSE CALL
23800 IBRD1(cro%, y1%(), cnt$)
23800 PRINT
23900 PRINT IBCNT%; "bytes of data transferred from Ch2"
23950 GOSUB 60000
24000 PRINT
24100 PRINT "Hit any key to continue"
24200 xx$ = INPUT$(1)
24210 INPUT "Do you wish to save the data?": xx$: IF xx$ = "y" OR xx$ = "Y" THEN
24220 ELSE 24300
24220 INPUT "Enter name of potential file : "; a$: pfnam$ = disk$ + a$
24230 INPUT "Enter name of current file : "; b$: ifnam$ = disk$ + b$
24240 OPEN "o", #1, pfnam$: FOR i = 0 TO 1023: PRINT #1, x%: NEXT i: CLOSE #1
24250 OPEN "o", #1, ifnam$: FOR i = 0 TO 1023: PRINT #1, y%: NEXT i: CLOSE
24300 GOTO 5000
24400 ' subroutine to run experiment from cro
24500 CLS
24600 txt$ = "TXT='LOCAL'": CALL IBWRT(cro%, txt$)
24700 CALL IBLOC(cro%); go to local mode
24800 PRINT "CRO now available for manual control"
24900 PRINT
25000 PRINT "Hit any key to transfer data."
25100 xx$ = INPUTS(1)
25200 CALL IBCLR(cro%)
25300 txt$ = "TXT='REMOTE'": CALL IBWRT(cro%, txt$)
25400 GOTO 20900
25450 'SUBROUTINE TO PLOT DATA TO SCREEN
25475 CLS
25600 INPUT "Plot from (M)emory or (D)isk"; xx$; IF xx$ = "M" OR xx$ = "m"
THEN 26400
26050 INPUT "Enter potential filename : ", b$
26100 INPUT "Enter current filename : ", a$
26200 OPEN "I", #1, disk$ + a$: FOR i = 1 TO 1022: INPUT #1, y% (i): NEXT i:
CLOSE #1
26300 OPEN "I", #2, disk$ + b$: FOR i = 1 TO 1022: INPUT #2, x% (i): NEXT i:
CLOSE #2
26400 SCREEN 2
26450 CLS
26500 WINDOW (-128, -128)-(127, 127)
26600 FOR i = 1 TO 1022: PSET (x% (i), y% (i)); NEXT
26650 IF sm% = 1 THEN RETURN
26700 PRINT "ENTER ANY KEY TO CONTINUE"
26800 xx$ = INPUTS(1)
26900 GOTO 5000
30000 ' subroutine to average scans
30100 CLS
30120 PRINT " This routine accepts previously stored scans"
30122 PRINT " and calculates an average for each point."
30124 PRINT
30200 av% = 1
30300 PRINT "Enter filename "; av%; : INPUT flna$(av%); flna$(av%) = disk$ + f
30400 IF flna$(av%) <> disk$ THEN av% = av% + 1: GOTO 30300
30450 av% = av% - 1: FOR ai% = 1 TO av%
30500 OPEN "I", ai%; flna$(ai%)
30600 NEXT ai%
30650 PRINT "Enter result filename :"; fln$: fln$ = disk$ + fln$
30700 FOR aver% = 0 TO 1023: f% = 0
30800 FOR ai% = 1 TO av%: INPUT #ai%, a%; f% = f% + a%: NEXT ai%; x%(aver%) = f% \ av%: NEXT aver%
30900 OPEN "O", #50, fln$: FOR ai% = 0 TO 1023
31000 PRINT #50, x%(ai%)
31100 NEXT ai%
31200 CLOSE
32000 GOTO 5000
40000 CLS ; INPUT "Smooth from (M)emory or (D)isk"; xx$; IF xx$ = "M" OR xx$ =
"m" THEN 40500
40100 INPUT "Enter current filename : "; a$: a$ = disk$ + a$
40200 INPUT "Enter potential filename : ", b$: b$ = disk$ + b$
40300 OPEN "I", #1, a$: FOR i = 1 TO 1022: INPUT #1, y%(i); NEXT i: CLOSE #1
40400 OPEN "I", #2, b$: FOR i = 1 TO 1022: INPUT #2, x%(i); NEXT i: CLOSE #2
40500 INPUT "Window size (this value must be an odd number)"; ws
40600 INPUT "Number of repeat smooths"; ns: hs = INT(ws / 2): bl% = 0: sm% = 1
40700 IF ns > 1 THEN INPUT "Do you wish to see a plot after each repetition"; xx$: IF
 xx$ = "Y" OR xx$ = "y" THEN bl% = 1
40800 FOR si = 1 TO ns: FOR j = hs TO 1022 - hs: su = 0
40900 FOR k = j - hs TO j + hs: su = su + y%(k); NEXT k: y1%(j) = INT(su / ws):
  NEXT j
41000 FOR j = 1 TO 1022: y%(j) = y1%(j); NEXT j
41100 IF bl% = 1 OR ns = 1 THEN GOSUB 26400
41200 NEXT si: sm% = 0
41300 INPUT "Do you wish to save the resultant smoothed file"; xx$: IF xx$ = "y" OR
 xx$ = "Y" THEN INPUT "Current filename"; a$ ELSE 42000
41400 a$ = disk$ + a$: OPEN "o", #1, a$: FOR i = 1 TO 1022: PRINT #1, y%(i):
  NEXT i: CLOSE #1
42000 GOTO 5000
50000 FOR i = 1 TO 1022: PRINT x%(i), y%(i); NEXT i: INPUT "Continue.."; xx$: IF
 xx$ = "y" OR xx$ = "Y" THEN 5000
50100 CLS
50200 PRINT "Error detected, retry whatever you just did......... seriously..."
50300 PRINT
50400 RESUME
60000 FOR i = 0 TO 511: x%(i * 2) = -x1%(i) \ 256: x%(i * 2 + 1) = -x1%(i) MOD 256
60050 y%(i * 2) = -y1%(i) \ 256: y%(i * 2 + 1) = -y1%(i) MOD 256
60100 NEXT i
60110 SCREEN 2: CLS: WINDOW (-128, -128)-(127, 127)
60200 FOR i = 0 TO 1023: IF x%(i) < 0 THEN x%(i) = -x%(i) - 128 ELSE x%(i) = -
  x%(i) + 127
60300 IF y%(i) < 0 THEN y%(i) = -y%(i) - 128 ELSE y%(i) = -y%(i) + 127
60400 PSET (x%(i), y%(i)); NEXT i: RETURN
PROGRAM SPOLO.FOR

DIGITAL SIMULATION PROGRAM BASED ON FELDBERG'S APPROACH
CALCULATION OF SURFACE CONCENTRATIONS RESULTING FROM
A DC CYCLIC POTENTIAL RAMP

THIS PROGRAM WAS WRITTEN BY R. O'HALLORAN AND ADAPTED
FOR USE ON THE DEAKIN DEC-20 BY K. HANCK. SIMULATION
OF SUCCESSIVE MULTI-STEP ELECTRON TRANSFERS
WERE ADDED BY K. HANCK. POTENTIAL DEPENDENCE OF ALPHA
ADDED BY P. J. MAHON.

THE SIMULATIONS OF PRECEDING AND FOLLOWING KINETICS
ARE VALID ONLY FOR THE CASE WHERE NCOUPL = 1

THE DATA WRITTEN INTO THE "PLOTFILE" IS IN LIST DIRECTED
FORMAT: POTENTIAL (MV), CURRENT (MILLIAMP)

FORMAT FOR DATA INPUT FILE

RECORD 1 IS IN 12A5 FORMAT AND RECORD 7 IS IN A6,2X,12 FORMAT
ALL OTHER INPUT IS THROUGH LIST DIRECTED I/O

C*****RECORD 1*****TITLE IN 12A5 FORMAT
C
C*****RECORD 2*****NSPEC,NCOUPL,NORM,DDMAX
C
NSPEC = NUMBER OF SPECIES
NCOUPL = NUMBER OF RED/OX COUPLES
NORM = NORMALIZING SPECIES
DDMAX = SIMULATOR DIFFUSION COEFFICIENT

C*****RECORD 3*****EZ(I),ALPHAZ(I),DALPHA(I),NELS(I),HETRAT(I),
HMRATF(I),HMRATR(I)
C
EZ(I) = EZERO OF RED/OX COUPLE I (VOLTS)
ALPHAZ(I) = TRANSFER COEFFICIENT OF COUPLE I AT EZERO
DALPHA(I) = POTENTIAL DEPENDENCE OF ALPHA
NELS(I) = NUMBER OF ELECTRONS OF COUPLE I
HETRAT(I) = ELECTRON TRANSFER RATE CONSTANT FOR COUPLE I
(CM/SEC)
HMRATF(I) = FORWARD HOMOGENEOUS RATE CONSTANT FOR COUPLE I
HMRATR(I) = REVERSE HOMOGENEOUS RATE CONSTANT FOR COUPLE I

C*****RECORD 4*****CONC(I),DCOF(I)
C
CONC(I) = CONCENTRATION OF SPECIES I (MOLAR)
DCOF(I) = DIFFUSION COEFFICIENT OF SPECIES I (CM**2/SEC)

C*****RECORD 5*****TEMP,RTVS,ESTRT,EFINAL,SURF
C
TEMP = ABSOLUTE TEMPERATURE
RTVS = SCAN RATE IN VOLTS/SEC
C ESTRT = STARTING POTENTIAL (VOLTS)
C EFINAL = SWITCHING POTENTIAL (VOLTS)
C SURF = ELECTRODE SURFACE AREA (CM**2)
C
C*****RECORD 6*****NTAPE,EINCR,IVAL
C
C NTAPE = FLAG FOR STORING DATA
C EINCR = POTENTIAL INCREMENT (VOLTS)
C IVAL = OUTPUT DENSITY
C
C*****RECORD 7*****WHICH,ITYPE
C
C WHICH = ELECTRODE TYPE (SPHERE OR PLANAR)
C ITYPE = REACTION TYPE (PRECEDING=-1,SIMPLE=0,
       FOLLOWING=1)
C
CHARACTER*5 FILEIN,PLTFIL,OUTFIL
CHARACTER*10 WHICH
DIMENSION TITLE(12),EZ(4),AI,PHAZ(4),RHSNRM(4),RTNORM(8),
& CONC(4),DCOF(4),DD(4),RT(8),RIS(4),
& E(C(4,350),TL(350),TR(350),FF(4),CXZ(4),
& RHF(4),DEL(4),NSPEC,NCOUPL,TMV5,TOTLN,TFINAL,
& FR,FFAR,K,SPHERE,RTVS,RHB(4),CHECK,DDMAX,SURF,DELPOT,
& KAYY,AMALOM,ATYPE(2),ITYPE,ESTEP,NELS(4),HMRAF(4),
& HMRATR(4),HETRAT(4),WHICH(2),APPN(4),CUR(4),RS(350),XIN(350),
& XMED(350),DIMID,DALDE(4),ALPHA(4)

C ********** INITIALIZATION **********
C
C DEFINITION OF CONSTANTS
C
CHECK=0.0
FK=0.5
DEN=EXP(FK)-1.
PI=3.14159
FR=96484.6/8.31441
WRITE (*,*) ' ENTER INPUT FILENAME'
READ(*,101)FILEIN
101 FORMAT(A5)
WRITE (*,*)' FILENAME FOR PLOT FILE'
READ(*,101)PLTFIL
OPEN (15,FILE=FILEIN)
WRITE (*,*)' DETAILED PRINTOUT'
READ(*,108)NPRINT
108 FORMAT(A2)
READ (15,29) TITLE
WRITE(*,58)
58 FORMAT(1X,'DIMER REACTION?')
READ(*,101)DIMID
C
C SYSTEM CONSTANTS
C
FFAR = 0, JJ = 0
C AMALGM = 3H NO
READ (15, *) NSPEC, NCOUPL, NORM, DDMAX
IF (NSPEC.EQ.0) GO TO 27
IF (NORM.EQ.0) NORM = 1
DO 90 I = 1, NCOUPL
90 READ(15, *) EZ(I), ALPHAZ(I), DALSE(I), NELS(I), HETRAT(I), HMRATF(I), & HMRATR(I)
DO 91 I = 1, NSPEC
91 READ(15, *) CONC(I), DCOF(I)
C
C EXPERIMENTAL CONSTANTS
C
READ (15, *) TEMP, RTVS, ESTRT, EFINAL, SURF
DELPOT = (ESTRT - EFINAL)
TMVS = 2. * DELPOT / RTVS
C
C PROGRAM CONSTANTS
C
READ (15, *) NTAPE, EINCR,IVAL
IF (NTAPE.LE.0) GO TO 200
WRITE (*, *) ' FILENAME FOR SURFACE CONCENTRATIONS?'
READ(*, 101) OUTFIL
OPEN (17, FILE = OUTFIL, STATUS = 'NEW')
200 READ (15, 35) WHICH(I), ITYPE
IF (ITYPE) 2, 3, 4
2 ATYPE(1) = 'PRECE'
ATYPE(2) = 'DING'
IF (HMRATR(I).EQ.0.0) HMRATR(I) = 1.0E-30
GO TO 5
3 ATYPE(1) = 'SIMPL'
ATYPE(2) = 'E'
GO TO 5
4 ATYPE(1) = 'FOLLO'
ATYPE(2) = 'WING'
IF (HMRATF(I).EQ.0.0) HMRATF(I) = 1.0E-30
GO TO 5
5 CONTINUE
C IPVAL = .0001/ EINCR
IF (EINCR.GT.0.0001) IPVAL = 1
IVAL = IPVAL
ESTEP = EINCR * AVAL
NFINAL = 2. * DELPOT / EINCR + 0.5
FFINAL = NFINAL
NVEMAX = 2.0 + (1.0 / FK) * ALOG(6. * DEN * SQRT(DDMAX * (FFINAL)) + 1.)
WRITE (*, *) NVEMAX
IM1 = NVEMAX + 1
DO 517 I = 1, IM1
FI = I
XIN(I) = (EXP(FK*(I-1)) - 1.0) / DEN
XMED(I) = (EXP(FK*(FI-0.5)) - 1.0) / DEN
517 CONTINUE
TFINAL = NFINAL
FRT=FR/TEMP
KAYY=2.*DELPOY(EINCR*IVAL)+0.5

WRITE OUT INPUT DATA
WRITE (*,36)
WRITE (*,49)FILEIN,PLTFIL
IF(NTAPE.GT.0)WRITE (*,50)OUTFIL
WRITE (*,37)NSPEC,NCOUPL,RTVS,SURF,TEMP,DDMAX
WRITE (*,38)ESTRT,EFINAL,EINCR,WHICH,AMALGM,ATYPE
IF(PLTFIL.NE.'NONE ')WRITE(16,28)TITLE
IF(PLTFIL.NE.'NONE ')WRITE(16,*)KAYY
IF(PLTFIL.NE.'NONE ')WRITE(16,*)TEMP,NELS(1),RTVS,DCOF(1)
IF(PLTFIL.NE.'NONE ')WRITE(16,*)SURF,ESTRT,EFINAL,CONC(1)

NORMALIZATION OF DIFFUSION COEFFICIENTS
DXMAX=DCOF(1)
DO 6 J=2,NSPEC
   DXMAX=AMAX1(DXMAX,DCOF(J))
   DO 7 J=1,NSPEC
5 DD(J)=DDMAX*DCOF(J)/DXMAX
   ATFAC=CONC(NORM)*1000.*SQRT(DD(NORM)*FRT*EINCR)
   DCFAC=96487.7*SURF*SQRT(RTVS*FRT)
6 CONTINUE
7 WRITE (*,46)
8 WRITE (*,39)SPHERE
   GO TO 10
9 WRITE (*,40)
   GOTO10
10 CONTINUE
11 WRITE (*,59)
59 FORMAT(/// CYLINDRICAL ELECTRODE IS BEING USED')
CONTINUE

NORMALIZATION OF RATE CONSTANTS
DO 11 J=1,NCOUPL
   RHSNRM(J)=HETRAT(J)/SQRT(DCOF(NORM)*RTVS*NELS(J)*FRT)
10 RHS(J)=RHSNRM(J)*SQRT(DD(NORM)*NELS(J)*FRT*EINCR)
   IF(DIMID.EQ.'YES') GOTO 31
11 DO 12 J=1,NCOUPL
12 RTNORM(2*J-1)=HMRATF(J)*TMVS
   RTNORM(2*J)=HMRATR(J)*TMVS
   RT(2*J-1)=RTNORM(2*J-1)/TFINAL
   RT(2*J)=RTNORM(2*J)/TFINAL
   GOTO 34
31 DO 32 J=1,NCOUPL
RTNORM(2*J-1)=HMRATF(J)*TMVS*CONC(NORM)
RTNORM(2*J)=HMRATR(J)*TMVS*CONC(NORM)
RT(2*J-I)=RTNORM(2*J-I)/TFINAL
32 RT(2*J)=RTNORM(2*J)/TFINAL
34 CONTINUE

C WRITE NORMALIZED PARAMETERS

C WRITE (*,41)
DO 92 I=1,NCOUPL
WRITE (*,42),EZ(I),ALPHAZ(I),DALDE(I),NELS(I),HETRAT(I),
&HMRATF(I),HMRATR(I)
92 CONTINUE

C WRITE (*,43)
WRITE (*,44) (I,CONC(I),DCOF(I),I=1,NSPEC)
WRITE (*,45) NORM

C WRITE (*,46)
WRITE (*,28) TITLE
IF (NPRINT.NE.'YE') GO TO 60
WRITE (*,36)
WRITE (*,47)

C ************** END OF INITIALIZATION **************

C ************** SETTING OF SURFACE BOUNDARY **************
C ************** CONDITIONS **************

C CONCENTRATION GRADIENT LOOP

C 60 DO 14 I=1,NVEMAX
DO 14 J=1,NSPEC
14 CC(J,I)=1000.*CONC(J)
KKKK=(NFINAL/2)+1

C CALCULATION OF SPHERICAL DIFFUSION CORRECTION

C FSUR=SURF*RTVS*DD(NORM)/(DCOF(NORM)*EINCR)
IF (WHICH(1).EQ.'PLANAR') GO TO 16
IF (WHICH(1).EQ.'CYLIND') GO TO 70
RR=SQRT(FSUR/(4.*PI))
WRITE (*,*),RR
TL(1)=1./XMED(1)
TR(1)=3.*((RR+1.)**2./((RR+1.)**3.-RR**3.)*)(XMED(2)-XMED(1))
DO 15 I=2,NVEMAX
RSUMI=RR+XIN(I)
RSUMO=RR+XIN(I+1)
VDIF=RSUMO**3.-RSUMI**3,
TL(I)=3.*(RSUMI**2.)/(VDIF*(XMED(I)-XMED(I-1)))*
15 TR(I)=3.*(RSUMO**2.)/(VDIF*(XMED(I+1)-XMED(I)))*
GO TO 89
70 WRITE (*,400)
400 FORMAT (1X,'ELECTRODE LENGTH (CM)?')
READ (*,*),ELENG
RAD=SURF/(2.*PI*ELENG)
CALCULATION OF CYLINDRICAL DIFFUSION CORRECTION
RR=RAD*(RTVS*DD(NORM)/(DCOF(NORM)*EINCR))**0.5
WRITE (*,*) RR,RAD
TL(1)=1./XMED(1)
TR(1)=2.*(RR+1.)/(RR+1.)**2.-RR**2.)*(XMED(2)-XMED(1))
DO 715 I=2,NVEMAX
RSUMI=RR+XIN(I)
RSUMO=RR+XIN(I+1)
VDIF=RSUMO**2.-RSUMI**2.
TL(I)=2.*RSUMI/(VDIF*(XMED(I)-XMED(I-1)))
TR(I)=2.*RSUMO/(VDIF*(XMED(I+1)-XMED(I)))
715 CONTINUE
GOTO 89
CONTINUE
IM1=NVEMAX+1
DO 17 I=1,IM1
FI=I
XIN(I)=(EXP(FK*(I-1))-1.0)/DEN
XMED(I)=(EXP(FK*(FI-0.5))-1.0)/DEN
CONTINUE
TL(1)=1./XMED(1)
TR(1)=1./(XMED(2)-XMED(1))
DO 18 I=2,NVEMAX
TL(I)=1./(XIN(I+1)-XIN(I))*(XMED(I)-XMED(I-1))
TR(I)=1./(XIN(I+1)-XIN(I))*(XMED(I+1)-XMED(I))
17 CONTINUE
89 CONTINUE

TIME-POTENTIAL K-LOOP

DO 25 IKK=1,NFINAL
K=IKK
IF (K.EQ.1) E=ESTRT
IF (K.GT.1) E=E.EINCR
IF (K.EQ.KKKK) E=EFINAL
IF (K.GT.KKKK) E=E+E2.*EINCR
IF (K.EQ.NFINAL) GOTO 26

****** CALCULATION OF HETEROGENEOUS RATE CONSTANTS ******

DO 19 JS=1,NCOUPL
ALPHA(JS)=ALPHAZ(JS)+DALDE(JS)*(E-EZ(JS))
EOVER=NELS(JS)*FRT*(E-EZ(JS))
RHF(JS)=RHS(JS)*EXP(-ALPHA(JS)*EOVER)
RHB(JS)=RHS(JS)*EXP((1.-ALPHA(JS))*EOVER)
19 CONTINUE

*************** CALCULATION OF FARADAIC FLUX ***************

TIMEE=K
GOTO999
IF (MOD(K,IVAL),NE.0)GOTO999
WRITE (*,*) K,NVE,1
WRITE (*,*) (CC(1,L),L=1,1)
CONTINUE
NVE=2.0+(1.0/FK)*ALOG(6.*DEN*SQT(DDMAX*TIMEE)+1.0)
IF(NVE,GTT,NVEMAX) WRITE(*,*) NVE
IF(TTYPE) 99,110,98

CONTINUE
C FOLLOW UP REACTION
RTL=1./TL(1)
FF(1)=((RHF(1)*CC(1,1)-RHB(1)*CC(2,1))/(1.+RTL*RHF(1)/DD( &1)+RTL*RHB(1)/DD(2))
FF(2)=FF(1)
FF(3)=0.0
APPN(1)=FF(1)/SQT(R1.*NELS(1))
CUR(1)=APPN(1)*NELS(1)*CONC(1)*SQT(DCOF(1)*NELS(1))
GO TO 20

CONTINUE
C PRECEDING REACTION
FF(1)=0.
FF(2)=((RHF(1)*CC(2,1)-RHB(1)*CC(3,1))/(1.+0.5*RHF(1)/DD( &1)+0.5*RHB(1)/DD(3))
FF(3)=FF(2)
APPN(1)=FF(2)/SQT(R1.*NELS(1))
CUR(1)=APPN(1)*NELS(1)*CONC(2)*SQT(DCOF(2)*NELS(1))
GO TO 20

SIMPLE REACTION
GO TO(111,112,113)NCOUPL

CONTINUE
C ONE CHARGE TRANSFER STEP
RTL=1./TL(1)
FF(1)=((RHF(1)*CC(1,1)-RHB(1)*CC(2,1))/(1.+RTL*RHF(1)/DD( &1)+RTL*RHB(1)/DD(2))
FF(2)=FF(1)
FF(3)=0.
FF(4)=0.
APPN(1)=FF(1)/SQT(R1.*NELS(1))
CUR(1)=APPN(1)*NELS(1)*CONC(1)*SQT(DCOF(1)*NELS(1))
GO TO 20

CONTINUE
C TWO CHARGE TRANSFER STEPS
FF(1)=((RHF(1)*CC(1,1)-RHB(1)*CC(2,1))/(1.+0.5*RHF(1)/DD( &1)+0.5*RHB(1)/DD(2))
FF2=((RHF(2)*CC(2,1)-RHB(2)*CC(3,1))/(1.+0.5*RHF(2)/DD(2)
&+0.5*RHB(2)/DD(3))
FF(2)=FF2-FF(1)
FF(3)=FF2
FF(4)=0.
APPN(1)=FF(1)/SQT(R1.*NELS(1))
APPN(2)=FF2/SQT(R2.*NELS(2))
CUR(1)=APPN(1)*NELS(1)*CONC(1)*SQT(DCOF(1)*NELS(1))
CUR(2)=APPN(2)*NELS(2)*CONC(1)*SQT(DCOF(2)*NELS(2))
GO TO 20

CONTINUE
C THREE CHARGE TRANSFER STEPS
FF(1)=((RHF(1)*CC(1,1)-RHB(1)*CC(2,1))/(1.+0.5*RHF(1)/DD( &1)+0.5*RHB(1)/DD(2))
FF2=\((RHF(2) \times CC(2,1) - RHB(2) \times CC(3,1))/(1.0 + 0.5 \times RHF(2)/DD(2)) \& + 0.5 \times RHB(2)/DD(3))\)
FF(2)=FF2-FF(1)
FF3=\((RHF(3) \times CC(3,1) - RHB(3) \times CC(4,1))/(1.0 + 0.5 \times RHF(3)/DD(3)) \& + 0.5 \times RHB(3)/DD(4))\)
FF(3)=FF3-FF2
FF(4)=FF3
APPN(1)=FF(1)/SQRZ(1.*NELS(1))
APPN(2)=FF(2)/SQRZ(1.*NELS(2))
APPN(3)=FF(3)/SQRZ(1.*NELS(3))
CUR(1)=APPN(1)*NELS(1)*CONC(1)*SQRZ(DCOF(1)*NELS(1))
CUR(2)=APPN(2)*NELS(2)*CONC(1)*SQRZ(DCOF(2)*NELS(2))
CUR(3)=APPN(3)*NELS(3)*CONC(1)*SQRZ(DCOF(3)*NELS(3))
KK=K-1

20 CALCULATION OF DC CURRENT FUNCTION AND SURFACE CONCENTRATIONS

21 TOTALN=0.
DCCUR=0.
DO 222 NC=1,NCOUPL
TOTALN=TOTALN+APPN(NC)
DCCUR=DCCUR+CUR(NC)
222 CONTINUE
TOTALN=TOTALN/AFAC
DCCUR=DCCUR*DCFAC/AFAC
POTL=E*1000.
DO 22 J=1,NSPEC
22 C XZ(J)=CC(J,1)-FF(J)/(2.*DD(J))
C IF(E.EQ.EFINAL)CSP=DCCUR
C
C LOCATION OF CATHODIC AND ANODIC PEAKS
C
IF(MOD(KK,IPVAL).NE.0)GOTO310
IF(K.GT.3)GOTO 295
SORT(K,1)=POTL
SORT(K,2)=DCCUR
GOTO 93
295 CONTINUE
DO 296 IPK=1,2
SORT(1,IPK)=SORT(2,IPK)
SORT(2,IPK)=SORT(3,IPK)
296 CONTINUE
93 CONTINUE
SORT(3,1)=POTL
SORT(3,2)=DCCUR
FIX(1)=ABS(SORT(1,2))
FIX(2)=ABS(SORT(2,2))
FIX(3)=ABS(SORT(3,2))
IF(K.LT.20)GOTO 310
IF(FIX(1).LE.FIX(2).AND.FIX(3).LE.FIX(2))GOTO 300
GOTO 310
300 JJ=JJ+1
PKI(JJ)=SORT(2,2)
PKE(JJ)=SORT(2,1)
CONTINUE

OUTPUT

IF(MOD(KK,IVAL),NE.0)GO TO 23
IF(NPRINT.EQ.'YE')WRITE (*,48) E,DCCUR,TOTLN,(CXZ(J),J=1,NSPEC)
IF(PLTFIL.NE.'NONE')WRITE(16,*)POTL,DCCUR
IF (NTAPE.GT.0) CALL STORE
GO TO 23
WRITE(*,*) FF(1),FF(2),CUR(1),DCCUR,CXZ(1),CXZ(2)
CONTINUE

********* DIFFUSION *********

**** AND INFLUENCE OF HOMOGENEOUS CHEMICAL REACTIONS *****

DO 24 J=1,NSPEC
I=1
CALL DELTA (I)
IF(WHICH(1).EQ.'SPHERE')GOTO500
IF(WHICH(1).EQ.'CYLIND')GOTO510
BL=1.
GOTO520
500 BL=3.*(RR**2.)/((RR+1.)***3.-RR**3.)
GOTO520
510 BL=2.*RR/((RR+1.)***2.-RR**2.)
520 CONTINUE
AAAA=CC(J,1)+TR(1)*DD(J)*(CC(J,2)-CC(J,1))-BL*FF(J)+DEL(J)
DO 24 I=2,NVE
CALL DELTA (I)
BBBB=CC(J,I)+(TR(I)*DD(J)*(CC(J,I+1)-CC(J,I))-TL(I)*DD(J)*
& (CC(J,I)-CC(J,I-1)))+DEL(J)
CC(J,I-1)=AAAA
AAAA=BBBB
24 CONTINUE
GOTO25
IF(MOD(KK,IVAL),NE.0)GOTO25
WRITE (*,*),K,NVE,I
WRITE (*,*), (CC(J,I),I=1,NVE)
25 CONTINUE
26 CONTINUE
DO 88 I=1,JI
WRITE (*,51,),PKE(I),PKI(I)
IF(PLTFIL.NE.'NONE')WRITE(16,51),PKE(I),PKI(I)
CONTINUE
R=ABS(PKI(2))/ABS(PKI(1))+0.485*ABS(CSP)/ABS(PKI(1))+0.086
WRITE(*,52),CSP
WRITE(*,53),R
88 CONTINUE
STOP

FORMAT (1X,12A5)
FORMAT (12A5)
FORMAT (A10,J2)
FORMAT (1H1)
FORMAT (' NUMBER OF SPECIES=',I2,', NUMBER OF COUPLES=',I2, &/', NUMBER OF VOLTAGE SCAN=',F12.4/, &'/ SURFACE AREA OF THE ELECTRODE=',F10.4/, &'/ TEMPERATURE=',F10.4/, DDMAX=',F10.4/) 38
FORMAT ('20H STARTING POTENTIAL=','F10.4/17H FINAL &POTENTIAL=','F10.4/21H POTENTIAL INCREMENT=','F10.7/','ELECTRODE &TYPE=','A5/','AMALGAM CASE ... ','A3/','15H REACTION TYPE=','A5//') 39
FORMAT ('12H SPHERICITY=','F10.4//') 40
FORMAT ('///32H PLANAR ELECTRODE IS BEING USED.') 41
FORMAT ('1X','COUPLE',3X,'EZERO',3X,'ALPHA',3X,'DALPDE', &3X,'N',6X,'KS',10X,'KHF',10X,'KHR') 42
FORMAT ('4X,I1,4X,F6.3,2X,F6.3,3X,F6.3,3X,I1,5X,3(E9.4,3X)) 43
FORMAT ('/// SPECE CONCENTRATION DIFFUSION COEFF') 44
FORMAT ('4X,I1,8X,E12.6,8X,E12.4') 45
FORMAT ('32H NORMALIZING SPECIES IS SPECIES I1)') 46
FORMAT ('1H )') 47
FORMAT('5X,POTENTIAL',5X,'CURRENT',9X,'APPN',6X,'CONC(1)', &5X,'CONC(2)',5X,'CONC(3)',5X,'CONC(4)') 48
FORMAT ('2X,F10.5,5X,E11.4,5(2X,F10.5)) 49
FORMAT('1X,'DATA INPUT FILE=',1X,'A5/',' PLOT FILE=',1X,'A5/) 50
FORMAT('1X,'SURFACE CONCENTRATIONS IN FILE=',1X,'A5/) 51
FORMAT('1X,'/','PEAK NUMBER ',1X,'1X,'- POTENTIAL=',E12.4, &' MV',10X,'CURRENT=',E12.4,' MAMP/) 52
FORMAT('1X,'CSP=',E12.4,' MAMP/) 53
FORMAT('1X,'IA/IC=',F10.4/) END 54
SUBROUTINE DELTA(I)
C INFLUENCE OF HOMOGENEOUS CHEMICAL REACTION
C STATEMENT 501 IS FOR PRECEDING REACTION
C STATEMENT 502 IS FOR SIMPLE REACTION
C STATEMENT 503 IS FOR FOLLOW UP REACTION
C IF (ITYPE) 1,2,3
1 DEL(1)=RT(2)*CC(2,J)-RT(1)*CC(1,I)
DEL(2)=DEL(1)
DEL(3)=0.0
GO TO 4
2 DO 5 NS=1,NSPEC
DEL(NS)=0.0
5 CONTINUE
GO TO 4
3 IF(DIMID.EQ.'YES')GOTO 6
DEL(1)=0.0
DEL(2)=RT(2)*CC(3,I)-RT(1)*CC(2,I)
DEL(3)=DEL(2)
GOTO 4
6
DEL(1)=0.0
DEL(2)=RT(1)*(CC(2,1)**2)/(CONC(NORM)*1000.)
DEL(3)=0.5*DEL(2)
4
CONTINUE
RETURN
END
SUBROUTINE STORE

C
STORING OUTPUT DATA
C
COMON TTITLE(12),EZ(4),ALPHA(4),RHSNRM(4),RTNORM(8),CONC(4),
&DCOF(4),DD(4),RT(8),RHS(4),
&CC(4,350),TL(350),TR(350),FF(4),CXZ(4),
&RHF(4),DEL(4),NSPEC,NORM,NCOUPL,TMVS,TEMP,TOTLN,TFINAL,
&FRT,FFAR,K,SHERE,RTVS,RHB(4),CHECK,DDMAX,SURF,DELPOT,
&KAYY,AMALGM,ATYPE(2),RTYPE,ESTEP,NELS(4),HRMATF(4),
&HMRTATR(4),HETRAT(4),WHICH(2),APPN(4),CUR(4),RS(350),XIN(350),
&XMD(350),DIDIM,ALPHA(4),APEL(4)
C
IF (K,GT.1) GO TO 4
CHECK=CHECK+1.0
IF (CHECK,GE.2.0) GO TO 1
WRITE (17,5) TITLE
1
CONTINUE
WRITE (17,6) DDMAX,KAYY,WHICH,AMALGM,ATYPE,ESTEP
IF (WHICH(1),EQ,'PLANA') GO TO 2
WRITE (17,7) NSPEC,NORM,NCOUPL,TMVS,TEMP,RTVS,SPHERE,
&DELMAT,DELPOT
GO TO 3
2
CONTINUE
WRITE (17,7) NSPEC,NORM,NCOUPL,TMVS,TEMP,RTVS,SURF,DELPOT
3
CONTINUE
DO 20 J=1,NSPEC
20
WRITE (17,*) CONC(J),DCOF(J)
DO 21 J=1,NCOUPL
21
WRITE (17,*) EZ(J),ALPHA(J),DALDE(J),NELS(J),HRTATR(J),
&HMRATR(J)
4
CONTINUE
WRITE (17,11) E,TOTLN,(CXZ(J),J=1,NSPEC)
RETURN
C
5
FORMAT (12A5)
6
FORMAT (F10.4,F10.4,F10.4,A3,2A5,E10.4)
7
FORMAT (31I7,8F10.4)
11
FORMAT (2F15.9,4E15.6)
END
PROGRAM BHOSCPSV.BAS FOR THE GLOBAL ANALYSIS OF_CYCLIC VOLTAMMOGRAMS FOR A SPHERICAL ELECTRODE GEOMETRY. WRITTEN BY PETER J. MAHON

DEFDBL A-Z
DEFINT I-J, M

DECLARE SUB adjcc (c#, i#, num%, pcri#)
DECLARE SUB pfit (fl$, pp(), py#, jh%, a, b, c)
DECLARE SUB fpa (fl$, pp(), c#, i#, num%, ntran%)
DECLARE SUB plot (fl$, pp(), clr%, lx#, ly#, pln%, phn%)
DECLARE SUB weight (fl$, pp(), c#, i#, sm#, ii#, ms#, num%, dte#, pif#, wi#, wnm#)
DECLARE SUB wls (fl$, pp(), wmod%, w#(), lx#(), ly#(), jl%, jh%, m#, c#)
DECLARE SUB noise (i#, num%, vr)
DECLARE SUB potpair (e#, i#, num%, switch%)
DECLARE SUB CROUT (NR%, MC%, NCC%, ZMCH%)
DECLARE SUB pwfit (fl$, wmod%, px#, py#, w#(), jl%, jh%, a#, b#, c#)
DECLARE SUB deriv (x#, der#, dte#, npt%, num%)
COMMON SHARED lpt%

GOSUB 1
GOTO 10

1 REM INITIALIZE
f' = 96484.6
rg = 8.31441
pi# = 3.1415926536#
size% = 1500
DIM fl$(2*size%), pp(4), i#(2*size%), c#(2*size%), co#(2*size%), sm#(2*size%), ii#(size%), ms#(size%), lx#(size%), mx#(size%), lx#(size%), ly#(size%), h#(2*size%), px#(size%), py#(size%), smp#(2*size%), wi#(size%), wnm#(size%), dte#(size%)
DIM SHARED XMAT1(10, 20)
wmod% = 0
lpt% = 1
OPEN "\DEV\pt1" FOR OUTPUT AS #4
RETURN

10 REM SCREEN MENU
CLS : SCREEN 0
PRINT : PRINT : PRINT " SPHERICAL BHO ANALYSIS"
PRINT " --------------------------": PRINT
PRINT " 1, READ RAW FILE"
PRINT " 2, READ SCALED DATA WITH EXPT. PARAMETERS"
PRINT " 3, ADJUST EXPT. PARAMETERS"
PRINT " 4, PERFORM ANALYSIS"
PRINT " 5, SAVE SCALED DATA WITH PRESENT EXPT. PARAMETERS"
PRINT " 6, APPLY iR CORRECTION"
PRINT " 7, APPLY SMOOTHING"
PRINT " 8, APPLY CHARGING CURRENT CORRECTION"
PRINT " 9, READ SIMULATED DATA (mV, mA)"
PRINT " 10, CHOOSE WEIGHTING FUNCTION OPTION"
PRINT "11, ADD RANDOM NOISE"
PRINT "12, SAVE OUTPUT DATA"
PRINT "13, ACTIVATE/DEACTIVATE THE PRINTER"
PRINT "14, EXIT"
PRINT : PRINT : INPUT "-input option (1-13)"; q
main = 1
IF q < 1 OR q > 14 THEN 10
ON q GOTO 1000, 2000, 3900, 4000, 5000, 6000, 7000, 8000, 9000, 10000, 11000,
12000, 13000, 14000
GOTO 10

1000 REM READ RAW DATA FILE
CLS
INPUT "current file"; c$
INPUT "potential file"; p$
OPEN c$ FOR INPUT AS #1
j% = 0
DO WHILE NOT EOF(1)
    j% = j% + 1
    INPUT #1, i#(j%)
LOOP
CLOSE #1
OPEN p$ FOR INPUT AS #1
j% = 0
DO WHILE NOT EOF(1)
    j% = j% + 1
    INPUT #1, e#(j%)
    lx#(j%) = j%
LOOP
CLOSE #1
num% = j% - 2
CALL plot(f1$(), pp(), 1, lx#, e#, 1, num%)
CALL plot(f1$(), pp(), 1, lx#, i#, 1, num%)
CALL plot(f1$(), pp(), 1, e#, i#, 1, num%)
SCREEN 0
INPUT "DO YOU WISH TO INVERT POTENTIAL SCALE"; a$
IF a$ = "Y" OR a$ = "y" THEN FOR j% = 1 TO num%; e#(j%) = -e#(j%); NEXT j%
INPUT "DO YOU WISH TO INVERT CURRENT SCALE"; a$
IF a$ = "Y" OR a$ = "y" THEN FOR j% = 1 TO num%; i#(j%) = -i#(j%); NEXT j%
INPUT "INITIAL POTENTIAL (V)" "; ci#
INPUT "SWITCHING POTENTIAL (V)" "; ch#
INPUT "INPUT POTENTIOSTAT SCALE (mV/V)"; scp
INPUT "INPUT C.R.O. SCALE (mV/DIV)" "; scc
scale = scp * scc / 1000000
emax# = -99999
emin# = 99999
FOR j% = 1 TO num%
    IF e#(j%) > emax# THEN emax# = e#(j%)
    IF e#(j%) < emin# THEN emin# = e#(j%)
NEXT j%
sum = 0: shigh = 0
FOR j% = 1 TO num%
    IF e#(j%) = emax# THEN shigh = shigh + j%; sum = sum + 1
NEXT j%
switch% = INT(shigh / sum)
j% = switch%
DO
j% = j% - 1
LOOP UNTIL j% = 1 OR e#(j%) = emin#
ptb% = j%
j% = switch%
DO
j% = j% + 1
LOOP UNTIL e#(j%) = emin# OR j% = num%
ptc% = j%
um% = ptc% - ptb% + 1
delt = cmx% - emin#
FOR j% = ptb% TO ptc%
IF j% <= switch% THEN e#(j%) = (j% - ptb%) * delt / (switch% - ptb%) + emin#
IF j% > switch% THEN e#(j%) = (ptc% - j%) * delt / (ptc% - switch%) + emin#
c#(j% - ptb% + 1) = (((ch# - ei#) * (c#(j%) - emin#)) / delt) + ei#
i#(j% - ptb% + 1) = i#(j%) * scalc * .0346
NEXT j%
CALL plot(fl$, pp(), 1, c#(), i#(), 1, num%)
PRINT ptb%, ptc%, num%, switch%
IF ptc% - switch% <= switch% - ptb% THEN switch% = switch% - ptb% + 1: CALL
popair(e#(), i#(), num%, switch%)
CALL plot(fl$, pp(), 1, c#(), i#(), 1, num%)
j% = 1: jh% = num% \ 10
FOR j% = j% TO jh%
lx#(j%) = j%
ly#(j%) = i#(j%)
NEXT j%
CALL wls(fl$, pp(), 2, wi#(), lx#(), ly#(), jl%, jh%, m#, c#)
ibeg = m# + c#
FOR j% = 1 TO num%
i#(j%) = i#(j%) - ibeg
NEXT j%
CALL plot(fl$, pp(), 1, c#(), i#(), 1, num%)
GOTO 10

2000 REM READ SCALED DATA
CLEAR
GOSUB 1
INPUT "filename"; o$
OPEN o$ FOR INPUT AS #1
INPUT #1, title$
INPUT #1, num%, t, n, s, d, e#, ch#, cb
FOR j% = 1 TO num%
INPUT #1, c#(j%), i#(j%)
IF i#(j%) > imax# THEN imax# = i#(j%); maxij% = j%
IF i#(j%) < imin# THEN imin# = i#(j%); minij% = j%
NEXT j%
CLOSE #1
CALL plot(fl$, pp(), 2, e#(), i#(), 1, num%)
rad# = (saa / (d * pi#)) ^ (1/2)
isp# = .7516 * n * f * saa * d * cb / rad#
ipl# = .4463 * n * f * saa * d ^ (1/2) * sr ^ (1/2) * cb * (n * f / (rg * t)) ^ (1/2) + isp
spher# = iwp# * 100 / ipl#
PRINT title$; " SPHERICITY=": spher; "%; " Epc="; ee#(maxij%); " Epa=";
e#(minij%)  
IF lpt% = 1 THEN PRINT #4, title$; " SPHERICITY="; spher, "%"; " Epc=";  
e#(maxi%); " Epa="; e#(minij%)  
DO  
LOOP UNTIL INKEY$ <> ""  
GOTO 10  

3900 REM ADJUST EXPT. PARAMETERS  
CLS : SCREEN 0  
PRINT : PRINT : PRINT : PRINT " CURRENT EXPT. PARAMETERS": PRINT  
PRINT " 1, TEMPERATURE (K) " ; t  
PRINT " 2, DIFFUSION CO-EFFICIENT (CM^2/SEC) " ; d * 10000  
PRINT " 3, SCAN RATE (V/SEC) " ; sr  
PRINT " 4, SURFACE AREA OF SPHERE (CM^2) " ; ssa * 10000  
PRINT " 5, NUMBER OF ELECTRONS " ; n  
PRINT " 6, CONCENTRATION (MOLAR) " ; cb / 1000  
PRINT " 7, EXIT"  
PRINT : PRINT : PRINT : INPUT " INPUT SELECTION"; qq  
SELECT CASE qq  
CASE IS = 1  
INPUT "NEW TEMPERATURE (K)"; t  
CASE IS = 2  
INPUT "NEW DIFFUSION COEFFICIENT (CM^2/SEC)"; d  
d = d / 10000  
CASE IS = 3  
INPUT "NEW SCAN RATE (V/S)"; sr  
CASE IS = 4  
INPUT "NEW SURFACE AREA (CM^2/SEC)"; ssa  
ssa = ssa / 10000  
CASE IS = 5  
INPUT "NEW NUMBER OF ELECTRONS"; n  
CASE IS = 6  
INPUT "NEW CONCENTRATION (MOLAR)"; cb  
cb = cb * 1000  
CASE IS = 7  
GOTO 10  
CASE ELSE  
END SELECT  
GOTO 3900  

4000 REM BHOS ANALYSIS  
FOR j% = 1 TO num%: fl$(j%) = "" : NEXT j%  
main = 0  
rad# = (ssa / (4 * pi#)) ^ (1 / 2)  
v# = 4 * pi# * rad# ^ 3 / 3  
dtc# = 2 * ABS(ei# - cb#) / ((num% - 1) * sr)  
b# = d * dtc# * (4 * pi# / (3 * v#)) ^ (2 / 3)  
p# = 1 - b#  
t# = 1  
FOR j% = 0 TO (num% - 1)  
Z# = j% * b# + b#  
IF Z# >= 2.25 THEN 4100  
k% = 2 + INT(9 * (Z# ^ (1 / 2)))  
r# = k% / (k% + Z#)  
FOR lk% = k% TO 1 STEP -1
r# = 1 + (.5 - lk%) * r# * Z# / (lk% * (lk% + .5))
NEXT lk%

r# = 2 * (Z# / pi#) ^ (1 / 2) + (1 - 2 * r# * (Z# / pi#) ^ (1 / 2)) * EXP(Z#)
GOTO 4200

4100 Z# = (2 * Z#) ^ (1 / 2)
PRINT Z#

k% = 2 + INT(45 / Z#)
r# = 1 / Z#
FOR lk% = k% TO 1 STEP -1
r# = 1 / (lk% * r# + Z#)
NEXT lk%
r# = (2 / pi#) ^ (1 / 2) * (r# + Z#)
4200 h#(j%) = 2 * q# - p# - r#
p# = q#
quart = r#
NEXT j%
l# = h#(0)
h#(0) = 0

la# = dte# * d ^ (1 / 2) / (rad# * b# * b#)

FOR j% = 1 TO num%
s# = 1# * int(j%)
FOR lj% = 0 TO j% - 1
s# = s# + #j% * hj%(lj%)
NEXT j%
sm#(j%) = s# * la#
IF sm%(j%) > mmax# THEN mmax# = sm%(j%)
NEXT j%

CALL plot(fl$(0), pp0, 1, e#0, sm#(0), 1, num%)
4300 GOTO 10000

4400 IF wmod% = 3 THEN 4900
IF wmod% = 0 OR wmod% = 1 THEN jh% = 1: jh% = num% \
\2: GOTO 4500
j% = 0
DO
j% = j% + 1
LOOP UNTIL sm%(j%) >= ewl / 100 * mmax#
jh% = j%
j% = num% \2
DO
j% = j% + 1
LOOP UNTIL sm%(j%) <= ewl / 100 * mmax#
jh% = num% - j%
4500 emid# = (e#(1) - e#(num% \2 + 1)) / 2 - e#(1)
FOR j% = jh% TO jh%
top# = sm#(num% - j% + 1) * j#(j%) - sm#(j%) * i#(num% - j% + 1)
i#(j%) = top# / (sm#(num% - j% + 1) - sm#(j%))
ms#(j%) = top# / (i#(j%) - i#(num% - j% + 1))
IF i#(j%) <= 0 OR ms#(j%) <= 0 THEN fl$(j%) = "n"
ix#(j%) = f * (e#(j%) + emid#) / (rg * t)
ms#(j%) = EXP(f * (e#(j%) + emid#) / (rg * t))
4600 NEXT j%
IF wmod% <= 1 THEN 4650
CALL weight(fl$(0), pp0, e#0, i#0, sm#0, ii#0, ms#0, num%, dte#, pi#, wi#, w#0)
CALL plot(fl$(0), pp0, 1, e#0, ms#0, 1, num% \2)
CALL deriv(ms#0, der#0, dte#, 20, num% \2)
CALL plot(fl$, pp0, 1, e#, der#, 1, num% \text{\textbackslash} 2)
FOR j% = 1 TO num% \textbackslash 2
IF der#(j%) \textgreater dermax# THEN dermax# = der#(j%): maxj% = j%
NEXT j%

dermax# = e#(maxj%)
4650 FOR j% = j1% TO jh%
IF fl$(j%) = "n" THEN 4700

lx#(j%) = mx#(j%)
ly#(j%) = 1 / ms#(j%)
4700 NEXT j%

CALL wls(fl$(i), pp, wmod%, wms#, lx#, ly#, j1%, jh%, m#, c#)
bm# = 1 / c#
IF bm# < 0 THEN CLS: INPUT "CALCULATION OF E 1/2 WILL FAIL (M<0), SO"

INPUT AN ESTIMATE FOR E 1/2"; ct#: ct# = ct# + emid#: GOTO 4750
cr# = -LOG(m# \ast bm#) \ast t / f
4750 FOR j% = j1% TO jh%
IF fl$(j%) = "n" THEN 4800

lx#(j%) = ix#(j%)
ly#(j%) = LOG(iy#(j%))
px#(j%) = e#(j%) - cr# + emid#
py#(j%) = LOG(iy#(j%)) \ast (ssa + f \ast cb))
4800 NEXT j%

CALL wls(fl$(i), pp, wmod%, wi#, lx#, ly#, j1%, jh%, m#, c#)
a1# = -m#
ic# = c#
diff# = (bm# / (ssa + f \ast cb)) \ast 2
bi# = EXP(ic# \ast (a1# + f \ast cr#) / (rg + t)))
ko# = bi# / (ssa + f \ast cb)
CLS: SCREEN 0
IF lpt% = 1 THEN PRINT #4, "Weighted Linear"
PRINT "E 1/2=": er# = emid#: TAB(40); "I=": bi#
PRINT "D=": diff#: TAB(40); "M=": bm#
PRINT "Alpha=:": al#: TAB(40); "Ks=:"; ko#
IF lpt% = 1 THEN PRINT #4, "E 1/2=": er# = emid#: TAB(40); "I=": bi#
IF lpt% = 1 THEN PRINT #4, "D=": diff#: TAB(40); "M=": bm#
IF lpt% = 1 THEN PRINT #4, "Alpha=:": al#: TAB(40); "Ks=:"; ko#
FOR j% = 1 TO num% \textbackslash 2
di# = #1(j%)- i#(num% - j% + 1)
IF di# > dimax# THEN dimax# = di#: dij% = j%
dm# = sm#(num% - j% + 1) - sm#(j%)
IF dm# > dmmax# THEN dmmax# = dm#: dmj% = j%
IF ms#(j%) <= bm# / 2 AND ms#(j% + 1) > bm# / 2 THEN emd2# = (e#(j%) + e#(j% + 1)) / 2
etest = INT(e#(j%) \ast 1000 + .5) / 1000
IF estet = .05 THEN died2# = i#(j%) - i#(num% - j% + 1)

NEXT j%

PRINT "E(i<i)<max=": e#(dij%); TAB(40); "(i<i)<max=": dimax#
PRINT "E(i<i)<1E1/2": died2#
PRINT "E(m<m)<max=": e#(dmj%); TAB(40); "(m<m)<max=": dmmax#
PRINT "E(M/2)=": emd2#: TAB(40); "E(m mu*/dE)=": dermax#
IF lpt% = 1 THEN PRINT #4, "E(i<i)<max=": e#(dij%); TAB(40); "(i<i)<max=": dimax#
IF lpt% = 1 THEN PRINT #4, "E(m<m)<max=": e#(dmj%); TAB(40); "(m<m)<max=": dmmax#
IF lpt% = 1 THEN PRINT #4, "E(M/2)="; emd2#; TAB(40); "E(d mu*/dE)max=";
dermax#
INPUT "EXAMINE da/dE (y/n)"; a$
IF a$ = "n" OR a$ = "N" THEN 4300
IF lpt% = 1 THEN PRINT #4, "Unweighted Quadratic"
CALL pfit(fl$(i), px$(i), py$(i), jl%, jh%, a, b, c)
PRINT "Unweighted"
PRINT "Alpha="; -rg * t * b / f; TAB(40); "Ks="; EXP(a)
PRINT "da/dE ="; -rg * t * c / f
IF lpt% = 1 THEN PRINT #4, "Alpha="; -rg * t * b / f; TAB(40); "Ks="; EXP(a)
IF lpt% = 1 THEN PRINT #4, "da/dE ="; -rg * t * c / f
DO: LOOP UNTIL INKEYS $ = ""
IF wmod% = 2 THEN 4300
CALL weight(fl$(i), pp(i), et(i), st(i), am(i), bs(i), st(i), num%, dt#, pi#, wi#)
IF lpt% = 1 THEN PRINT #4, "Weighted Quadratic"
CALL pwfit(fl$(i), wmod%, px$(i), py$(i), wi$(i), jl%, jh%, a, b, c)
PRINT "Weighted"
PRINT "Alpha="; -rg * t * b / f; TAB(40); "Ks="; EXP(a)
PRINT "da/dE ="; -rg * t * c / f
IF lpt% = 1 THEN PRINT #4, "Alpha="; -rg * t * b / f; TAB(40); "Ks="; EXP(a)
IF lpt% = 1 THEN PRINT #4, "da/dE ="; -rg * t * c / f
DO: LOOP UNTIL INKEYS $ = ""
GOTO 4300

4900 smmmax# = f * ssa * d ^ (1 / 2) * cb
PRINT "1, Imax="; smmmax#
PRINT "2, Imax = Your Choice"
4902 INPUT "Which Option"; eee
IF eee < 1 OR eee > 2 THEN 4902
IF eee = 2 THEN INPUT "new Imax"; smmmax#
jl% = 1
jh% = num% \ 2 - 2
ehalf% = (et(maxi%)) + et(mini%)) / 2
izero# = 9999999999
FOR j% = num% \ 2 TO num%
IF ABS(et(j%)) < izero# THEN izero# = i#(j%); szero# = sm#(j%); ezero# = e#(j%)
NEXT j%
ehalf# = czero# - (rg * t / f) * LOG((smmmax# - szero#) / smzero#)
PRINT "1, E1/2 ="; ehalf1#
PRINT "2, E1/2 ="; ehalf2#
PRINT "3, E1/2 = Your Choice"
4905 INPUT "Which Option"; eee
IF eee < 1 OR eee > 3 THEN 4905
IF eee = 1 THEN ehalf# = ehalf1#
IF eee = 2 THEN ehalf# = ehalf2#
IF eee = 3 THEN INPUT "new E1/2"; ehalf#
FOR j% = 1 TO jh%
smix# = sm#(j%) * (EXP(f * (et(j%)) - ehalf#) / (rg * t) + 1)
wi#(j%) = i#(j%) ^ 2 * (smmmax# - sm#(j%)) ^ 2
IF smmmax# <= smmix# OR i#(j%) < 0 THEN fl$(j%) = "n": GOTO 4910
px#(j%) = rg * t * LOG((smmmax# - smc#) / i#(j%)) / f
py#(j%) = et(j%) - ehalf#
4910 NEXT j%
CALL plot(fl$(i), pp(i), et(i), st(i), w#(i), jh%)
IF lpt% = 1 THEN PRINT #4, "Weighted Linear CPSV"
CALL wls(rl$( ), pp$( ), 1, wi$( ), px$( ), py$( ), 1, jh%, m#, c#)
al# = 1 / m#
ko# = EXP(c# * al# * f / (rg * t)) * (d ^ (1 / 2))
PRINT "Weighted"
PRINT "alpha ="; al#
PRINT "ko ="; ko#
PRINT "E1/2 ="; ehalf#
PRINT "diffusion coefficient"; d
IF lpt% = 1 THEN PRINT #4, "alpha ="; al#; "ko ="; ko#
IF lpt% = 1 THEN PRINT #4, "E1/2 ="; ehalf#; "diffusion coefficient"; d
DO
LOOP UNTIL INKEY$ <> ""
FOR j% = 1 TO jh%
smc# = sm#(j%) * (EXP(f * (ef(j%) - ehalf#) / (rg * t)) + 1)
IF smmax# <= smc# OR is#(j%) < 0 THEN fl$(j%) = "n": GOTO 4920
px#(j%) = rg * t * LOG(smmax# - smc#) / is#(j%) / f
py#(j%) = ef(j%) - ehalf#
4920 NEXT j%
IF lpt% = 1 THEN PRINT #4, "Unweighted Linear CPSV"
CALL wls(rl$( ), pp$( ), 0, wi$( ), px$( ), py$( ), 1, jh%, m#, c#)
al# = 1 / m#
ko# = EXP(c# * al# * f / (rg * t)) * (d ^ (1 / 2))
PRINT "Unweighted"
PRINT "alpha ="; al#
PRINT "ko ="; ko#
PRINT "E1/2 ="; ehalf#
PRINT "diffusion coefficient"; d
IF lpt% = 1 THEN PRINT #4, "alpha ="; al#; "ko ="; ko#
IF lpt% = 1 THEN PRINT #4, "E1/2 ="; ehalf#; "diffusion coefficient"; d
DO: LOOP UNTIL INKEY$ <> ""
FOR j% = 1 TO jh%
smc# = sm#(j%) * (EXP(f * (ef(j%) - ehalf#) / (rg * t)) + 1)
wi#(j%) = is#(j%) ^ 2 * (smmax# - smc#(j%)) ^ 2
IF smmax# <= smc# OR is#(j%) < 0 THEN fl$(j%) = "n": GOTO 4930
py#(j%) = rg * t * LOG((smmax# - smc#) / is#(j%)) / f
px#(j%) = ef(j%) - ehalf#
4930 NEXT j%
IF lpt% = 1 THEN PRINT #4, "Weighted Quadratic CPSV"
CALL pwfit(rl$( ), 1, px$( ), py$( ), wi$( ), jh%, al#, b#, c#)
ko# = EXP(-a# * f / (rg * t)) * d ^ (1 / 2)
PRINT "Weighted"
PRINT "alpha ="; b#
PRINT "dalphade ="; c#
PRINT "ko ="; ko#
PRINT "E1/2 ="; ehalf#
PRINT "diffusion coefficient"; d
IF lpt% = 1 THEN PRINT #4, "alpha ="; b#; "dalphade ="; c#; "ko ="; ko#
IF lpt% = 1 THEN PRINT #4, "E1/2 ="; ehalf#; "diffusion coefficient"; d
DO
LOOP UNTIL INKEY$ <> ""
FOR j% = 1 TO jh%
smc# = sm#(j%) * (EXP(f * (ef(j%) - ehalf#) / (rg * t)) + 1)
IF smmax# <= smc# OR is#(j%) < 0 THEN fl$(j%) = "n": GOTO 4940
py#(j%) = rg * t * LOG((smmax# - smc#) / is#(j%)) / f
px#(j%) = ef(j%) - ehalf#
4940 NEXT j%
IF j% = 1 THEN PRINT #4, "Unweighted Quadratic CPSV"
CALL pwt((f$%), 0, px$(a#), py$(b#), w%(c#), j%(d#), a#, b#, c#)
k0% = EXP(-(a# * f / (rg * t)) * d ^ (1 / 2))
PRINT "Unweighted"
PRINT "alpha ="; b#
PRINT "dalpha/dE ="; c#
PRINT "ko ="; ko#
PRINT "E1/2 ="; ehalf#
PRINT "diffusion coefficient"; d
IF j% = 1 THEN PRINT #4, "alpha ="; b#; "dalpha/dE ="; c#; "ko ="; ko#
IF j% = 1 THEN PRINT #4, "E1/2 ="; ehalf#; "diffusion coefficient"; d
DO: LOOP UNTIL INKEY$ <> ""
GOTO 4300

5000 REM SAVE SCALED DATA
CLS
INPUT "filename": o$
INPUT "title": tit$
OPEN o$ FOR OUTPUT AS #1
PRINT #1, tit$
PRINT #1, num%
PRINT #1, t, n, sr, d, ssa, ei#, eh#, cb
FOR j% = 1 TO num%
PRINT #1, e#(j%), i#(j%)% NEXT j%
CLOSE #1
GOTO 10

6000 REM IR CORRECTION
CLS : PRINT : PRINT : PRINT : PRINT : PRINT
INPUT ": UNCOMPENSATED RESISTANCE (OHMS)"; ru
IF j% = 1 THEN PRINT #4, "Uncompensated Resistance ="; ru; "ohms"
nnum% = num%
ei# = ei#(1)
eh# = eh#(1)
FOR j% = 1 TO num%
eo#(j%) = ei#(j%) + i#(j%) * ru
h#(j%) = i#(j%)% IF eo#(j%) > ei# THEN ei# = eo#(j%)% IF eo#(j%) < eh# THEN eh# = eo#(j%)% NEXT j%
inc# = (ei# - eh#) * 2 / (num% + 1)
j1% = 1
c#(1) = ei#
FOR i% = 2 TO num% \ 2 + 1
    c# = ei# - (i% - 1) * inc#
c#(i%) = c#
FOR j% = j1% TO num% \ 2
    IF j% < 1 THEN j% = 1
    IF c# <= eo#(j%) AND c# > eo#(j% + 1) THEN i#(j%) = h#(j%) + (h#(j% + 1) - h#(j%)) * (c# - eo#(j%)) / (eo#(j% + 1) - eo#(j%)); j1% = j% - 1; j% = num% \ 2 + 2
NEXT j%
NEXT i%
j1% = num% \ 2 + 1
FOR i% = nnum\% \ TO \ nnum\%
e# = e# + (1\% - nnum\% \ \* 2) \* inc#
e#(i%) = e#
FOR j% = j1\% \ TO \ nnum\%
IF e# >= cos#(j%) \ \& \ e# < cos#(j% + 1) \ THEN \ i#(i%) = h#(j%) + (h#(j% + 1) -
        h#(j%)) \* (e# - eo#(j%)) / (eo#(j% + 1) - eo#(j%)); j1\% = j% - 1; j% = num\%
NEXT j%
NEXT i%
nnum\% = nnum\%
CALL plot(fl$, pp(), 1, e#, i#, 1, nnum\%)
GOTO 10

7000 REM SMOOTHING
CLS : SCREEN 0
PRINT "CHOOSE MODE OF SMOOTHING"
PRINT "1, 3-POINT TRIANGULAR WINDOW SMOOTHING"
PRINT "2, FOURIER SMOOTHING"
PRINT "3, 9-POINT LEAST SQUARES WINDOW SMOOTHING"
PRINT "4, EXIT"
PRINT ; INPUT "MODE OF SMOOTHING"; i%
FOR j% = 1 TO nnum\%
eo#(j%) = i#(j%)
NEXT j%
ON i% GOTO 7010, 7020, 7030, 7040
7010 CALL plot(fl$, pp(), 2, e#, i#, 1, num\%)
FOR j% = 2 TO nnum\% - 1
i#(j%) = eo#(j%) / 2 + (eo#(j% - 1) + eo#(j% + 1)) / 4
NEXT j%
CALL plot(fl$, pp(), 0, e#, i#, 1, num\%)
GOTO 7040
7020 INPUT "NUMBER OF TRANSFORMATIONS"; ntran\%
CALL plot(fl$, pp(), 2, e#, i#, 1, num\%)
CALL rpa(fl$, pp(), e#, i#, 1, num\%)
GOTO 7040
7030 CALL plot(fl$, pp(), 2, e#, i#, 1, num\%)
i#(1) = (eo#(1) \* 99 + eo#(2) \* 54 + eo#(3) \* 39 + eo#(4) \* 14 + eo#(5) \* -21) / 145
i#(2) = (eo#(2) \* 54 + (eo#(1) + eo#(3)) \* 54 + eo#(4) \* 39 + eo#(5) \* 14 + eo#(6) \* -21)/199
i#(3) = (eo#(3) \* 54 + (eo#(2) + eo#(4)) \* 54 + (eo#(1) + eo#(5)) \* 39 + eo#(6) \* 14 +
eo#(7) \* -21) / 238
i#(4) = (eo#(4) \* 54 + (eo#(3) + eo#(5)) \* 54 + (eo#(2) + eo#(6)) \* 39 + (eo#(1) +
eo#(7)) \* 14 + eo#(8) \* -21) / 252
FOR j% = 5 TO nnum\% - 4
i#(j%) = eo#(j%) \* 59 + (eo#(j% - 1) + eo#(j% + 1))/54 + (eo#(j% - 2) + eo#(j% + 2)) \* 39 + (eo#(j% - 3) + eo#(j% + 3)) \* 14 + (eo#(j% - 4) + eo#(j% + 4)) \* -21
i#(j%) = i#(j%) / 231
NEXT j%
i#(num\% - 3) = (eo#(num\% - 3) \* 59 + (eo#(num\% - 4) + eo#(num\% - 2)) \* 54 +
(eo#(num\% - 5) + eo#(num\% - 1)) \* 39 + (eo#(num\% - 6) + eo#(num\%)) \* 14 +
eo#(num\% - 7) \* -21) / 252
i#(num\% - 2) = (eo#(num\% - 2) \* 59 + (eo#(num\% - 3) + eo#(num\% - 1)) \* 54 +
(eo#(num\% - 4) + eo#(num\%)) \* 39 + eo#(num\% - 5) \* 14 + eo#(num\% - 6) \* -21)/238
i#(num\% - 1) = (eo#(num\% - 1) \* 59 + (eo#(num\% - 2) + eo#(num\%)) \* 54 +
8000 REM ADJUST CHARGING CURRENT
INPUT "CHARGING CURRENT CORRECTION AS A %OF ip"; perip#
IF jpt% = 1 THEN PRINT #4, "Charging Current Correction"; perip#; "%"
CALL adjct(e#, i#, num%, perip#)
CALL plot(fl$,0, pp(), 1, e#, i#, 1, num%)
GOTO 10

9000 REM READ SIMULATED DATA (mV.mA)
CLEAR
GOSUB 1
CLS
INPUT "filename": o$
OPEN o$ FOR INPUT AS #1
INPUT #1, title$
INPUT #1, num%
INPUT #1, t, n, sr, d
INPUT #1, ssa, ei#, ch#, cb
num% = num% - 1
d = d / 10000
ssa = ssa / 10000
cb = cb * 1000
FOR j% = 0 TO num%
INPUT #1, e#(j%), i#(j%)
e#(j%) = -c#(j%) / 1000
i#(j%) = i#(j%) / 1000
IF e#(j%) > imax# THEN imax# = e#(j%): maxj% = j%
IF e#(j%) < imin# THEN imin# = e#(j%): minj% = j%
NEXT j%
CLOSE #1
CALL plot(fl$,0, pp(), 1, e#, i#, 1, num%)
e# = (e#(1) + e#(num%)) / 2
rad# = (ssa / (4 * pi#)) ^ (1 / 2)
isp# = 7.516 * n * f * ssa * d * cb / rad#
ipl# = .44463 * n * f * ssa * d ^ (1 / 2) * sr ^ (1 / 2) * cb * (n * f / (rg * t)) ^ (1 / 2) + isp
spher = isp# * 100 / ipl#
PRINT title$; " SPHERICITY="; spher; "%"; " Epc="; e#(maxj%); " Epa="; e#(minj%)
IF jpt% = 1 THEN PRINT #4, : PRINT #4, : PRINT #4,
IF jpt% = 1 THEN PRINT #4, o$; " SPHERICITY="; spher; "%"; " Epc="; e#(maxj%); " Epa="; e#(minj%)
DO
LOOP UNTIL INKEY$ <> ""
GOTO 10

10000 REM CHOOSE WEIGHTING FUNCTION
CLS : SCREEN 0
FOR j% = 1 TO num%
f$(j%) = ""
NEXT j%
PRINT : PRINT : PRINT : PRINT : PRINT
PRINT " CHOOSE A WEIGHTING FUNCTION"
PRINT " 0, NO WEIGHTING (THIS IS THE DEFAULT)"
PRINT " 1, OLDHAM WEIGHTING"
PRINT " 2, EVANS WEIGHTING"
PRINT " 3, SAVEANT CPSV"
PRINT " 4, EXIT"
INPUT " CHOICE"; wmod%
IF wmod% < 0 OR wmod% > 4 THEN 10000
ON wmod% GOTO 10100, 10200, 10300, 10
GOTO 4400
10100 wmod% = 1
IF lpt% = 1 THEN PRINT #4, PRINT #4, "BHO analysis"
GOTO 10400
10200 wmod% = 2
PRINT : INPUT " LOWER LIMIT (<50%)"; ewl
PRINT : INPUT " UPPER LIMIT (>50%)"; ewh
IF lpt% = 1 THEN PRINT #4, PRINT #4, "Evans Weighting - "; ewl; "% to "; ewh;
%"
GOTO 10400
10300 wmod% = 3
IF lpt% = 1 THEN PRINT #4, PRINT #4, "CPSV Analysis"
10400 IF main = 1 THEN 10 ELSE 4400

11000 REM ADD RANDOM NOISE
CLS
INPUT "VARIANCE AS % OF ip"; vr
CALL noise(i#, ip%, vr)
CALL plot(fl$, pp, 1, e#, i#, 1, ip%)
PRINT vr
GOTO 10

12000 REM SAVE OUTPUT DATA
CLS
jlo% = 1
jho% = num% \\ 2
INPUT "FILENAME OF OUTPUT FILE"; o$
INPUT "OUTPUT DENSITY"; dd%
PRINT "j=%; j %"; jh = "; jh; "; total number="; num% \\ 2
INPUT "LOWER DATA LIMIT"; jlo%
INPUT "UPPER DATA LIMIT"; jho%
OPEN o$ FOR OUTPUT AS #1
PRINT #1, title$
PRINT #1, num%, t, n, sr, d, ssa, ci#, ch#, cb
PRINT #1, "E(V)-> i(A)-> mu->"
PRINT #1, "E(V)<- i(A)<- mu<".
PRINT #1, "m* w(m*)"
PRINT #1, "i* w(i*)"
FOR j% = jlo% TO jho% STEP dd%
PRINT #1, e#(j%), i#(j%), sm#(j%)
PRINT #1, e#(num% - j% + 1), i#(num% - j% + 1), sm#(num% - j% + 1)
PRINT #1, j%, sm#(j%), wm#(j%)
PRINT #1, j%, i#(j%), wi#(j%)
NEXT j%
CLOSE #1
GOTO 10

13000 IF lpt% = 0 THEN INPUT "ACTIVATE THE PRINTER (y/n)"; a$: IF a$ = "Y" OR a$ = "y" THEN lpt% = 1: OPEN "DEVlp1" FOR OUTPUT AS #4: GOTO 13010
IF lpt% = 1 THEN INPUT "DEACTIVATE THE PRINTER (y/n)"; a$: IF a$ = "Y" OR a$ = "y" THEN CLOSE 4: lpt% = 0: GOTO 10
GOTO 13000
13010 IF lpt% = 1 THEN PRINT #4, o$: " SPHERICITY="; sph; "%"; " Epc="; eff(maxi%); " Epa="; e#(mini%)
GOTO 10
14000 END

SUB adjcc (e#, i#, num%, perip#)
FOR j% = 1 TO num% \ 2
IF i#(j%) > imax# THEN imax# = i#(j%)
NEXT j%
FOR j% = num% \ 2 TO num%
i#(j%) = i#(j%) + perip# * imax# / 100
NEXT j%
END SUB

----------Subroutine CROUT(NR%,MC%,NCC%,ZMCH%)----------
SUB CROUT (NR%, MC%, NCC%, ZMCH%)
2970 DIM LP(10)
2980 IF NR% > MC% THEN 3200
2990 dt = 1: IF ERR = 0: QNRS% = NR% - 1: FOR QI% = 1 TO NR%: LP(QI%) = QI%: NEXT QI%: IF NCC% < 0 THEN 3200
3000 IF NCC% < 0 THEN 3200
3010 QNTC% = NR% + NR%: QI% = 1: FOR QK% = NR% + 1 TO QNTC%: FOR
QKX% = 1 TO NR%: XMAT1(QKX%, QK%) = 0!: NEXT QKX%:
XMAT1(QI%, QK%) = 1!: Q1% = QI% + 1: NEXT QK%: GOTO 3030
3020 QNTC% = NR% + NCC%
3030 IF QNTC% < NR% THEN 3200
3040 FOR QI% = 1 TO NR%: QTEMP = 0!: FOR QI% = QI% TO QNCTC%: IF QI% = 1 THEN 3060
3050 QKX% = 1: FOR QK% = 1 TO QI% - 1: XMAT1(QI%, QI%) = XMAT1(QI%, QI%): XMAT1(QI%, QK%) = XMAT1(QK%, QI%): QKX% = QKX% + 1:
NEXT QK%
3060 IF QI% > NR% THEN 3090
3070 IF ABS(XMAT1(QI%, QI%)) <= QTTEMP THEN 3090
3080 QTTEMP = ABS(XMAT1(QI%, QI%)): QNX% = QI%
3090 NEXT QI%: IF QI% = NR% THEN 3120
3100 IF QNX% = QI% THEN 3120
3110 QTTEMP% = LP(QNX%): LP(QNX%) = LP(QI%): LP(QI%) = QTTEMP%:
QLPIS% = QNX%: FOR QK% = 1 TO NR%: QTEMP = XMAT1(QK%, QI%): XMAT1(QK%, QI%) = XMAT1(QK%, QLPIS%): XMAT1(QK%, QK%) = QTEMP: NEXT QK%: dt = -dt
3120 dt = dt * XMAT1(QI%, QI%): IF ZMCH% - ABS(XMAT1(QI%, QI%)) > 0 THEN 3210
3130 FOR QI% = QI% + 1 TO QNCTC%: XMAT1(QI%, QI%) = XMAT1(QI%, QI%): NEXT QI%: IF QI% = 1 THEN 3160
3140 IF QI% = NR% THEN 3160
3150 FOR QM% = QP% + 1 TO NR%: QKX% = 1: FOR QKY% = 1 TO QI% - 1:
   XMAT1(QM%, QP%) = XMAT1(QM%, QI%): XMAT1(QM%, QKX%) =
   XMAT1(QKX%, QI%): QKX% = QKX% + 1: NEXT QKY%: NEXT QM%
3160 NEXT QI%: FOR QI% = 1 TO NR% - 1: QREV% = NR% - QI%: QKRS% =
   NR% + 1 - QI%: FOR QRCT% = NR% + 1 TO QNTC%: QKCS% = QREV% +
   1: FOR QK% = QKRS% TO NR%: XMAT1(QREV%, QRCT%) =
   XMAT1(QKCS%, QRCT%) * XMAT1(QREV%,
   QK%): QKCS% = QKCS% + 1: NEXT QK%: NEXT QRCT%: NEXT QI%:
3170 IF QP% = QI% THEN 3190
3180 QNX% = LP(QI%): LP(QI%) = LP(QNX%): LP(QNX%) = QNX%: QIXS% =
   QI%: QIY% = QNX%: FOR QIX% = NR% + 1 TO QNTC%: QTEMP =
   XMAT1(QIXS%, QIX%): XMAT1(QIXS%, QIX%) = XMAT1(QIY%, QIX%):
   XMAT1(QIY%, QIX%) = QTEMP: NEXT QIX%: GOTO 3170
3190 NEXT QI%: GOTO 3220
3200 IERR = 2: dt = 999999999#: GOTO 3220
3210 IERR = 1: GOTO 3220
3220 END SUB

SUB deriv (x#, der#, dte#, npt#, num%)
FOR j% = 1 TO nump
IF j% > npt# + 1 AND j% < num% - npt# THEN norm = 0: dx# = 0: FOR nsg# = 1
TO npt#: dx# = dx# + ((x#(j% - nsg#)) * nsg#: norm = norm
+ 2 * nsg#^2: NEXT nsg#: der#(j%) = dx# / (norm * dte#)
NEXT j%
END SUB

SUB fpa (fl$, pp(), c#, i#, num%, ntran)
DIM real#(300), imag#(300), lx#(300), ly#(300)
pi# = 3.1415926536#
ntran% = 1
bfl# = (i##(num%) - i#(1)) / num%
g# = 0
FOR j% = 2 TO num%
   i#(j%) = i##(j%): bfl# * (j% - 1)
   g# = g# + i#(j%)
   NEXT j%
real#(0) = g# / num%
7110 IF ntran% <= ntran% THEN 7120 FOR k% = ntran% TO ntran% - 1
   sumr# = 0
   sumi# = 0
   FOR j% = 2 TO num% - 1
      s# = SIN(2 * pi# * (j% - 1) * k% / num%)
      c# = COS(2 * pi# * (j% - 1) * k% / num%)
      sumr# = sumr# + i#(j%) * c#
      sumi# = sumi# + i#(j%) * s#
      NEXT j%
   real#(k%) = sumr# / num%
   imag#(k%) = -sumi# / num%
   lx#(k%) = k%
   ly#(k%) = real#(k%)^2 + imag#(k%)^2
   NEXT k%
CALL plot(fli$, pp(), 1, lx#, ly#, ntran%, ntran% - 1)
IF ntran% > ntran% THEN ntran% = ntran%
7120 f1# = 0: f2# = 0
FOR k% = 1 TO ntran% - 1
f1# = f1# + real#(k%)
f2# = f2# + k% * 2 * real#(k%)
f0# = 1 - k% * 2 / (ntran% * ntran%)
real#(k%) = f0# * real#(k%)
imag#(k%) = f0# * imag#(k%)
NEXT k%
if#(1) = if#(1) + real#(0) + 2 * (f1# - f2# / (ntran% * ntran%))
FOR j% = 2 TO num%
sum# = 0
FOR k% = 1 TO ntran% - 1
s# = SIN(2 * pi# * k% * (j% - 1) / num%)
c# = COS(2 * pi# * k% * (j% - 1) / num%)
sum# = sum# + real#(k%) * c# - imag#(k%) * s#
NEXT k%
if#(j%) = if#(1) + (j% - 1) * bf# + real#(0) + 2 * sum#
NEXT j%
END SUB

SUB noise (i#(), num%, vr)
DIM ni%(300)
kint% = 100
FOR j% = 1 TO num% \ 2
IF i#(j%) > imax# THEN imax# = i#(j%)
NEXT j%
PRINT "method of noise"
PRINT " 1. Oldham noise"
PRINT " 2. Computer noise"
INPUT "choice"; c%
ON c% GOTO 11110, 11120
11110 pi# = 3.1415926536#
k% = 0
mu = 0
bn# = 199017
s# = 2 * (vr * imax# / 100) ^ 2
j% = 2 * num%
n# = 2 * num%
11100 n# = 24298 * n# + 99991
n# = 1 + n# - bn# * INT(n# / bn#)
ni%(n#) = 1 + INT(n# / bn# * kint%)
ni%(ni%) = ni%(ni%) + 1
j% = j% - 1
IF j% \ 2 = j% / 2 THEN 11200
x# = (s# * LOG(bn#/n#)) ^ (1/2)
GOTO 11100
11200 x# = mu + x# * COS(2 * pi# * n# / bn#)
k% = k% + 1
if#(k%) = if#(k%) + x#
IF j% > 0 THEN 11100 ELSE 11300
11120 FOR j% = 1 TO num%
x# = (RND(1) -.5) * imax# * vr / 100
i#(j%) = i#(j%) + x#
NEXT j%
11300 FOR j% = 1 TO kint%
snisd# = snisd# + (ni%(j%) - 2 * num% / kint%) ^ 2 / (2 * num% / kint%)
NEXT j%
chisq# = snisd#
PRINT chisq#, kint%
DO
LOOP UNTIL INKEY$ <> ""
END SUB

SUB pfit (fl$, px(), py(), jl%, jh%, a, b, c)
DIM pny#(1500), pp(4)
FOR j% = jl% TO jh%
IF fl$(j%) = "n" THEN 20000
smx = smx + px#(j%)
snu = snu + px#(j%) ^ 2
smy = smy + py#(j%)
smysq = smysq + py#(j%) ^ 2
smxu = smxu + px#(j%) ^ 3
smusq = smusq + px#(j%) ^ 4
smxy = smxy + py#(j%) * px#(j%)
smuy = smuy + py#(j%) * px#(j%) ^ 2
20000 NEXT j%
pnum% = jh% - jl% + 1
A1 = snu - smx ^ 2 / pnum%
B1 = smxu - smx * snu / pnum%
B2 = smusq - smu ^ 2 / pnum%
A3 = smxy - smx * smy / pnum%
B3 = smuy - smu * smy / pnum%
A2 = B1
c = (A3 - A1 * b) / A2
a = (smy - b * smx - c * snu) / pnum%
sy = smysq - smy ^ 2 / pnum%
FOR j% = jl% TO jh%
IF fl$(j%) = "n" THEN 20010
pny#(j%) = a + b * px#(j%) + c * px#(j%) ^ 2
spny = spny + pny#(j%)
spnysq = spnysq + pny#(j%) ^ 2
20010 NEXT j%
syd = spnysq - spny ^ 2 / pnum%
rsq = syd / sy
CALL plot(fl$, pp(), 1, px(), py(), jl%, jh%)
PRINT a, b, c, rsq
IF lpt% = 1 THEN PRINT #4, "a=": a; "b=": b; "c=": c; "r^2="; rsq
CALL plot(fl$, pp(), 0, px(), pny#(), jl%, jh%)
END SUB

SUB plot (fl$, pp(), clr%, lx#(), ly#(), pln%, phn%)
REM clr% = (0:nc,p) (1:c,p) (2:c, np) (3:nc, np)
IF clr% = 0 OR clr% = 3 THEN 999
CLS
FOR j% = pln% TO phn%
IF fl$(j%) <> "n" THEN 30005
NEXT j%
30005 pp(2) = lx#(j%); pp(1) = lx#(j%)
pp(4) = ly#(j%); pp(3) = ly#(j%)
FOR j% = pln% TO phn%
IF f$%j% = "n" THEN 30010
IF lx%(j%) >= pp(1) THEN pp(1) = lx%(j%)
IF lx%(j%) <= pp(2) THEN pp(2) = lx%(j%)
IF ly%(j%) >= pp(3) THEN pp(3) = ly%(j%)
IF ly%(j%) <= pp(4) THEN pp(4) = ly%(j%)
30010 NEXT j%
9999 SCREEN 2
WINDOW (0, 0)-(pp(1) - pp(2), 1.1 * (pp(3) - pp(4)))
FOR j% = pln% TO phn%
IF f$%j% <> "n" THEN PSET (lx%(j%) - pp(2), ly%(j%) - pp(4))
NEXT j%
IF clr% = 1 OR clr% = 2 THEN PRINT pp(2); pp(4); ":<>"; pp(1); pp(3)
IF clr% = 2 OR clr% = 3 THEN 9999
DO
q$ = INKEY$
LOOP WHILE q$ = "m"
IF q$ <> "f" AND q$ <> "F" THEN 9999
INPUT "filename": o$
OPEN o$ FOR OUTPUT AS #1
FOR j% = pln% TO phn%
IF f$%j% <> "n" THEN x% = lx%(j%): y% = ly%(j%): PRINT #1, x%, y%
NEXT j%
CLOSE #1
9999 END SUB

DEFSNG A-Z
SUB potpair (e%(i%), i%(j%), num%, switch%)
DIM co%(1500), io%(1500)
e#% = e%(1)
eh# = e%(switch%)
inc# = ABS(e%(2) - e%(1))
nswitch% = switch%
FOR j% = 1 TO num%
eo%(j%) = e%(j%)
io%(j%) = i%(j%)
NEXT j%
PRINT "THE POTENTIAL INCREMENT ON THE FORWARD SWEEP IS="; inc#
PRINT "DO YOU WISH TO CHANGE THE INCREMENT (Y/N)"; o$
IF o$ = "y" OR o$ = "Y" THEN INPUT "NEW INCREMENT": inc%: nswtch% =
ABS(e#% - eh#) / inc% + 1
nnum% = 2 * nswtch% - 1
j1% = 1
FOR i% = 1 TO nswtch% + 1
e#% = e#% - (i% - 1) * inc%
e%(i%) = e#%
NEXT i%
FOR j% = j1% TO switch%
IF e#% < co%(j%) AND e#% > eo%(j% + 1) THEN i%(j%) = io%(j%) + (io%(j% + 1) -
io%(j%)) * (e#% - eo%(j%)) / (co%(j% + 1) - co%(j%)); j1% = j%: j% = switch%
NEXT j%
NEXT i%
j1% = switch% + 1
FOR i% = nswtch% + 1 TO num%
c#% = ch#% + (i% - nswtch%) * inc%
c%(i%) = c#%
FOR j% = j1% TO num%
IF e# > eo#(j%) AND e# < eo#(j% + 1) THEN
  ih#(j%) = io#(j%) + (io#(j% + 1) - io#(j%)) * (e# - eo#(j%)) / (eo#(j% + 1) - eo#(j%));
  j1% = j%; j% = num%
NEXT j%
NEXT i%
PRINT num%
num% = num%
switch% = nswitch%
END SUB

DEFINT I-J, M
DEFDBL A-H, K-L, N-Z
SUB pwfit(n$i(), wmd%, px#(), py#(), w#(), j1%, jh%, a#, b#, c#)
DIM pny#(1500), pp(4)
IF wmd% = 1 THEN 30000
FOR j% = j1% TO jh%
  w#(j%) = 1
NEXT j%
30000 FOR j% = j1% TO jh%
IF n$i(j%) = "n" THEN 30100
swmx# = swmx# + w#(j%) * px#(j%)
swmu# = swmu# + w#(j%) * px#(j%) ^ 2
swmy# = swmy# + w#(j%) * py#(j%)
swmysq# = swmysq# + w#(j%) * py#(j%) ^ 2
swmxu# = swmxu# + w#(j%) * px#(j%) ^ 3
swmusq# = swmusq# + w#(j%) * px#(j%) ^ 4
swmxy# = swmxy# + w#(j%) * px#(j%) * py#(j%)
swmu# = swmu# + w#(j%) * py#(j%) * px#(j%)
sw# = sw# + w#(j%)
pnum% = pnum% + 1
30100 NEXT j%
NR1% = 3; MC1% = 3; NCC1% = 1; ZMCH% = 0; IRHS% = NR1% + NCC1%
XMAT1(1, 1) = swmu#
XMAT1(1, 2) = swmx#
XMAT1(1, 3) = sw#
XMAT1(1, IRHS%) = swmy#
XMAT1(2, 1) = swmxu#
XMAT1(2, 2) = swmu#
XMAT1(2, 3) = swmx#
XMAT1(2, IRHS%) = swmxy#
XMAT1(3, 1) = swmusq#
XMAT1(3, 2) = swmxu#
XMAT1(3, 3) = swmu#
XMAT1(3, IRHS%) = swmuy#
CALL CROUT(NR1%, MC1%, NCC1%, ZMCH%)
c# = XMAT1(1, IRHS%)
b# = XMAT1(2, IRHS%)
a# = XMAT1(3, IRHS%)
sy# = swmysq# - swmy# ^ 2 / sw#
FOR j% = j1% TO jh%
IF n$i(j%) = "n" THEN 30200
pny#(j%) = a# + b# * px#(j%) + c# * px#(j%) ^ 2
spny# = spny# + w#(j%) * pny#(j%)
spmysq# = spmysq# + w#(j%) * pny#(j%) ^ 2
30200 NEXT j%
syd# = spnysq# - spn# ^ 2 / sw#
rsq# = syd# / sy#
CALL plot(flS(), pp(), 1, px#(), py#(), j#%, jh#%)
PRINT a#, b#, c#, rsq#
IF j% = 1 THEN PRINT "a="; a#; "b="; b#; "c="; c#; "r^2="; rsq#
CALL plot(flS(), pp(), 0, px#(), pny#(), j#%, jh#%)
END SUB

SUB weight (flS(), pp(), ef#, i#, sm#(), ii#, ms#, num#, det#, pi#, wi#, wm#())
  eta = 1
FOR j% = 1 TO num% \ 2
  b% = num% - j% + 1
  rd = 4 * (det# / pi#) ^ (1 / 2) / 3
  bot = (sm#(b%) - rd * i#(b%)) ^ 2 + (sm#(j%) - rd * i#(j%)) ^ 2 + det# * (i#(j%) ^ 2 * LOG(2.27 * b%) + i#(b%) ^ 2 * LOG(2.27 * j%) / pi#)
  IF i#(j%) <= 0 THEN wi#(j%) = (sm#(b%) - sm#(j%)) ^ 2 / (eta ^ 2 * det# * LOG(180!
    * j% * b% / pi# + eta ^ 2 * bot / i#(j%) ^ 2)
  IF ms#(j%) <= 0 THEN wm#(j%) = (sm#(b%) * i#(j%) - sm#(j%) * i#(b%)) ^ 2 / (2 *
    eta ^ 2 + eta ^ 2 * bot / ms#(j%) ^ 2)
  IF wi#(j%) > wimax THEN wimax = wi#(j%); wij% = j%
  IF wm#(j%) > wmax THEN wmax = wm#(j%); wmj% = j%
NEXT j%
CALL plot(flS(), pp(), 1, e#, wi#, 1, num% / 2)
PRINT "E(w(ln i)*max)="; e#(wij%)
DO LOOP UNTIL INKEY$ <> ""
CALL plot(flS(), pp(), 1, e#, wm#(), 1, num% / 2)
PRINT "E(w(1/m)*max)="; e#(wmj%)
DO LOOP UNTIL INKEY$ <> ""
END SUB

SUB wls (flS(), pp(), wmd%, w#(), lx#(), ly#(), j1%, jh%, m#, c#)
  IF wmd% = 1 THEN 100
  FOR j#% = j1% TO jh%
NEXT j%
100 sx# = 0; sy# = 0; sxy# = 0; ssq# = 0; sys# = 0; sw# = 0
FOR j#% = j1% TO jh%
IF flS(j#%) = "n" THEN 40010
sx# = sx# + w#(j#%) * lx#(j#%)
sy# = sy# + w#(j#%) * ly#(j#%)
sxy# = sxy# + w#(j#%) * lx#(j#%) * ly#(j#%)
ssq# = ssq# + w#(j#%) * lx#(j#%) * lx#(j#%)
sys# = sys# + w#(j#%) * ly#(j#%) * ly#(j#%)
sw# = sw# + w#(j#%)
40010 NEXT j#%
m# = (sw# * sxy# - sx# * sy#) / (sw# * ssq# - sx# * sx#)
c# = -(sx# * sxy# - sy# * ssq#) / (sw# * ssq# - sx# * sx#)
CALL plot(flS(), pp(), 1, lx#(), ly#(), j1%, jh%)
FOR j#% = j1% TO jh%
IF flS(j#%) <> "n" THEN ly#(j#%) = m# * lx#(j#%) + c#
NEXT j#%
rsq# = (sw# * sxy# - sx# * sy#) ^ 2 / ((sw# * ssq# - sx# ^ 2) * (sw# * sys# - sy# ^
2))
PRINT m#, c#, rsq#
IF lpt% = 1 THEN PRINT #4, "m="; m#; "c="; c#; "r^2="; rsq#
CALL plot(f$(), pp(), 0, lx#(), ly#(), ji%, jh%)
FOR j% = ji% TO jh%
  w%(j%) = 0
NEXT j%
END SUB
DECLARE SUB adjcc (e#, i#, num%, perip!)
DECLARE SUB pfit (fl$, pp#, py#, jl%, jh%, a, b, c)
DECLARE SUB fpa (fl$, pp#, e#, i#, num%, ntran)
DECLARE SUB plot (fl$, pp#, clr%, lx#, iy#, pln%, phn%,
DECLARE SUB weight (fl$, pp#, e#, i#, sm#, ii#, m$, num%, dt#, pi#, wi#, wmi#))
DECLARE SUB wls (fl$, pp#, wmod%, w#, ly#, iy#, ji%, jh%, m#, c#)
DECLARE SUB noise (i#, num%, vr)
DECLARE SUB potpair (e#, i#, num%, switch%)

GOSUB 1
GOTO 10

1 REM INITIALIZE
f = 96484.6
rg = 8.31441
pi# = 3.1415926536#
size% = 1500
DIM fl$(2 * size%), pp(4), i#(2 * size%), e#(2 * size%), co#(2 * size%), sm#(2 * size%),
i#(size%), m#(size%), li#(size%), mx#(size%), lx#(size%), ly#(size%),
h#(2 * size%), px#(size%), py#(size%), smp#(2 * size%),
wi#(size%), wmi#(size%)
wmod% = 0
RETURN

10 REM SCREEN MENU
CLS : SCREEN 0
PRINT : PRINT : PRINT " PLANAR BHO ANALYSIS"
PRINT " ------------------" : PRINT
PRINT " 1, READ RAW FILE"
PRINT " 2, READ SCALED DATA WITH EXPT. PARAMETERS"
PRINT " 3, ADJUST EXPT. PARAMETERS"
PRINT " 4, PERFORM ANALYSIS"
PRINT " 5, SAVE SCALED DATA WITH PRESENT EXPT. PARAMETERS"
PRINT " 6, APPLY IR CORRECTION"
PRINT " 7, APPLY SMOOTHING"
PRINT " 8, APPLY CHARGING CURRENT CORRECTION"
PRINT " 9, READ SIMULATED DATA (mV, mA)"
PRINT " 10, CHOOSE WEIGHTING FUNCTION OPTION"
PRINT " 11, ADD RANDOM NOISE"
PRINT " 12, SAVE OUTPUT DATA"
PRINT " 13, EXIT"
PRINT : PRINT : PRINT : PRINT : INPUT " INPUT OPTION (1-13):" ; qq
main = 1
IF qq < 1 OR qq > 13 THEN 10
ON qq GOTO 1000, 2000, 3000, 4000, 5000, 6000, 7000, 8000, 9000, 10000, 11000, 12000, 13000
GOTO 10

1000 REM READ RAW DATA FILE
CLS
INPUT "current file"; c$
INPUT "potential file"; p$
OPEN c$ FOR INPUT AS #1
j% = 0
DO WHILE NOT EOF(1)
j% = j% + 1
INPUT #1, i#(j%)
LOOP
CLOSE #1
OPEN p$ FOR INPUT AS #1
j% = 0
DO WHILE NOT EOF(1)
j% = j% + 1
INPUT #1, e#(j%)
lx#(j%) = j%
LOOP
CLOSE #1
num% = j% - 2
CALL plot(fl$(), pp(), 1, lx#(), e#(), 1, num%)
CALL plot(fl$(), pp(), 1, lx#(), i#(), 1, num%)
CALL plot(fl$(), pp(), 1, e#(), i#(), 1, num%)
SCREEN 0
INPUT "DO YOU WISH TO INVERT POTENTIAL SCALE"; a$
IF a$ = "Y" OR a$ = "y" THEN FOR j% = 1 TO num%; e#(j%) = -e#(j%): NEXT j%
INPUT "DO YOU WISH TO INVERT CURRENT SCALE"; a$
IF a$ = "Y" OR a$ = "y" THEN FOR j% = 1 TO num%; i#(j%) = -i#(j%): NEXT j%
INPUT "INITIAL POTENTIAL (V)" ; ci#
INPUT "SWITCHING POTENTIAL (V)" ; ch#
INPUT "INPUT POTENTIOSTAT SCALE (mA/V)" ; scp
INPUT "INPUT C.R.O. SCALE (mV/DIV)" ; scc
scale = scp * scc / 1000000
cmax# = -99999
emin# = 99999
FOR j% = 1 TO num%
IF e#(j%) > cmax# THEN cmax# = e#(j%)
IF e#(j%) < emin# THEN emin# = e#(j%)
NEXT j%
snum = 0; shigh = 0
FOR j% = 1 TO num%
IF e#(j%) = cmax# THEN shigh = shigh + j%: snum = snum + 1
NEXT j%
sswitch% = INT(shigh / snum)
j% = switch%
DO
j% = j% - 1
LOOP UNTIL j% = 1 OR e#(j%) = emin#
put% = j%
j% = switch%
DO
j% = j% + 1
LOOP UNTIL e#(j%) = emin# OR j% = num%
ptc% = j%
num% = ptc% - ptb% + 1
delt = cmmax# - cmmin#
FOR j% = ptb% TO ptc%
IF j% <= switch% THEN e#(j%) = (j% - ptb%) * delt / (switch% - ptb%) + cmmin#
IF j% > switch% THEN e#(j%) = (ptc% - j%) * delt / (ptc% - switch%) + cmmin#
c#(j% - ptb% + 1) = ((ch# - ci#) * (e#(j%) - cmmin#)) / delt + ei#
i#(j% - ptb% + 1) = i#(j%) * scale * .0346
NEXT j%
PRINT ptc%, ptc%, num%, switch%
IF ptc% - switch% <= switch% - ptb% THEN switch% = switch% - ptb% + 1: CALL.
potpair(e#, i#, num%, switch%)
j1% = 1: jh% = num% \ 10
FOR j% = j1% TO jh%
x#(j%) = j%
y#(j%) = i#(j%)
NEXT j%
CALL wls(fl$(), pp(), 2, wi#(), 1x#(), 1y#(), j1%, jh%, m#, c#)
ibeg = m# + c#
FOR j% = 1 TO num%
i#(j%) = i#(j%) - ibeg
NEXT j%
CALL plot(fl$(), pp(), 1, e#, i#, 1, num%)
GOTO 10

2000 REM READ SCALED DATA
CLEAR
GOSUB 1
INPUT "filename"; o$
OPEN o$ FOR INPUT AS #1
INPUT #1, title$
INPUT #1, num%, t, n, sr, d, rad#, ei#, eh#, cb
FOR j% = 1 TO num%
INPUT #1, e#(j%), i#(j%)
NEXT j%
CLOSE #1
CALL plot(fl$(), pp(), 2, e#, i#, 1, num%)
dsa = pi# * rad#^2
isp = .7516 * n * f * dsa * d * cb / rad#
ipl = .4463 * n * f * dsa * d^2 * sr^2 * cb * (n * f / (rg * t)) * (1 / 2) + isp
'spher = isp * 100 / ipl
PRINT title$; "SPHERICITY="; spher; "%"
DO
LOOP UNTIL INKEYS <> ""
GOTO 10

3000 REM ADJUST EXPT. PARAMETERS
CLS : SCREEN 0
PRINT : PRINT : PRINT : PRINT " CURRENT EXPT. PARAMETERS": PRINT
PRINT " 1, TEMPERATURE (K) "; t
PRINT " 2, DIFFUSION CO-EFFICIENT (CM^2/sec) "; d * 10000
PRINT " 3, SCAN RATE (V/SEC) " ; sr
PRINT " 4, RADIUS OF DISK (CM) "; rad# * 100
PRINT " 5, NUMBER OF ELECTRONS " ; n
PRINT " 6, CONCENTRATION (MOLAR) " ; cb / 1000
PRINT " 7, EXIT"
PRINT : PRINT : PRINT : INPUT "  INPUT SELECTION"; qq
SELECT CASE qq
CASE IS = 1
INPUT "NEW TEMPERATURE (K)"; t
CASE IS = 2
INPUT "NEW DIFFUSION COEFFICIENT (CM^2/SEC)"; d
   d = d / 10000
CASE IS = 3
INPUT "NEW SCAN RATE (V/S)"; sr
CASE IS = 4
INPUT "NEW RADIUS (CM)"; rad#
   rad# = rad# / 100
CASE IS = 5
INPUT "NEW NUMBER OF ELECTRONS"; n
CASE IS = 6
INPUT "NEW CONCENTRATION (MOLAR)"; cb
   cb = cb * 1000
CASE IS = 7
GOTO 10
CASE ELSE
END SELECT
GOTO 3000

4000 REM BHOP ANALYSIS
main = 0
dsa = pi# * rad#^2
v# = 4 * pi# * rad#^3 / 3
dt# = 2 * ABS(c# - ch#) / ((num% - 1) * sr)
FOR bj% = 2 TO num%
   sums# = 0
   FOR j% = 1 TO bj% - 1
      sums# = sums# + i%(j%) * (((bj% - j% + 1)^(3/2)) - 2 * ((bj% - j%)^(3/2)) +
         ((bj% - j% - 1)^(3/2)))
   NEXT j%
   sm#(bj%) = 4 / 3 * (dt# / pi#)^(1/2) * (i%(bj%) + sums#)
   IF sm#(bj%) > mmax THEN mmax = sm#(bj%)
   NEXT bj%
   CALL plot(fl$(), pp(), 1, c#(), sm#(), 1, num%)
4300 GOTO 10000
4400 IF wmod% = 3 THEN 4900
IF wmod% = 0 OR wmod% = 1 THEN j1% = 1; jh% = num% \ 2; GOTO 4500
j% = 0
DO
j% = j% + 1
LOOP UNTIL sm#(j%) >= ewl / 100 * mmax
j1% = j%
j% = num% \ 2
DO
j% = j% + 1
LOOP UNTIL sm#(j%) <= ewh / 100 * mmax
jh% = num% \ j%
4500 emit# = (e#(1) - e#((num% \ 2 + 1)) / 2 - e#(1)
FOR j% = j1% TO jh%
top# = sm#((num% - j% + 1) * i%(j%) - sm#(j%)) * i%(num% - j% + 1)
ii#(j%) = top# / (sm#(num% - j% + 1) - sm#(j%))
ms#(j%) = top# / (i#(j%) - i#(num% - j% + 1))
IF ii#(j%) <= 0 OR ms#(j%) <= 0 THEN fl$(j%) = "n"
ix#(j%) = f * (e#(j%) + emid#) / (rg * t)
mx#(j%) = EXP(f * (e#(j%) + cmid#)) / (rg * t)
4600 NEXT j%
IF wmod% = 1 THEN CALL weight(fl$(), pp(), c#, i#, sm#, ii#, ms#, num%,
   dtt#, pif#, wi#, wmo#)())
IF wmod% = 1 THEN CALL plot(fl$(), pp(), 1, c#, ms#, 1, num% \ 2)
FOR j% = j1% TO jh%
IF fl$(j%) = "n" THEN 4700
lx#(j%) = mx#(j%)
ly#(j%) = 1 / ms#(j%)
4700 NEXT j%
CALL wls(fl$(), pp(), wmod%, wmo#, lx#, ly#, j1%, jh%, m#, c#)
bm# = 1 / c#
IF bm# < 0 THEN CLS : INPUT "CALCULATION OF E 1/2 WILL FAIL (M<0), SO"
   INPUT AN ESTIMATE FOR E 1/2"; er# = cr# + emid#: GOTO 4750
4750 FOR j% = j1% TO jh%
IF fl$(j%) = "n" THEN 4800
lx#(j%) = ix#(j%)
ly#(j%) = LOG(i#(j%))
p#(j%) = c#(j%) - er# + emid#
p#(j%) = LOG(i#(j%) / (dsa * f * cb))
4800 NEXT j%
CALL wls(fl$(), pp(), wmod%, wi#, lx#, ly#, j1%, jh%, m#, c#)
al# = -m#
1c# = c#
diff# = (bm# / (dsa * f * cb)) ^ 2
bi# = EXP(ic# - (al# * f * er#) / (rg * t)))
ko# = bi# / (dsa * f * cb)
CLS : SCREEN 0
PRINT "E/2=="; cr# - emid#: TAB(40); "I=-"; bi#
PRINT "D=\"; diff#: TAB(40); "M=\"; bm#
PRINT "Alpha=\"; al#: TAB(40); "Ks=\"; ko#
FOR j% = 1 TO num% \ 2
di# = i#(j%) - i#(num% - j% + 1)
IF di# > dimax# THEN dimax# = di#: dij% = j%
dm# = sm#(num% - j% + 1) - sm#(j%)
IF dm# > dmmax# THEN dmmax# = dm#: dmj% = j%
IF ms#(j%) <= bm# / 2 AND ms#(j% + 1) > bm# / 2 THEN emd2# = (e#(j%) + e#(j% + 1)) / 2
etest = INT(e#(j%) * 1000 + .5) / 1000
IF etest = .05 THEN died2# = i#(j%) - i#(num% - j% + 1)
NEXT j%
PRINT "E(i<1)max=\"; e#(di#)
PRINT "E(i<1)E 1/2=\"; died2#
PRINT "E(m<mg)max=\"; e#(dmj#)
PRINT "E(M/2)=\"; emd2#
INPUT "EXAMINE da/de (y/n)"; a$
a$ = "n" OR a$ = "N" THEN 4300
CALL pfit(fl$(), px#, py#, j1%, jh%, a, b, c)
PRINT "Alpha=\"; -rg * t * b / f: TAB(40); "Ks=\"; EXP(a)
PRINT "da/de =\"; -rg * t * c / f
DO
LOOP UNTIL INKEYS <> ""
4900 jh% = num% \ 2
ehalf# = (e#(maxij%) + e#(minij%)) / 2
FOR j% = 1 TO jh% - 1
smc# = smc#(j%) * (EXP(f * (e#(j%) - ehalf#) / (rg * i)) + 1)
px#(j%) = rg * t * LOG((smc#(jh%) - smc#(j%)) / smc#(j%)) / f
py#(j%) = e#(j%) - ehalf#
4910 NEXT j%
4920 CALL wls(fl$, fl$, 0, wi#(), px#(), py#(), 1, jh% - 1, m#, c#)
al# = 1 / m#
INPUT "Diffusion Coefficient"; diff#
k0# = EXP(al# * f / (rg * i)) * (diff# ^ (1 / 2))
PRINT "alpha ="; al#
PRINT "k0 ="; k0#
PRINT "E1/2 ="; ehalf#
PRINT "diffusion coefficient"; diff#
DO
LOOP UNTIL INKEYS <> ""
GOTO 4300

5000 REM SAVE SCALED DATA
CLS
INPUT "filename"; os$
INPUT "title"; title$
OPEN os$ FOR OUTPUT AS #1
PRINT #1, title$
PRINT #1, num%, t, n, sr, d, rad#, ei#, eh#, cb
FOR j% = 1 TO num%
PRINT #1, e#(j%), i#(j%)
NEXT j%
CLOSE #1
GOTO 10

6000 REM IR CORRECTION
CLS : PRINT : PRINT : PRINT : PRINT : PRINT
INPUT " INPUT UNCOMPENSATED RESISTANCE (OHMS)"; ru
nnnum% = num%
ei# = e#(1)
eh# = e#(1)
FOR j% = 1 TO num%
e#(j%) = e#(j%) + i#(j%) * ru
h#(j%) = j#(j%)
IF e#(j%) > hi# THEN ei# = e#(j%)
IF e#(j%) < hi# THEN eh# = e#(j%)
NEXT j%
CALL plot(fl$, pp(), 1, eo#, i#(), 1, num%)
inc# = ABS((ei# - eh#) * 2 / (1 + nnum%))
j1% = 1
c#(1) = ci#
FOR i% = 2 TO nnum\ 2 + 1
c# = ci# - (i% - 1) * inc#
c#(i%) = c#
FOR j% = j1% TO nnum\ 2 + 1
IF j% < 1 THEN j% = 1
IF e# <= eo#(j%) AND e# > eo#(j% + 1) THEN i#(i%) = h#(j%) + (h#(j% + 1) -
  h#(j%)) * (e# - eo#(j%)) / (eo#(j% + 1) - eo#(j%)); j1% = j% - 1; j% = num% \ 2 +
  2
NEXT j%
NEXT i%

j1% = num% \ 2 + 1
FOR i% = num% \ 2 TO num%;
  e# = ch# + (i% - num% \ 2) * inc#
  c#(j%) = c#
  FOR j% = j1% TO num%;
  IF e# >= eo#(j%) AND e# < eo#(j% + 1) THEN i#(i%) = h#(j%) + (h#(j% + 1) -
  h#(j%)) * (e# - eo#(j%)) / (eo#(j% + 1) - eo#(j%)); j1% = j% - 5; j% = num%
NEXT j%
NEXT i%

num% = num%
CALL plot(fl$, pp(), 1, c#, i%, 1, num%)
GOTO 10

7000 REM SMOOTHING
CLS : SCREEN 0
PRINT "CHOOSE MODE OF SMOOTHING"
PRINT "1, 3-POINT TRIANGULAR WINDOW SMOOTHING"
PRINT "2, FOURIER SMOOTHING"
PRINT "3, 9-POINT LEAST SQUARES WINDOW SMOOTHING"
PRINT "4, EXIT"
PRINT : INPUT "MODE OF SMOOTHING"; i%
FOR j% = 1 TO num%
i#(j%) = i#(j%)
NEXT j%
ON i% GOTO 7010, 7020, 7030, 7040
7010 CALL plot(fl$, pp(), 2, c#, i#, 1, num%)
FOR i% = 2 TO num% - 1
  i#(i%) = eo#(i%) / 2 + (eo#(i% - 1) + eo#(i% + 1)) / 4
NEXT i%
CALL plot(fl$, pp(), 0, c#, i#, 1, num%)
GOTO 7040
7020 INPUT "NUMBER OF TRANSFORMATIONS"; ntran%
CALL plot(fl$, pp(), 2, c#, i#, 1, num%)
CALL fp(data, pp(), c#, i#, num%, ntran%)
CALL plot(fl$, pp(), 1, c#, i#, 1, num%)
GOTO 7040
7030 CALL plot(fl$, pp(), 2, c#, i%, 1, num%)
i#(1) = (eo#(1) * 59 + eo#(2) * 54 + eo#(3) * 39 + eo#(4) * 14 + eo#(5) * -21) / 145
i#(2) = (eo#(2) * 59 + (eo#(1) + eo#(3)) * 54 + eo#(4) * 39 + eo#(5) * 14 + eo#(6) * -
  21) / 199
i#(3) = (eo#(3) * 59 + (eo#(2) + eo#(4)) * 54 + (eo#(1) + eo#(5)) * 39 + eo#(6) * 14 +
  eo#(7) * -21) / 238
i#(4) = (eo#(4) * 59 + (eo#(3) + eo#(5)) * 54 + (eo#(2) + eo#(6)) * 39 + (eo#(1) +
  eo#(7)) * 14 + eo#(8) * -21) / 252
FOR j% = 5 TO num% - 4
i#(j%) = eo#(j%) * 59 + (eo#(j% - 1) + eo#(j% + 1)) * 54 + (eo#(j% - 2) + eo#(j% + 2))
  * 39 + (eo#(j% - 3) + eo#(j% + 3)) * 14 + (eo#(j% - 4) + eo#(j% + 4)) * -21
i#(j%) = i#(j%) / 231
NEXT j%
i#(num% - 3) = (eo#(num% - 3) * 59 + (eo#(num% - 4) + eo#(num% - 2)) * 54 +
(eo%(num% - 5) + eo%(num% - 1)) * 39 + (eo%(num% - 6) + eo%(num%)) * 14 +
eo%(num% - 7) * -21 / 252
i%(num% - 2) = (eo%(num% - 2) * 59 + (eo%(num% - 3) + eo%(num% - 1)) * 54 +
(eo%(num% - 4) + eo%(num%)) * 39 + eo%(num% - 5) * 14 + eo%(num% - 6) * -21) / 238
i%(num% - 1) = (eo%(num% - 1) * 59 + (eo%(num% - 2) + eo%(num%)) * 54 +
eo%(num% - 3) * 39 + eo%(num% - 4) * 14 + eo%(num% - 5) * -21) / 199
i%(num%) = (eo%(num%) * 59 + eo%(num% - 1) * 54 + eo%(num% - 2) * 39 +
eo%(num% - 3) * 14 + eo%(num% - 4) * -21) / 145
CALL plot(fis(), pp(), 0, c#(), i#(), 1, num%)
7040 GOTO 10

8000 REM ADJUST CHARGING CURRENT
INPUT "CHARGING CURRENT CORRECTION AS A %OF ip": perip
CALL adjcc(e(), i(), num%, perip)
CALL plot(flS(), pp(), 1, c#(), i#(), 1, num%)
GOTO 10

9000 REM READ SIMULATED DATA (mV,mA)
CLEAR
GOSUB 1
CLS
INPUT "filename": o$
OPEN o$ FOR INPUT AS #1
INPUT #1, title$
INPUT #1, num%
INPUT #1, t, n, sr, d
INPUT #1, rsa, e#, ch#, cb
num% = num% - 1
d = d / 10000
rsa = rsa / 10000
cb = cb * 1000
FOR j% = 0 TO num%
INPUT #1, e%(j%), i%(j%)
c%(j%) = -e%(j%) / 1000
i%(j%) = i%(j%) / 1000
IF i%(j%) > imax# THEN imax# = i%(j%): maxij% = j%
IF i%(j%) < imin# THEN imin# = i%(j%): minij% = j%
NEXT j%
CLOSE #1
CALL plot(flS(), pp(), 2, c#(), i#(), 1, num%)
ei# = (e#(1) + e#(num%)) / 2
rad# = (dxa / (4 * pi#)) ^ (1 / 2)
isp = .7516 * n * f * dxa * d * cb / rad#
ipl = .4463 * n * f * dxa * d ^ (1 / 2) * sr ^ (1 / 2) * cb * (n * f / (rg * t)) ^ (1 / 2) + isp
spher = isp * 100 / ipl
PRINT title$: " SPHERICITY="; spher; "%"; " Epc="; e#(maxij%); " Epa="; e#(minij%)
DO
LOOP UNTIL INKEY$ <> ""
GOTO 10

10000 REM choose weighting function
CLS : SCREEN 0
PRINT : PRINT : PRINT : PRINT : PRINT
PRINT "CHOOSE A WEIGHTING FUNCTION"
PRINT "0, NO WEIGHTING (THIS IS THE DEFAULT)"
PRINT "1, OLDHAM WEIGHTING"
PRINT "2, EVANS WEIGHTING"
PRINT "3, SAVEANT CPSV"
PRINT "4, EXIT"
INPUT "CHOICE": wmod%
IF wmod% < 0 OR wmod% > 4 THEN 10000
ON wmod% GOTO 10100, 10200, 10300, 10
GOTO 4400
10100 wmod% = 1
GOTO 10400
10200 wmod% = 2
PRINT : INPUT "LOWER LIMIT (<50%)": ewl
PRINT : INPUT "UPPER LIMIT (>50%)": ewh
GOTO 10400
10300 wmod% = 3
10400 IF main = 1 THEN 10 ELSE 4400

11000 REM ADD RANDOM NOISE
CLS
INPUT "VARIANCE AS % OF ip": vr
CALL noise(i#, num%, vr)
CALL plot(fl$, pp(), 1, e#, i#, 1, num%)
PRINT vr
GOTO 10

12000 REM SAVE OUTPUT DATA
CLS
jlo% = 1
jho% = num% \ 2
INPUT "FILENAME OF OUTPUT FILE": o$
INPUT "OUTPUT DENSITY": dd%
PRINT "j=": jlo%, ", jh = ": jho%, ", total number =": num% \ 2
INPUT "LOWER DATA LIMIT": jlo%
INPUT "UPPER DATA LIMIT": jho%
OPEN o$ FOR OUTPUT AS #1
PRINT #1, title$
PRINT #1, num%, i, n, sr, d, dsa, ei#, eh#, cb
PRINT #1, "E(V)--> i(A)--> w(m*)"
PRINT #1, "E(V)<= i(A)<= w(i*)"
PRINT #1, "m* w(m*)"
PRINT #1, "i* w(i*)"
FOR j% = jlo% TO jho% STEP dd%
PRINT #1, e#(j%), i#(j%), sm#(j%)
PRINT #1, e#(num% - j% + 1), i#(num% - j% + 1), sm#(num% - j% + 1)
PRINT #1, j%, ms#(j%), wm#(j%)
PRINT #1, j%, ii#(j%), wi#(j%)
NEXT j%
CLOSE #1
GOTO 10

13000 END

SUB adjcc (e#(), i#(), num%, perip)
FOR j% = 1 TO num% \2
IF i%(j%) > imax THEN imax = i%(j%)
NEXT j%
FOR j% = num% \2 TO num%
i%(j%) = i%(j%) + perip * imax / 100
NEXT j%
END SUB

SUB fpa (fl$(0), pp$(0), e$(0), i$(0), num%, ntran%)
DIM real#(300), imag#(300), lx#(300), ly#(300)
pi# = 3.1415926536#
ntrano% = 1
bf# = (i%(num%) - i%(1)) / num%
g# = 0
FOR j% = 2 TO num%
i%(j%) = i%(j%) - i%(1) - bf# * (j% - 1)
g# = g# + i%(j%)
NEXT j%
real#(0) = g# / num%
7110 IF ntran% <= ntran0% THEN 7120
FOR k% = ntran0% TO ntran% - 1
sumr# = 0
sumi# = 0
FOR j% = 2 TO num% - 1
s# = SIN(2 * pi# * (j% - 1) * k% / num%)
c# = COS(2 * pi# * (j% - 1) * k% / num%)
sumr# = sumr# + i%(j%) * c#
sumi# = sumi# + i%(j%) * s#
NEXT j%
real#(k%) = sumr#/num%
imag#(k%) = -sumi#/num%
lx#(k%) = k%
ly#(k%) = real#(k%)^2 + imag#(k%)^2
NEXT k%
CALL plot(fl$(0), pp$(0), 1, lx$(0), ly$(0), ntran0%, ntran% - 1)
IF ntran% > ntran0% THEN ntran0% = ntran%
7120 f1# = 0: f2# = 0
FOR k% = 1 TO ntran% - 1
f1# = f1# + real#(k%)
f2# = f2# + k%^2 * 2 * real#(k%)
f0# = 1 - k%^2 / (ntran% * ntran%)
real#(k%) = f0# * real#(k%)
imag#(k%) = f0# * imag#(k%)
NEXT k%
i%(1) = i%(1) + real#(0) + 2 * (f1# - f2#/ (ntran% * ntran%))
FOR j% = 2 TO num%
sum# = 0
FOR k% = 1 TO ntran% - 1
s# = SIN(2 * pi# * k% * (j% - 1) / num%)
c# = COS(2 * pi# * k% * (j% - 1) / num%)
sum# = sum# + real#(k%) * c# - imag#(k%) * s#
NEXT k%
i%(j%) = i%(1) + (j% - 1) * bf# + real#(0) + 2 * sum#
NEXT j%
END SUB
SUB noise (i#, num%, vr)
DIM ni%(500)
kint% = 100
FOR j% = 1 TO num% \
IF i#(j%) > imax# THEN imax# = i#(j%)
NEXT j%
PRINT "method of noise"
PRINT " 1, Oldham noise"
PRINT " 2, Computer noise"
INPUT "choice"; c%
ON c% GOTO 11110, 11120
11110 pi# = 3.1415926536#
k% = 0
mu = 0
bn# = 199017
s# = 2 * (vr * imax# / 100) ^ 2
j% = 2 * num%
n# = 2 * num%
11100 n# = 24298 * n# + 99991
n# = 1 + n# - bn# * INT(n# / bn#)
ni% = 1 + INT(n# / bn# * kint%)
ni%(ni%) = ni%(ni%) + 1
j% = j% - 1
IF j% \
IF j% = 2 = j% / 2! THEN 11200
x# = (s# * LOG(bn# / n#)) ^ (1/2)
GOTO 11100
11200 x# = mu + x# * COS(2 * pi# * n# / bn#)
k% = k% + 1
i#(k%) = i#(k%) + x#
IF j% > 0 THEN 11100 ELSE 11300
11120 FOR j% = 1 TO num%
x# = (RND(1) - .5) * imax# * vr / 100
i#(j%) = i#(j%) + x#)
NEXT j%
11300 FOR j% = 1 TO kint%
snitsq# = snitsq# + (ni%(j%) - 2 * num% / kint%) ^ 2 / (2 * num% / kint%)
NEXT j%
chisq# = snitsq#
PRINT chisq#, kint%
DO
LOOP UNTIL INKEY$ <> ""
END SUB

SUB pfit (fl$(i), px#, py#, jl%, jh%, a, b, c)
DIM pny#(1500), pp(4)
FOR j% = jl% TO jh%
IF fl$(j%) = "n" THEN 20000
smx = smx + px#(j%)
smu = smu + px#(j%) ^ 2
smy = smy + py#(j%)
smysq = smysq + py#(j%) ^ 2
smxu = smxu + px#(j%) ^ 3
smusq = smusq + px#(j%) ^ 4
smxy = smxy + py#(j%) * px#(j%)
NEXT j%
smuy = smuy + py#(j%) * px#(j%) ^ 2
20000 NEXT j%
pnum% = jh% - jl% + 1
a1 = smu - smux ^ 2 / pnum%
b1 = smux - smu / pnum%
b2 = smusq - smu ^ 2 / pnum%
a3 = smxy - smu * smy / pnum%
b3 = smuy - smu * smy / pnum%
a2 = b1
b = (a2 * b3 - b2 * a3) / (a2 * b1 - a1 * b2)
c = (a3 - a1 * b) / a2
a = (smy - b * smx - c * smu) / pnum%
sy = smysq - smy ^ 2 / pnum%
FOR j% = jl% TO jh%
IF f1$(j%) = "n" THEN 20010
pny#(j%) = a + b * px#(j%) + c * px#(j%) ^ 2
spny = spny + pny#(j%)
spnysq = spnysq + pny#(j%) ^ 2
20010 NEXT j%
syd = spnysq - spny ^ 2 / pnum%
rsq = syd / sy
CALL plot(fl$(0), pp(), 1, px#(), py#(), jl%, jh%)
PRINT a, b, c, rsq
CALL plot(fl$(0), pp(), 0, px#(), pny#(), jl%, jh%)
END SUB

SUB plot (fl$(0), pp(), clr%, lx#(), ly#(), pln%, phn%)
REM clr% = (0:nc,p) (1:c,p) (2:c,np) (3:nc,np)
IF clr% = 0 OR clr% = 3 THEN 999
CLS
pp(2) = lx#(pln%); pp(1) = lx#(pln%)
pp(4) = ly#(pln%); pp(3) = ly#(pln%)
FOR j% = pln% TO phn%
IF f1$(j%) = "n" THEN 30010
IF lx#(j%) >= pp(1) THEN pp(1) = lx#(j%)
IF lx#(j%) <= pp(2) THEN pp(2) = lx#(j%)
IF ly#(j%) >= pp(3) THEN pp(3) = ly#(j%)
IF ly#(j%) <= pp(4) THEN pp(4) = ly#(j%)
30010 NEXT j%
999 SCREEN 2
WINDOW (0, 0)-(pp(1) - pp(2), 1.1 * (pp(3) - pp(4)))
FOR j% = pln% TO phn%
IF f1$(j%) <> "n" THEN PSET (lx#(j%) - pp(2), ly#(j%) - pp(4))
NEXT j%
IF clr% = 1 OR clr% = 2 THEN PRINT pp(2); pp(4); "<>"; pp(1); pp(3)
IF clr% = 2 OR clr% = 3 THEN 9999
DO
LOOP WHILE INKEY$ = ""
99999 END SUB

SUB potpair (c#(), i#(), num%, switch%)
DIM ec#(1500), io#(1500)
ci# = c#(1)
eh# = e#(switch%)
inc# = ABS(e#(2) - e#(1))
nswitch% = switch%
FOR j% = 1 TO num%
c#(j%) = c#(j%)
io#(j%) = i#(j%)
NEXT j%
PRINT "THE POTENTIAL INCREMENT ON THE FORWARD SWEEP IS="; inc#
INPUT "DO YOU WISH TO CHANGE THE INCREMENT (Y/N)"; o$
IF o$ = "y" OR o$ = "Y" THEN INPUT "NEW INCREMENT"; inc#
inc# = nswitch% = ABS(c#(j) - ch#) / inc# + 1
nnum% = 2 * nswitch% - 1
j1% = 1
FOR i% = 1 TO nswitch% + 1
e# = e# - (1% - 1) * inc#
c# = c#
FOR j% = j1% TO switch%
IF e# < eo#(j%) AND e# > eo#(j% + 1) THEN i#(i%) = io#(j%) + (io#(j% + 1) -
   io#(j%)) * (e# - eo#(j%)) / (eo#(j% + 1) - eo#(j%)); j1% = j%: j% = switch%
NEXT j%
NEXT i%
j1% = switch% + 1
FOR i% = 1 TO nnum%
e# = e# + (1% - nswitch%) * inc#
e#(i%) = e#
FOR j% = j1% TO num%
IF e# > eo#(j%) AND e# < eo#(j% + 1) THEN i#(i%) = io#(j%) + (io#(j% + 1) -
   io#(j%)) * (e# - eo#(j%)) / (eo#(j% + 1) - eo#(j%)); j1% = j%: j% = num%
NEXT j%
NEXT i%
PRINT nnum%
nnum% = nnum%
switch% = nswitch%
END SUB

SUB weight (fl$, pp(), e#(), i#(), sm#(), ii#(), ms#(), num%, dt#, pi#, wi#(), wm#())
et% = 1
FOR j% = 1 TO num% \ 2
b% = num% - j% + 1
rd = 4 * (dt# / pi#) \ (1 / 2) / 3
bot = (sm#(b%) - rd * i#(b%)) \ 2 + (sm#(b%) - rd * i#(j%)) \ 2 + dt# * (i#(j%) \ 2 *
   LOG(2.27 * b%) + i#(b%) \ 2 * LOG(2.27 * j%)) / pi#;
IF i#(j%) <= 0 THEN wi#(j%) = (sm#(b%) - sm#(j%)) \ 2 / (eta \ 2 * dt# * LOG(180!
   * j% ^ b%) / pi# + eta \ 2 * bot / i#(j%)) \ 2)
IF ms#(j%) <= 0 THEN wm#(j%) = (sm#(b%) * i#(j%) - sm#(j%) * i#(b%)) \ 2 / (2 *
et# \ 2 + eta \ 2 * bot / ms#(j%)) \ 2)
IF wi#(j%) > wimax THEN wimax = wi#(j%); wi#% = j%
IF wm#(j%) > wmax THEN wmax = wm#(j%); wmax% = j%
NEXT j%
CALL plot(fl$, pp(), 2, e#(), wi#(), 1, num% / 2)
PRINT "E(wln i#max)="; e#(wi#%)
DO
LOOP UNTIL INKEYS $ <> "" 
CALL plot(fl$, pp(), 2, e#(), wm#(), 1, num% / 2)
PRINT "E(w(1/m#)max)="; e#(wm#%)
DO
LOOP UNTIL INKEYS $ <> ""
END SUB

SUB wls (fl$(()), pp(), wmd%, w#(), lx(), ly(), j1%, jh%, m#, c#)
IF wmd% = 1 THEN 100
FOR j%= j1% TO jh%
  w#(j%) = 1
  NEXT j%
100 sx# = 0: sy# = 0: sxy# = 0: ssxq# = 0: sysq# = 0: sw# = 0
  FOR j%= jl% TO jh%
    IF fl$(j%) = "n" THEN 40010
    sx# = sx# + w#(j%) * lx(j%)
    sy# = sy# + w#(j%) * ly(j%)
    sxy# = sxy# + w#(j%) * lx(j%) * ly(j%)
    ssxq# = ssxq# + w#(j%) * lx(j%) * lx(j%)
    sysq# = sysq# + w#(j%) * ly(j%) * ly(j%)
    sw# = sw# + w#(j%)
  40010 NEXT j%
  m# = (sw# * sxy# - sx# * sy#) / (sw# * ssxq# - sx# * sx#)
  c# = - (sx# * sxy# - sy# * ssxq#) / (sw# * ssxq# - sx# * sx#)
  CALL plot(fl$(()), pp(), 1, lx(), ly(), j1%, jh%)
  FOR j%= jl% TO jh%
    IF fl$(j%) <> "n" THEN ly(j%) = m# * lx(j%) + c#
  NEXT j%
rsq# = ((sw# * sxy# - sx# * sy#)^2 / ((sw# * ssxq# - sx#^2) * (sw# * sysq# - sy#^2)))
PRINT m#, c#, rsq#
CALL plot(fl$(()), pp(), 0, lx(), ly(), j1%, jh%)
END SUB
""" PROGRAM MICSIM.BAS
""" WRITTEN BY S.W. FELDBERG
""" MODIFIED BY P.J. MAHON

DEFDLL A-Z
DEFINT I-J, M

DECLARE SUB HELP ()
DECLARE SUB INIT ()
DECLARE SUB DISKGRID ()
DECLARE SUB PRINTINPUTDATA ()
DECLARE SUB PROFILE ()
DECLARE SUB WAITFORME ()
DECLARE SUB PLOT (PX(), PY(), PP(), IPLN, IPHN, CP)
COMMON SHARED AI1(), AI2(), DAI()
COMMON SHARED BI1(), BI2(), DBI()
COMMON SHARED PX(), PY()
COMMON SHARED BETAY, BETAY1, BETAR, BETAR1, ALPHA, ALPIN,
DALPDE,
COMMON SHARED K0RW, DRW, R0RW, VRW, N
COMMON SHARED PI, TIME, TMAX, D0, R0, VDT, SPH
COMMON SHARED YMIX, IRMAX, YMT, IRMT, IR0, MTMAX, AREASUM,
ESTART, EREV, BAAB
COMMON SHARED IPLN, IPHN, IRDIM, IYDIM, NR, MC, NCC, ZMCH, WE,
WF, WB, FRT, EAPP, EHAF, RL.
DIM SHARED AI1(40, 50), AI2(40, 50), DAI(40, 50), F0(40), AREA(40)
DIM SHARED BI1(40, 50), BI2(40, 50), DBI(40, 50)
DIM SHARED DY1(40, 50), DY2(40, 50), DR1(50), DR2(50), YMD1(40), RMD1(50)
DIM SHARED XMAT1(5, 10), PX(1500), PY(1500), PP(4), P1X(1500), P1Y(1500)
IRDIM = 50
IYDIM = 40
NR = 2; MC = 2; NCC = 1; ZMCH = 0
FUSUM1 = 0
PI = 3.1415927#
F = 96487.7
R = 8.3144
TEMP = 298.15
CBULK = .0000001
FRT = F / (R * TEMP)
CLS
PRINT
PRINT "Program MICSIM.BAS"
PRINT
PRINT "CV Disk simulation using expanding grid in y and r (from r=r0)."
PRINT " Use DF algorithm for FQEF.D."
PRINT
PRINT " Simulation of ",
PRINT " e + A <---> B (k0,alpha)"
PRINT
PRINT "For HELP in using this program type H; & any other key to continue."
H$ = INPUT$(1)
IF H$ = "H" OR H$ = "h" THEN CALL HELP
FRT = 96487.7# / (3.141399999999999# * 298#)
PI = 3.1415927#
ESTART = -.3
EREV = .2
NHALF = 2
E0AB = 0
K0RW = 1E+20
ALPIN = .5#
DALPDE = 0
VRW = .001
DRW = .00001
R0RW = .01
N = 1

100 REM SCREEN MENU
CLS : SCREEN 0
PRINT "Current Parameters"
PRINT "0, Begin Simulation"
PRINT "1, Starting Potential (V)", USING "###.#####"; ESTART
PRINT "2, Reversal Potential (V)", USING "###.#####"; EREV
PRINT "3, Number of Half Cycles", USING "###.#####"; NHALF
PRINT "4, Standard Potential of AB (V)", USING "###.#####"; E0AB
PRINT "5, Electron Transfer Rate of AB (cm/s)", USING "###.#####"; K0RW
PRINT "6, Alpha for AB", USING "###.#####"; ALPIN
PRINT "7, D(Alpha)/dE for AB", USING "###.#####"; DALPDE
PRINT "8, Scan Rate (V/s)", USING "###.#####"; VRW
PRINT "9, Diffusion Coefficient (cm^2/2/s)", USING "###.#####"; DRW
PRINT "10, Disk Radius (cm)", USING "###.#####"; R0RW
PRINT "11, Temperature (K)", USING "###.#####"; TEMP
PRINT "12, No. of electrons", USING "###.#####"; N
PRINT "13, Exit"
PRINT : INPUT "Input Selection"; IN
SELECT CASE IN
CASE IS = 0: GOTO 400
CASE IS = 1: INPUT "New Potential (V)"; ESTART
CASE IS = 2: INPUT "New Potential (V)"; EREV
CASE IS = 3: INPUT "New Number of Half Cycles"; NHALF
CASE IS = 4: INPUT "New Potential (V)"; E0AB
CASE IS = 5: INPUT "New Rate"; K0RW
CASE IS = 6: INPUT "New Alpha"; ALPIN
CASE IS = 7: INPUT "New d(Alpha)/dE"; DALPDE
CASE IS = 8: INPUT "New Scan Rate"; VRW
CASE IS = 9: INPUT "New Diffusion Coefficient (cm^2/2/s)"; DRW
CASE IS = 10: INPUT "New Disk Radius (cm)"; R0RW
CASE IS = 11: INPUT "New Temperature (K)"; TEMP
CASE IS = 12: INPUT "New No. of electrons"; N
CASE IS = 13: END
END SELECT
FRT = 96487.7# / (8.31439999999999999999 # * TEMP)
GOTO 100

400 SPH = DRW / (FRT * VRW * R0RW ^ 2)
   '----------------Calculate Simulation Parameters--------------'
   Calculate minimum R0
   R0 = SQR(50)
   IF R0 < 25 THEN R0 = 25
   ' Calculate min. R0 or max. vdt based on sphericity and D=.00001/vdt^2
   VDT = .001
   R01 = SQR(.00001 / (FRT * VDT ^ 3 * SPH))
   IF R01 < R0 THEN
VDT = (SQR(.00001 / (FRT * SPH)) / R0) ^ .6666666666#
ELSE
   R0 = R01
END IF
D0 = .00001 / VDT ^ 2
K0DT = K0RW * R0RW * D0 / (DRW * R0)
SPHSIM = D0 / (FRT * VDT * R0 ^ 2)
IF ABS(SPHSIM - SPH) / SPH > .000001 THEN PRINT "Screwed up something."
STOP
'------------------------------
IF VDT > .0001 GOTO 700
PRINT "vd = "; VDT; " Too small; Need double precision and that isn't "
PRINT "practical on a PC; also, computation will take too long."
600 PRINT " To continue type C; to quit restart type R"
Q$ = INPUT$(1)
IF Q$ = "C" OR Q$ = "c" THEN GOTO 700
IF Q$ = "r" OR Q$ = "R" THEN GOTO 100
GOTO 600
700 IF EREV - ESTART < 0 THEN VDT = -VDT
EAPP = ESTART - VDT / 2
MTREV = ABS((EREV - ESTART) / ABS(VDT))
MTMAX = MTREV * NHALF
TMAX = MTMAX
BETAY = .5#
BETAR = .5
BETAY1 = EXP(BETAY) - 1#
BETAR1 = EXP(BETAR) - 1
MTOUT = INT(ABS(.001 / VDT))
MTLAB = 15 * MTOUT
CALL INIT
CALL DISKGRID
CALL PRINTINPUTDATA
PRINT " E fnorm(cv) fnorm(ss) current(A)"
'-------------------------------Do it-------------------------------
INUM = 0
FOR MT = 1 TO MTMAX
EAPP = EAPP + VDT
IF MTREV = MT + 1 THEN VDT = -VDT: EAPP = EAPP + VDT
T = MT
ALPHA = (EAPP - E0AB) * DALPDE + ALPIN
KEFDT = K0DT * EXP(-ALPHA * N * FRT * (EAPP - E0AB))
KEBDT = K0DT * EXP((1 - ALPHA) * N * FRT * (EAPP - E0AB))
WF = KEFDT / (1 + KEFDT / DY1(1) + KEBDT / DY1(1))
WB = KEBDT / (1 + KEFDT / DY1(1) + KEBDT / DY1(1))
IYMT = INT(LOG(6 * BETAY1 * SQR(D0 * T) + 1) / BETAY)
IF IYMT > IYMAX - 1 THEN IYMT = IYMAX - 1
IRMT = IR0 + INT(LOG(6 * BETAR1 * SQR(D0 * T) + 1) / BETAR)
IF IRMT > IRMAX - 1 THEN IRMT = IRMAX - 1
Q$ = INKEY$
IF Q$ = "h" OR Q$ = "H" THEN CALL HELP
IF Q$ = "p" OR Q$ = "p" THEN CALL PROFILE: CALL WAITFORME
IF Q$ <= "q" AND Q$ <= "Q" THEN GOTO 900
CALL PRINTINPUTDATA
PRINT "Restart (Y/aok)";
R$ = INPUT$(1)
IF RS = "$y" OR R$ = "$y" THEN GOTO 100
PRINT "User Interrupt": END
900 IF QS = "$I" OR Q$ = "$i" THEN CALL PLOT(PIX(), PY(), PP0, 1, INUM, 0):
CALL PRINTINPUTDATA: CALL WAITFORME

'-----Solve for changes for iy=1; ir<=i0- ( electroactive part)-----
FOR IR = 1 TO I0R
NUMA = WF + DY2(1) + DR1(IR) + DR2(IR)
DENA = 1 + NUMA
XMAT1(1, 1) = DENA
XMAT1(1, 2) = -WB
XMAT1(1, 3) = DY2(1) * A12(2, IR) + DR2(IR) * A12(1, IR + 1) + DR1(IR) * A12(1, IR - 1) + WB * BI1(1, IR) - NUMA * A11(1, IR)
NUMB = WB + DY2(1) + DR1(IR) + DR2(IR)
DENB = 1 + NUMB
XMAT1(2, 1) = -WF
XMAT1(2, 2) = DENB
XMAT1(2, 3) = DY2(1) * B12(2, IR) + DR2(IR) * B12(1, IR + 1) + DR1(IR) * B12(1, IR - 1) + WB * A11(1, IR) - NUMB * BI1(1, IR)
DEN = XMAT1(1, 1) * XMAT1(2, 2) - XMAT1(1, 2) * XMAT1(1, 2)
DAI1(1, IR) = (XMAT1(1, 3) * XMAT1(2, 2) - XMAT1(1, 2) * XMAT1(1, 2)) / DEN
DBI1(1, IR) = (XMAT1(1, 1) * XMAT1(2, 3) - XMAT1(2, 1) * XMAT1(1, 3)) / DEN
F0(IR) = -WF * (A11(1, IR) + DAI1(1, IR)) + WB * (BI1(1, IR) + DBI1(1, IR))
NEXT IR.

'-----Solve for changes for iy=1; ir>i0- ( electrode inactive part)-----
FOR IR = I0R + 1 TO IRMT
NUMA = DY2(1) + DR1(IR) + DR2(IR)
DENA = 1 + NUMA
DAI1(1, IR) = (DY2(1) * A12(2, IR) + DR2(IR) * A12(1, IR + 1) + DR1(IR) * A12(1, IR - 1) - NUMA * A11(1, IR)) / DENA
NUMB = DY2(1) + DR1(IR) + DR2(IR)
DENB = 1 + NUMB
DBI1(1, IR) = (DY2(1) * B12(2, IR) + DR2(IR) * B12(1, IR + 1) + DR1(IR) * B12(1, IR - 1) - NUMB * BI1(1, IR)) / DENB
NEXT IR.

'-----Solve for changes for iy>1 and all ir--(DR1(0)=0)-----
FOR IY = 2 TO IYMT
FOR IR = 1 TO IRMT
NUMA = DY1(IY) + DY2(IY) + DR1(IR) + DR2(IR)
DENA = 1 + NUMA
DAI1(IY, IR) = (DY2(IY) * A12(IY + 1, IR) + DY1(IY) * A12(IY - 1, IR) + DR2(IR) * A12(IY, IR + 1) + DR1(IR) * A12(IY, IR - 1) - NUMA * A11(IY, IR)) / DENA
NUMB = DY1(IY) + DY2(IY) + DR1(IR) + DR2(IR)
DENB = 1 + NUMB
DBI1(IY, IR) = (DY2(IY) * B12(IY + 1, IR) + DY1(IY) * B12(IY - 1, IR) + DR2(IR) * B12(IY, IR + 1) + DR1(IR) * B12(IY, IR - 1) - NUMB * BI1(IY, IR)) / DENB
NEXT IR
NEXT IY

'---Reset---
FOR IY = 1 TO IYMT
FOR IR = 1 TO IRMT
NEXT IR
NEXT IY

------------------------Output------------------------

IF MT / MOUT <> INT(MT / MOUT) THEN GOTO 950
 F0SUM = 0
 FOR IR = 1 TO IRO
   F0SUM = F0SUM + F0(IR) * AREA(IR)
 NEXT IR
 F0NORMCV = -F0SUM / SQR(D0 * FRT * ABS(VDT))
 F0NORMD = -F0SUM / ((4 / PI) * D0 / R0)
 Curr = F0NORMD * 4 * N * F * DRW * CBULK * R0RW
 INUM = INUM + 1
 P1X(INUM) = EAPP
 P1Y(INUM) = F0NORMD
 IF MT / MTLAB <> INT(MT / MTLAB) THEN GOTO 925
 PRINT
 PRINT " E fnorm(cv) fnorm(ts) current(A)"
925 PRINT USING "###.#####  "; EAPP, F0NORMCV, F0NORMD, Curr
950 NEXT MT
1000 INPUT "COMPARING WITH EXPERIMENTAL CURVE": A$
   IF A$ = "N" OR A$ = "n" THEN CALL PLOT(P1X(), P1Y(), PP(), 1, INUM, 0):

GOTO 1010
 INPUT "FILENAME": O$
 OPEN O$ FOR INPUT AS #1
 INPUT #1, TITLES
 FOR I = 1 TO IDAT
   INPUT #1, PX(I), PY(I)
 NEXT I
 CLOSE #1
 CLS
 INPUT "Change sign of the simulated current": y$
 IF y$ = "n" OR y$ = "N" THEN 1005
 FOR I = 1 TO INUM
   P1Y(I) = -P1Y(I)
 NEXT I
1005 CALL PLOT(P1X(), P1Y(), PP(), 1, INUM, 0)
 CALL PLOT(PX(), PY(), PP(), 1, IDAT, 1)
 PRINT O$
 DO
 LOOP UNTIL INKEY$ <> ""
 CLS
 CALL PLOT(P1X(), P1Y(), PP(), 1, INUM, 2)
 CALL PLOT(PX(), PY(), PP(), 1, IDAT, 3)
1010 PRINT O$
 DO
 LOOP UNTIL INKEY$ <> ""
 INPUT "OUTPUT DATA TO FILE": A$
 IF A$ <> "y" AND A$ <> "Y" THEN 100
 INPUT "OUTPUT AS CURRENT DATA": O$
 CFAC = 1
 IF O$ = "Y" OR O$ = "y" THEN INPUT "BULK CONCENTRATION (M)";
   CBULK: CFAC = 4 * 1 * 96487.7 * CBULK * DRW * R0RW / 1000
 INPUT "FILENAME": A$
SUB DISKGRID STATIC
  ' Compute operative DY1(IY) and DY2(IY) for diffusion normal to disk.
  FOR IY = 1 TO IYMAX
    DY2(IY) = D0 * EXP(2 * BETAY * (.75 - IY))
    DY1(IY) = D0 * EXP(2 * BETAY * (1.25 - IY))
    YMID(IY) = (EXP(BETAY * (IY - .5)) - 1) / BETAY1
    IF IY = 1 THEN DY1(1) = D0 / YMID(1)
  NEXT IY
  ' Compute operative DR1(IY) and DR2(IY) for radial cylindrical diffusion.
  ' First, for r>r0:
  FOR IR = IR0 + 1 TO IRMAX
    I = IR - IR0
    DR = EXP(BETAR * (I - 1))
    R2 = R0 + (EXP(BETAR * I) - 1) / BETAR1
    R1 = R2 - DR
    DRBAR2 = EXP(BETAR * (I - .5))
    DRBAR1 = EXP(BETAR * (I - 1.5))
    RRMD = (EXP(BETAR * (I - .5)) - 1) / BETAR1
    RMID(IR) = R0 + RRMD
    DR2(IR) = D0 / (DRBAR2 * (DR - .5 * DR ^ 2 / R2))
    DR1(IR) = D0 / (DRBAR1 * (DR + .5 * DR ^ 2 / R1))
    IF I = 1 THEN DR1(IR) = D0 / (2 * RRMD * (DR + .5 * DR ^ 2 / R0))'mid ir0+1
    to mid ir0
  NEXT IR
  ' Then, for r<r0
  FOR IR = 2 TO IR0
    I = IR0 + 1 - IR
    DR = EXP(BETAR * (I - 1))
    R2 = R0 - (EXP(BETAR * (I - 1)) - 1) / BETAR1
    R1 = R2 - DR
    AREA(IR) = (R2 ^ 2 - R1 ^ 2) / R0 ^ 2
    RRMD = (EXP(BETAR * (I - .5)) - 1) / BETAR1
    RMID(IR) = R0 - RRMD
    DRBAR2 = EXP(BETAR * (I - 1.5))
    DRBAR1 = EXP(BETAR * (I - .5))
    DR2(IR) = D0 / (DRBAR2 * (DR - .5 * DR ^ 2 / R2))
    DR1(IR) = D0 / (DRBAR1 * (DR + .5 * DR ^ 2 / R1))
    IF I = 1 THEN DR2(IR) = D0 / (2 * RRMD * (DR - .5 * DR ^ 2 / R0))
    IF IR = 2 THEN DR1(IR) = D0 / (RMID(IR) * (DR + .5 * DR ^ 2 / R1))
  NEXT IR
  DR1(1) = 0
  R2 = R0 - (EXP(BETAR * (IR0 - 1)) - 1) / BETAR1
  AREA(1) = (R2 / R0) ^ 2
  DR2(1) = D0 / (RMID(2) * .5 * R2)
END SUB
'------------------------------------------------- Subroutine HELP'-------------------------------------------------
3820 SUB HELP STATIC
3830 PRINT "This program has a number of useful interrupts:"
3840 PRINT
3850 PRINT "Type"
3860 PRINT "--------------------------------------------------------------"
3870 PRINT " H Summons this HELP routine."
3880 PRINT ""
3890 PRINT " I Gives a listing of all parameters (some of this stuff"
3900 PRINT " will be simulation junk that is of no interest to most)."
3910 PRINT
3920 PRINT " P Gives Some concentration and flux profiles."
3930 PRINT
3940 PRINT " Q Exit Program"
3950 PRINT
3960 PRINT "Hit any key to continue."
3970 QS = INPUT$(1)
3980 PRINT "--------------------------------------------------------------"
3990 END SUB

SUB INT STATIC
IYMAX = LOG(6 * BETAY1 * SQR(D0 * TMAX) + 1) / BETAY
IYMAXSS = LOG(1000 * BETAY1 * R0 + 1) / BETAY
IF IYMAX > IYMAXSS THEN IYMAX = IYMAXSS
IR0 = INT(LOG(R0 / BETAR1 + 1) / BETAR)
IRMAX = IR0 + LOG(6 * BETAR1 * SQR(D0 * TMAX) + 1) / BETAR
IRMAXSS = IR0 + LOG(1000 * BETAR1 * R0 + 1) / BETAR
IF IRMAX > IRMAXSS THEN IRMAX = IRMAXSS
IF IRMAX < IRDIM THEN GOTO 2000
PRINT "iymax (=";', IYMAX; ") exceeds dimension (";', IRDIM; "): change something."
STOP
2000 IF IYMAX < IYDIM THEN GOTO 2050
PRINT "iymax (=";', IYMAX; ") exceeds dimension (";', IYDIM; "): change something."
STOP
2050 FOR IY = 1 TO IYMAX
  FOR IR = 1 TO IRMAX
    WE = EXP(FRT * (ESTART - E0AB))
    ASTART = WE / (1 + WE)
    BSTART = 1 / (1 + WE)
    A12(IY, IR) = ASTART: A12(IY, IR) = ASTART
    B12(IY, IR) = BSTART: B12(IY, IR) = BSTART
  NEXT IR
NEXT IY
END SUB

SUB PLOT (PX(), PY(), PP(), IPLN, IPHN, CP)
PP(3) = PY(5): PP(4) = PY(5)
IF CP > 0 THEN 5000
PP(1) = PX(1): PP(2) = PX(1)
5000 FOR J = IPLN TO IPHN
  IF PY(J) >= PP(3) THEN PP(3) = PY(J)
  IF PY(J) <= PP(4) THEN PP(4) = PY(J)
  IF CP > 0 THEN 5100
  IF PX(J) >= PP(1) THEN PP(1) = PX(J)
IF PX(J) <= PP(2) THEN PP(2) = PX(J)

5100 NEXT J
SCREEN 2
IF CP = 0 OR CP = 1 THEN WINDOW (0, -1!)-(PP(1) - PP(2), 1.25)
IF CP = 2 OR CP = 3 THEN WINDOW (0, -1.05)-(PP(1) - PP(2), 2.25)
FOR J = IPLN TO IPHN
   IF CP = 0 OR CP = 1 THEN PSET (PX(J) - PP(2), PY(J) / PP(3))
   IF CP = 2 OR CP = 3 THEN PSET (PX(J) - PP(2), -PY(J) / PP(4))
NEXT J
PRINT USING "####.####"; PP(2);
PRINT " ";
PRINT USING "####.####"; PP(4);
PRINT " <- > ";
PRINT USING "####.####"; PP(1);
PRINT " ";
PRINT USING "####.####"; PP(3)
END SUB

'-------------------------Subroutine PRINTINPUTDATA-------------------------------
SUB PRINTINPUTDATA STATIC
   PRINT "Critical Input Parameters:"
   PRINT " sph = ";
   PRINT USING "####.#### " ; SPH
   PRINT " alpha = ";
   PRINT USING "####.#### " ; ALP
   PRINT USING "####.#### " ; DALP
   PRINT " k0rw = ";
   PRINT USING "####.#### " ; K0RW
   PRINT " Estart = ";
   PRINT USING "####.#### " ; ESTART
   PRINT " Erev = "
   PRINT USING "####.#### " ; EREV
   PRINT
   PRINT "Simulation stuff:"
   PRINT " D0 = "; D0
   PRINT " betay = "; BETAY
   PRINT " bextar = "; BETAR
   PRINT " r0 = ";
   PRINT USING "####.#### " ; R0
   PRINT " dvt = "; VDT
   PRINT " mmax = "; MTMAX
   PRINT " tmax = ";
   PRINT USING "####.#### " ; TMAX
   PRINT " iymax = "; IYMAX
   PRINT " irmax = "; IRMAX
   PRINT " ir0 = "; IR0
END SUB

'-------------------------Subroutine PROFILE-------------------------------
SUB PROFILE STATIC
   PRINT
   IR = 1
   PRINT " y b(y,1) b(y,iro) b(y,irmx)"
   FOR IY = 1 TO IYMT - 1
PRINT USING "#.########.nn "; YMID(IY), BI2(IY, 1), BI2(IY, IR0), BI2(IY, IRMAX)
NEXT IY
CALL WAITFORME
PRINT : PRINT
PRINT "  ir   f(ir)   area(ir)  f(ir)*area(ir)"
AREASUM = 0: F0SUM = 0
FOR IR = 1 TO IR0
  F0SUM = F0SUM + F0(IR) * AREA(IR)
NEXT IR
FOR IR = 1 TO IR0
  AREASUM = AREASUM + AREA(IR)
  PRINT USING "#.########.nn "; IR, F0(IR), AREA(IR), F0(IR) * AREA(IR) / F0SUM
NEXT IR
PRINT "areasum = "; AREASUM
PRINT : PRINT
END SUB

'-----------------------------Subroutine WAITFORME-----------------------------

SUB WAITFORME STATIC
PRINT
PRINT "Hit Q to quit; any other key to continue."
WS$ = INPUT$(1)
IF WS$ = "Q" OR WS$ = "q" THEN END
END SUB
DEFDLB A-Z

DECLARE SUB xweight (flS(), pp#, i#, j#, imax#, num%, w#, chalf#, tomes)
DECLARE SUB adjcc (c#, i#, num%, petrip)
DECLARE SUB pfit (flS(), px#, py#, j#, jh#, a#, b#, c#, rsq#)
DECLARE SUB pwfit (flS(), wmd%, px#, py#, w#, j#, jh#, a#, b#, c#, rsq#)
DECLARE SUB fpa (flS(), pp#, c#, i#, num%, ntran%)
DECLARE SUB plot (flS(), pp#, clr%, lx#, ly#, pln%, phn%)
DECLARE SUB weight (flS(), pp#, c#, i#, imax#, num%, w#, chalf#)
DECLARE SUB wls (flS(), pp#, wmd%, w#, lx#, ly#, j#, jh#, m#, c#, rsq#)
DECLARE SUB noise (i#, num%, vr)
DECLARE SUB potpair (c#, i#, num%, switch%)
DECLARE SUB CROUT (NR%, MC%, NCC%, ZMCH%)
COMMON SHARED n, t, f, rg, pi#
GOSUB 1
GOTO 10

1 REM INITIALIZE

n = 1
f = 96484.6
rg = 8.31441
pi# = 3.1415926536#
size% = 1500
DIM flS(2 * size%), pp#, i#(2 * size%), c#(2 * size%), Eo#(2 * size%), sm#(2 * size%), i#(size%), m#(size%), lx#(size%), ly#(size%), h#(2 * size%), px#(size%), py#(size%), smp#(2 * size%), w#(size%), wt#(size%), wtm#(size%)

DIM SHARED XMATI(10, 20)
wm0d% = 0
RETURN

10 REM SCREEN MENU
CLS : SCREEN 0
PRINT : PRINT : PRINT " S.S. MICRODISC ANALYSIS"
PRINT " --------------------------": PRINT
PRINT " 1, READ RAW FILE"
PRINT " 2, READ SCALED DATA WITH EXPT. PARAMETERS"
PRINT " 3, ADJUST EXPT. PARAMETERS"
PRINT " 4, PERFORM ANALYSIS"
PRINT " 5, SAVE SCALED DATA WITH PRESENT EXPT. PARAMETERS"
PRINT " 6, APPLY IR CORRECTION"
PRINT " 7, APPLY SMOOTHING"
PRINT " 8, APPLY CHARGING CURRENT CORRECTION"
PRINT " 9, READ SIMULATED DATA (mV, mA)"
PRINT " 10, ADD RANDOM NOISE"
PRINT " 11, SAVE OUTPUT DATA"
PRINT " 12, EXIT"
PRINT : PRINT : PRINT : PRINT : PRINT : INPUT " INPUT OPTION (1-12):"; qq
main = 1
IF qq < 1 OR qq > 12 THEN 10
ON qq GOTO 1000, 2000, 3999, 4000, 5000, 6000, 7000, 8000, 9000, 10000, 11000, 12000
GOTO 10

1000 REM READ RAW DATA FILE
CLS
INPUT "current file"; c$
INPUT "potential file"; p$
OPEN c$ FOR INPUT AS #1
j% = 0
DO WHILE NOT EOF(1)
j% = j% + 1
INPUT #1, i$(j%)
LOOP
CLOSE #1
OPEN p$ FOR INPUT AS #1
j% = 0
DO WHILE NOT EOF(1)
j% = j% + 1
INPUT #1, e$(j%)
lx$(j%) = j%
LOOP
CLOSE #1
num% = j% - 2
CALL plot(fl$(0), pp(0), 1, lx$(0), e$(0), 1, num%)
CALL plot(fl$(0), pp(0), 1, lx$(0), i$(0), 1, num%)
CALL plot(fl$(0), pp(0), 1, e$(0), i$(0), 1, num%)
SCREEN 0
INPUT "DO YOU WISH TO INVERT POTENTIAL SCALE"; a$
IF a$ = "Y" OR a$ = "y" THEN FOR j% = 1 TO num%; e$(j%) = -e$(j%): NEXT j%
INPUT "DO YOU WISH TO INVERT CURRENT SCALE"; a$
IF a$ = "Y" OR a$ = "y" THEN FOR j% = 1 TO num%; i$(j%) = -i$(j%): NEXT j%
INPUT "INITIAL POTENTIAL (V)" ; e$
INPUT "SWITCHING POTENTIAL (V)" ; e$
INPUT "INPUT POTENTIOSTAT SCALE (mA/V)" ; scp
INPUT "INPUT C.R.O. SCALE (mV/DIV)" ; scc
scale = scp * scc / 1000000
emax# = 999999
emin# = 999999
FOR j% = 1 TO num%
IF e$(j%) > emax# THEN emax# = e$(j%)
IF e$(j%) < emin# THEN emin# = e$(j%)
NEXT j%
sum = 0: shigh = 0
FOR j% = 1 TO num%
IF e$(j%) = emax# THEN shigh = shigh + j%; sum = sum + 1
NEXT j%
switch% = INT(shigh / sum)
j% = switch%
DO
j% = j% - 1
LOOP UNTIL j% = 1 OR e$(j%) = emin#
ptb% = j%
num% = switch% - ptb% + 1

delt = emax# - cmin#

FOR j% = ptb% TO switch%

IF j% <= switch% THEN c#(j%) = (j% - ptb%) * delt / (switch% - ptb%) + emin#

ELSE c#(j%) = ((eh# - c#(j%)) * (c#(j%) - cmin#)) / delt + c#

END IF

i#(j%) = i#(j%) * scale * .0346

NEXT j%

CALL plot(fsl(), pp(), 1, e#(), i#(), 1, num%)

PRINT "ptb%, num%, switch%"

j% = 1: jh% = num% \ 6

FOR j% = j% TO jh%

lx%(j%) = c#(j%)

ly%(j%) = i%(j%)

NEXT j%

CALL wls(fsl(), pp(), 2, w#(), lx#(), ly#(), jl%, jh%, m#, c#, rsq#)

FOR j% = 1 TO num%

i%(j%) = i%(j%) - e%(j%) * m% - c%

NEXT j%

CALL plot(fsl(), pp(), 1, e#(), i#(), 1, num%)

GOTO 10

2000 REM READ SCALED DATA FILE

CLEAR

GOSUB 1

INPUT "Does file have exp. parameters"; a$

INPUT "filename"; o$

INPUT "Is data cyclic"; c$

OPEN o$ FOR INPUT AS #1

IF a$ = "Y" OR a$ = "y" THEN 2100

DO WHILE NOT EOF(1)

i% = i% + 1

INPUT #1, e%(i%), i%(i%)

LOOP

num% = i%

GOTO 2200

2100 INPUT #1, title$

INPUT #1, num%, t, n, sr, d, rad, ei#, eh#, cb

switch% = num% \ 2

FOR j% = 1 TO num%

INPUT #1, e%(j%), i%(j%)

IF e%(j%) = eh# THEN switch% = j%

NEXT j%

2200 CLOSE #1

IF e%(1) > e%(num% / 2) THEN 2300

CLS

PRINT "Warning - Data is for an oxidation and calculation will fail!"

INPUT "Convert to a reduction"; a$

IF a$ = "y" OR a$ = "Y" THEN FOR j% = 1 TO num%; e%(j%) = -e%(j%); NEXT j%

2300 IF c$ = "N" OR c$ = "n" THEN 2400

CALL plot(fsl(), pp(), 2, e#(), i#(), 1, num%)

IF c$ = "N" OR c$ = "n" THEN 2400

INPUT "Use only (F)orward cycle or (A)verage branches"; a$

IF a$ = "f" OR a$ = "F" THEN num% = num% \ 2: GOTO 10

CALL potpair(e#(), i#(), num%, switch%)

FOR j% = 1 TO switch%
i#(j%) = (i#(j%) + i#(num% - j% + 1)) / 2
NEXT j%
num% = switch%
2400 CALL plot(fl$, pp(), 2, c#, i#, 1, num%)
DO LOOP UNTIL INKEY$ <> "" GOTO 10

3999 REM ADJUST EXPT. PARAMETERS
CLS : SCREEN 0
PRINT : PRINT : PRINT : PRINT " CURRENT EXPT. PARAMETERS" : PRINT
PRINT " 1. TEMPERATURE (K) " ; t
PRINT " 2. DIFFUSION CO-EFFICIENT (CM^2/SEC) "; d * 10000
PRINT " 3. SCAN RATE (V/SEC) "; sr
PRINT " 4. RADIUS OF DISK (CM) "; rad * 100
PRINT " 5. NUMBER OF ELECTRONS " ; n
PRINT " 6. CONCENTRATION (MOLAR) " ; cb / 1000
PRINT " 7. EXIT"
PRINT : PRINT : PRINT : INPUT " INPUT SELECTION" ; qq
SELECT CASE qq
CASE IS = 1
INPUT "NEW TEMPERATURE (K)" ; t
CASE IS = 2
INPUT "NEW DIFFUSION COEFFICIENT (CM^2/SEC)" ; d
   d = d / 10000
CASE IS = 3
INPUT "NEW SCAN RATE (V/S)" ; sr
CASE IS = 4
INPUT "NEW RADIUS (CM)" ; rad
   rad = rad / 100
CASE IS = 5
INPUT "NEW NUMBER OF ELECTRONS" ; n
CASE IS = 6
INPUT "NEW CONCENTRATION (MOLAR)" ; cb
   cb = cb * 1000
CASE IS = 7
GOTO 10
CASE ELSE
END SELECT
GOTO 3999

4000 REM NORMALIZED STEADY STATE ANALYSIS
imax# = 1
INPUT "Is this a simulation (Y/N)?" ; a$
IF a$ = "y" OR a$ = "Y" THEN INPUT "Plateau Current" ; imax#: smp#(29) = imax#:
   GOTO 4010
   j1% = 1 ; jh% = num% \ 4
FOR j% = j1% TO jh%
   lx#(j%) = j%
   ly#(j%) = i#(j%)
NEXT j%
CALL wls(fl$, pp(), 2, w#, lx#, ly#, j1%, jh%, m#, c#, rsq#)
bckslp = m#
FOR j% = 1 TO num%
i#(j%) = i#(j%) - j% * bckslp
NEXT j%
CALL plot(fl$, pp(), 2, e#, i#, 1, num%)
DO
LOOP UNTIL INKEY$ <> ""
jl% = num% - num% \ 20; jh% = num%
sum# = 0
FOR j% = jl% TO jh%
sum# = sum# + i#(j%)
NEXT j%
imax# = sum# / (jh% - jl% + 1)
4010 eoneq = 0: etwoq = 0: ethrq = 0
sumone = 0: summwo = 0: sumthr = 0
FOR j% = 1 TO num%
fl$(j%) = ""
q# = i#(j%) / imax#
IF q# > .23 AND q# < .27 THEN eoneq = eoneq + e#(j%): sumone = sumone + 1
IF q# > .48 AND q# < .52 THEN etwoq = etwoq + e#(j%): summwo = summwo + 1: je%
    = j%
IF q# > .73 AND q# < .77 THEN ethrq = ethrq + e#(j%): sumthr = sumthr + 1
NEXT j%
tomes = eoneq / sumone - etwoq / summwo
ehalf = etwoq / summwo
CALL plot(fl$, pp(), 2, e#, i#, 1, num%)
PRINT "E1/2=", ehalf, "Tomes="; tomes
smp#(27) = ehalf
smp#(28) = tomes
PRINT : PRINT : PRINT
PRINT title$
PRINT imax#
PRINT "Sph factor = "; SQR(d * rg * t / (n * f * sr)) / rad
smp#(1) = SQR(d * rg * t / (n * f * sr)) / rad
INPUT "Continue with analysis"; a$
IF a$ <> "y" AND a$ <> "Y" THEN 10
INPUT "(Q)uasi-reversible or (I)rreversible"; a$
INPUT "Type of analysis for Eo (W)eighted or (I)terative"; e$
IF e$ = "i" OR e$ = "I" THEN 4030
CALL xweight(fl$, pp(), e#, i#, imax#, num%, w#, ehalf, tomes)
FOR j% = 1 TO num%
q# = i#(j%) / imax#
IF q# < 0 OR q# > 1 THEN fl$(j%) = "n": GOTO 4120
ly#(j%) = 1 / q#
lx#(j%) = EXP(n * f * (e#(j%) - ehalf#) / (rg * t))
4120 NEXT j%
CALL wls(fl$, pp(), 1, w#, lx#, ly#, 1, num%, m#, c#, rsq#)
Eo = LOG(c# / m#) * rg * t / (n * f) + ehalf#
PRINT "Eo="; Eo
GOTO 4040
4030 CALL weight(fl$, pp(), e#, i#, imax#, num%, w#, ehalf#)
4031 FOR j% = je% - 10 TO je% + 10
q# = i#(j%) / imax#
IF q# < .005 OR q# > .995 THEN fl$(j%) = "n": GOTO 4020
ly#(j%) = 1 / q#
lx#(j%) = EXP(n * f * e#(j%) / (rg * t))
4020 NEXT j%
PRINT je%
CALL wls(fl$, pp$, -1, w#$, lx#$, ly#$, je% - 10, je% + 10, m#, c#, rsq#)
Eo = LOG(c# / m#) * rg * t / (n * f)
PRINT "Eo=": Eo
IF LEO = Eo THEN 4040
LEo = Eo
FOR j% = 1 TO num%
IF INT(e#(j%) * 1000) / 1000 = INT(Eo * 1000) / 1000 THEN 4035
NEXT j%
4035 IF j% <= je% THEN je% = j% ELSE je% = j% - 1
GOTO 4031
4040 IF aS = "T" OR a$ = "i" THEN 4300
INPUT "Eo": Eo
sm$p(2) = Eo
FOR j% = 1 TO num%
fl$(j%) = ""
qu# = i#(j%) / imax#(i#(j%) - j% * bckslp) / imax#
IF q# < 0 OR q# > 1 THEN fl$(j%) = "n": GOTO 4000
theta# = 1 + EXP(n * f * (e#(j%) - Eo) / (rg * t))
lhs# = 1 / (q# * theta#)
a# = 6 * lhs# * 6
b# = 3 * pi# * lhs# - 2 - 3 * pi#
c# = -2
dct# = b# ^ 2 - 4 * a# * c#
IF dct# < 0 THEN 4100
h1# = (-b# + SQR(dct#)) / (2 * a#)
h2# = (-b# - SQR(dct#)) / (2 * a#)
w# = (1 - q#) / q# - lhs#
Z# = lhs# + 1
rhs# = 2 * Ko / (3 * pi# * q# * h1#)
IF h1# <= 0 THEN fl$(j%) = "n": GOTO 4010
ly#(j%) = LOG(2 * theta# / (3 * pi# * h1#))
lx#(j%) = e#(j%) - Eo
IF j% > 1 THEN PRINT e#(j%), (ly#(j%) - ly(j% - 1)) * rg * t / (n * f * (lx#(j%) - x#(j% - 1)))
4100 NEXT j%
CALL wls(fl$, pp$, 0, w#$, lx#$, ly#$, 1, num%, m#, c#, rsq#)
PRINT "Unweighted"
PRINT "ko (m/s)= ", EXP(-c#) * 4 * d / (pi# * rad)
PRINT "alpha =": m# * rg * t / (n * f)
PRINT "Ko = "; EXP(-c#)
sm$p(3) = m#
sm$p(4) = c#
sm$p(5) = rsq#
sm$p(6) = EXP(-c#) * 4 * d / (pi# * rad)
sm$p(7) = m# * rg * t / (n * f)
sm$p(30) = EXP(-c#)
DO: LOOP UNTIL INKEY$ <> ""
CALL weight(fl$, pp$, e#(), i#(), imax#, num%, w#$(), ehalf#)
CALL wls(fl$, pp$, 1, w#$, lx#$, ly#$, 1, num%, m#, c#, rsq#)
PRINT "Weighted"
PRINT "ko (m/s)= ", EXP(-c#) * 4 * d / (pi# * rad)
PRINT "alpha =": m# * rg * t / (n * f)
PRINT "Ko = "; EXP(-c#)
sm$p(8) = m#
sm$p(9) = c#
smp#(10) = rsq#
smp#(11) = EXP(-c#) * 4 * d / (pi# * rad)
smp#(12) = m# * rg * t / (n * f)
smp#(31) = EXP(-c#)

DO: LOOP UNTIL INKEY$ <> ""
CALL pfit(fl$(), 1x$, ly$, 1, num%, a#, b#, c#, rsq#)
PRINT "Unweighted"
PRINT "ko (m/s) = "; EXP(-a#) * 4 * d / (pi# * rad)
PRINT "alpha = "; b# * rg * t / (n * f)
PRINT "dalpha/dE = "; c# * rg * t / (n * f)
PRINT "Ko = "; EXP(-a#)
smp#(13) = c#
smp#(14) = b#
smp#(15) = a#
smp#(16) = rsq#
smp#(17) = EXP(-a#) * 4 * d / (pi# * rad)
smp#(18) = b# * rg * t / (n * f)
smp#(19) = c# * rg * t / (n * f)
smp#(32) = EXP(-a#)

DO: LOOP UNTIL INKEY$ <> ""
CALL weight(fl$(), pp(), c#(), i#(), imax#, num%, w#(), chalf#)
CALL pwt(fl$(), 1, lx$, ly$, w#(), 1, num%, aff, bff, cff#, rsq#)
PRINT "weighted"
PRINT "ko (m/s) = "; EXP(-a#) * 4 * d / (pi# * rad)
PRINT "alpha = "; b# * rg * t / (n * f)
PRINT "dalpha/dE = "; c# * rg * t / (n * f)
PRINT "Ko = "; EXP(-a#)
smp#(20) = c#
smp#(21) = b#
smp#(22) = a#
smp#(23) = rsq#
smp#(24) = EXP(-a#) * 4 * d / (pi# * rad)
smp#(25) = b# * rg * t / (n * f)
smp#(26) = c# * rg * t / (n * f)
smp#(33) = EXP(-a#)

DO: LOOP UNTIL INKEY$ <> ""
FOR j% = 1 TO num%; fl$() = ""; NEXT j%
GOTO 4500
4300 INPUT "Eo"; Eo
FOR j% = 1 TO num%
fl$() = ""
q# = i#(j%) / imax#
IF q# < 0 OR q# > 1 THEN fl$() = "n"; GOTO 4400
lhs# = 1 / q# - 1
a# = 4 * lhs#
b# = 3 * pi# ^ 2 * lhs# - 2 * pi#
c# = -3 * pi# ^ 2
det# = b# ^ 2 - 4 * a# * c#
IF det# < 0 THEN 4400
h1# = (-b# + SQR(det#)) / (2 * a#)
h2# = (-b# - SQR(det#)) / (2 * a#)
lx$(j%) = c#(j%) - Eo
ly$(j%) = LOG(h1#)
4400 NEXT j%
CALL wls(fl$(), pp(), 2, w#, lx$, ly$, 1, num%, m#, c#, rsq#)
PRINT "Unweighted"
PRINT "ko (m/s)= "; EXP(c#) * 4 * d / (pi# * rad)
PRINT "alpha ="; -m# * rg * t / (n * f)
PRINT "Ko = "; EXP(c#)
smp#(3) = m#
smp#(4) = c#
smp#(5) = rsq#
smp#(6) = EXP(c#) * 4 * d / (pi# * rad)
smp#(7) = -m# * rg * t / (n * f)
smp#(30) = EXP(c#)
DO: LOOP UNTIL INKEY$ <> ""
CALL weight(fl$, pp(), e#, i#, imax#, num%, w#, chalf#)
CALL wsls(fl$, pp(), 1, w#, lx#, ly#, 1, num%, m#, c#, rsq#)
PRINT "Weighted"
PRINT "ko (m/s)= "; EXP(c#) * 4 * d / (pi# * rad)
PRINT "alpha ="; -m# * rg * t / (n * f)
PRINT "Ko = "; EXP(c#)
smp#(8) = m#
smp#(9) = c#
smp#(10) = rsq#
smp#(11) = EXP(c#) * 4 * d / (pi# * rad)
smp#(12) = -m# * rg * t / (n * f)
smp#(31) = EXP(c#)
DO: LOOP UNTIL INKEY$ <> ""
CALL pfitt(fl$, lx#, ly#, 1, num%, a#, b#, c#, rsq#)
PRINT "Unweighted"
PRINT "ko (m/s)= "; EXP(a#) * 4 * d / (pi# * rad)
PRINT "alpha ="; -b# * rg * t / (n * f)
PRINT "alpha/dE ="; -c# * rg * t / (n * f)
PRINT "Ko = "; EXP(a#)
smp#(13) = c#
smp#(14) = b#
smp#(15) = a#
smp#(16) = rsq#
smp#(17) = EXP(a#) * 4 * d / (pi# * rad)
smp#(18) = -b# * rg * t / (n * f)
smp#(19) = -c# * rg * t / (n * f)
smp#(32) = EXP(a#)
DO: LOOP UNTIL INKEY$ <> ""
CALL weight(fl$, pp(), e#, i#, imax#, num%, w#, chalf#)
CALL pfwfit(fl$, 1, lx#, ly#, w#, 1, num%, a#, b#, c#, rsq#)
PRINT "Weighted"
PRINT "ko (m/s)= "; EXP(a#) * 4 * d / (pi# * rad)
PRINT "alpha ="; -b# * rg * t / (n * f)
PRINT "alpha/dE ="; -c# * rg * t / (n * f)
PRINT "Ko = "; EXP(a#)
smp#(20) = c#
smp#(21) = b#
smp#(22) = a#
smp#(23) = rsq#
smp#(24) = EXP(a#) * 4 * d / (pi# * rad)
smp#(25) = -b# * rg * t / (n * f)
smp#(26) = -c# * rg * t / (n * f)
smp#(33) = EXP(a#)
DO: LOOP UNTIL INKEY$ <> ""
FOR j% = 1 TO num%: fl$=j% = "": NEXT j%
4500 INPUT "Print results to printer"; b$
IF b$ <> "y" AND b$ <> "Y" THEN 10
LPRINT title$
LPRINT num%, t, n, sr, d, rad, ei#, ch#, cb
LPRINT "Sphericity factor =": smp#(1)
LPRINT "Eo =": smp#(2), "Current maxima =": smp#(29)
LPRINT "Eb/2 =": smp#(27), "Tomes =": smp#(28)
IF a$ = "q" OR a$ = "Q" THEN LPRINT "Quasi-reversible"
IF a$ = "r" OR a$ = "R" THEN LPRINT "Irreversible"
LPRINT "Unweighted linear"
LPRINT "m =": smp#(3), "a =": smp#(4), "rsq =": smp#(5)
LPRINT "ko =": smp#(6), "alpha =": smp#(7), "Ko =": smp#(30)
LPRINT "Weighted linear"
LPRINT "m =": smp#(8), "a =": smp#(9), "rsq =": smp#(10)
LPRINT "ko =": smp#(11), "alpha =": smp#(12), "Ko =": smp#(31)
LPRINT "Unweighted quadratic"
LPRINT "c(X^2) =": smp#(13), "b(X) =": smp#(14), "a =": smp#(15), "rsq =": smp#(16)
LPRINT "ko =": smp#(17), "alpha =": smp#(18)
LPRINT "dalpha/dE": smp#(19), "Ko =": smp#(32)
LPRINT "Weighted quadratic"
LPRINT "c(X^2) =": smp#(20), "b(X) =": smp#(21), "a =": smp#(22), "rsq =": smp#(23)
LPRINT "ko =": smp#(24), "alpha =": smp#(25)
LPRINT "dalpha/dE": smp#(26), "Ko =": smp#(33)
GOTO 10

5000 REM SAVE SCALED DATA FILE
CLS
INPUT "filename": o$
INPUT "title": title$
OPEN o$ FOR OUTPUT AS #1
PRINT #1, title$
PRINT #1, num%, t, n, sr, d, rad, ei#, ch#, cb
FOR j% = 1 TO num%
PRINT #1, e#(j%), i#(j%)
NEXT j%
CLOSE #1
GOTO 10

6000 REM IR CORRECTION
CLS : PRINT : PRINT : PRINT : PRINT : PRINT
INPUT " INPUT UNCOMPENSATED RESISTANCE (OHMS)": ru
num%= .95 * num%
ci# = e#(1)
ch# = e#(1)
FOR j% = 1 TO num%
Eo#(j%) = e#(j%) + i#(j%) * ru
IF Eo#(j%) > ci# THEN ci# = Eo#(j%)
IF Eo#(j%) < ch# THEN ch# = Eo#(j%)
NEXT j%
inc# = (ei# - ch#) * 2 / num%
j1% = 1
FOR i% = 1 TO num% \ 2
e# = ei# - i% * inc#
e#(i%) = e#
FOR j% = j1% TO num% \ 2
IF e# < Eo#(j%) AND e# > Eo#(j% + 1) THEN i#(j%) = i#(j%) + (i#(j% + 1) - i#(j%)) * 
(e# - Eo#(j%)) / (Eo#(j% + 1) - Eo#(j%)); j1% = j%: j% = num% \ 2
NEXT j%
NEXT i%
j1% = num% \ 2 + 1
FOR i% = nnum% \ 2 TO nnum%
e# = e# + (i% - nnum% \ 2) * inc#
e#(i%) = e
NEXT j%
NEXT i%
num% = nnum%
CALL plot(fi$,0, pp(), 1, e#, i#, 1, nnum%)
GOTO 10

7000 REM SMOOTHING
CLS : SCREEN 0
PRINT "CHOOSE MODE OF SMOOTHING"
PRINT "1, 3-POINT TRIANGULAR WINDOW SMOOTHING"
PRINT "2, FOURIER SMOOTHING"
PRINT "3, 9-POINT LEAST SQUARES WINDOW SMOOTHING"
PRINT "4, EXIT"
PRINT : INPUT "MODE OF SMOOTHING": i%
FOR j% = 1 TO num%
Eo#(j%) = i#(j%) 
NEXT j%
ON i% GOTO 7010, 7020, 7030, 7040
7010 CALL plot(fl$,0, pp(), 2, e#, i#, 1, num%)
FOR j% = 2 TO num% - 1
i#(j%) = Eo#(j%) / 2 + (Eo#(j% - 1) + Eo#(j% + 1)) / 4
NEXT j%
CALL plot(fl$,0, pp(), 0, e#, i#, 1, num%) 
GOTO 7040
7020 INPUT "NUMBER OF TRANSFORMATIONS": ntran%
CALL plot(fl$,0, pp(), 2, e#, i#, 1, num%)
CALL fpa(fl$,0, pp(), e#, i#, num%, ntran%)
CALL plot(fl$,0, pp(), 1, e#, i#, 1, num%)
GOTO 7040
7030 CALL plot(fl$,0, pp(), 2, e#, i#, 1, num%)
i#(1) = (Eo#(1) * 59 + Eo#(2) * 54 + Eo#(3) * 39 + Eo#(4) * 14 + Eo#(5) * -21) / 145
i#(2) = (Eo#(2) * 59 + (Eo#(1) + Eo#(3)) * 54 + Eo#(4) * 39 + Eo#(5) * 14 + Eo#(6) * -21) / 199
i#(3) = (Eo#(3) * 59 + (Eo#(2) + Eo#(4)) * 54 + (Eo#(1) + Eo#(5)) * 39 + Eo#(6) * 14 + Eo#(7) * -21) / 238
i#(4) = (Eo#(4) * 59 + (Eo#(3) + Eo#(5)) * 54 + (Eo#(2) + Eo#(6)) * 39 + (Eo#(1) + Eo#(7)) * 14 + Eo#(8) * -21) / 252
FOR j% = 5 TO num% - 4
i#(j%) = Eo#(j%) * 59 + (Eo#(j% - 1) + Eo#(j% + 1)) * 54 + (Eo#(j% - 2) + Eo#(j% + 2)) * 39 + (Eo#(j% - 3) + Eo#(j% + 3)) * 14 + (Eo#(j% - 4) + Eo#(j% + 4)) * -21
i#(j%) = i#(j%) / 231
NEXT j%
i#(num% - 3) = (Eo#(num% - 3) * 59 + (Eo#(num% - 4) + Eo#(num% - 2)) * 54 +
(Eo#(num% - 5) + Eo#(num% - 1)) * 39 + (Eo#(num% - 6) + Eo#(num%)) * 14 + Eo#(num% - 7) * -21) / 252
i#(num% - 2) = (Eo#(num% - 2) * 59 + (Eo#(num% - 3) + Eo#(num% - 1)) * 54 + Eo#(num% - 4) + Eo#(num%)) * 39 + Eo#(num% - 5) * 14 + Eo#(num% - 6) * -21) / 238
i#(num% - 1) = (Eo#(num% - 1) * 59 + (Eo#(num% - 2) + Eo#(num%)) * 54 + Eo#(num% - 3) * 39 + Eo#(num% - 4) * 14 + Eo#(num% - 5) * -21) / 199
i#(num%) = (Eo#(num%) * 59 + Eo#(num% - 1) * 54 + Eo#(num% - 2) * 39 + Eo#(num% - 3) * 14 + Eo#(num% - 4) * -21) / 145
CALL plot(f1$, pp(), 0, e#, i#, 1, num%)
7040 GOTO 10

8000 REM ADJUST CHARGING CURRENT
INPUT "CHARGING CURRENT CORRECTION AS A % OF Ip"; perip
CALL adjcc(e#, i#, num%, perip)
CALL plot(f1$, pp(), 1, e#, i#, 1, num%)
GOTO 10

9000 REM READ SIMULATED DATA (mV, mA)
CLEAR
GOSUB 1
CLS
INPUT "filename"; o$
OPEN o$ FOR INPUT AS #1
INPUT #1, title$
INPUT #1, num%
INPUT #1, t, n, sr, d
INPUT #1, ssa, e#, eh#, cb
num% = num% - 1
d = d / 10000
ssa = ssa / 10000
cb = cb * 1000
FOR j% = 0 TO num%
INPUT #1, e#(j%), i#(j%)
e#(j%) = -e#(j%) / 1000
i#(j%) = i#(j%) / 1000
IF i#(j%) > imax# THEN imax# = i#(j%); maxj% = j%
IF i#(j%) < imin# THEN imin# = i#(j%); minj% = j%
NEXT j%
CLOSE #1
CALL plot(f1$, pp(), 2, e#, i#, 1, num%)
cif = (e#(1) + e#(num%)) / 2
rad# = (ssa / (4 * pi#)) ^ (1 / 2)
isp = .7516 * n * f * ssa * d * cb / rad#
ipl = .4463 * n * f * ssa * d ^ (1 / 2) * sr ^ (1 / 2) * cb * (n * f / (rg * t)) ^ (1 / 2) + isp
sphere = isp * 100 / ipl
PRINT title$; " SPHERICITY="; sphere; "%"; " Epc="; e#(maxj%); " Epa="; e#(minj%)
DO
LOOP UNTIL INKEYS <> ""
GOTO 10

10000 REM ADD RANDOM NOISE
CLS
INPUT "VARIANCE AS % OF Ip"; vr
CALL noise(i(#), num%, vr)
CALL plot(i$(#), pp(), 1, e#(), i#(), 1, num%)
PRINT vr
GOTO 10

11000 REM SAVE OUTPUT DATA
CLS
jlo% = 1
jho% = num% \ 2
INPUT "FILENAME OF OUTPUT FILE"; o$
INPUT "OUTPUT DENSITY"; dd%
PRINT "jl="; jl%; "; jh="; jh%; "; total number="; num% \ 2
INPUT "LOWER DATA LIMIT"; jlo%
INPUT "UPPER DATA LIMIT"; jho%
OPEN o$ FOR OUTPUT AS #1
PRINT #1, title$
PRINT #1, num%, t, n, sr, d, ssa, ei#, eh#, cb
PRINT #1, "E(V)-> i(A)-> mu*->"
PRINT #1, "E(V)<- i(A)<- mu*<-"
PRINT #1, "m* w(m*)"
PRINT #1, "i* w(i*)"
FOR j% = jlo% TO jho% STEP dd%
PRINT #1, ei%(j%), i%(j%), sm%(j%)
PRINT #1, ei%(num% - j% + 1), i%(num% - j% + 1), sm%(num% - j% + 1)
PRINT #1, j%, ms%(j%), w%(j%)
PRINT #1, j%, i%(j%), w%(j%)
NEXT j%
CLOSE #1
GOTO 10

12000 END

SUB addc(e#(), i#(), num%, perip)
FOR j% = 1 TO num% \ 2
IF i%(j%) > imax THEN imax = i%(j%)
NEXT j%
FOR j% = num% \ 2 TO num%
    i%(j%) = i%(j%) + perip * imax / 100
NEXT j%
END SUB

DEFINT I-J, M
-------------------Subroutine CROUT(NR%,MC%,NCC%,ZMCH%)-------------------
2960 SUB CROUT(NR%, MC%, NCC%, ZMCH%) STATIC
2970 DIM LP(10)
2980 IF NR% > MC% THEN 3200
2990 DT = 1; IERR = 0; QNRS% = NR% - 1; FOR QI% = 1 TO NR%: LP(QI%) = QI%; NEXT QI%; QI% IF NCC% < 0 THEN 3200
3000 IF NCC% <> 0 THEN 3200
3010 QNTC% = NR% + NR%; Q1% = 1: FOR QK% = NR% + 1 TO QNTC%: FOR QKX% = 1 TO NR%; XMAT1(QKX%, QK%) = 0!: NEXT QKX%;
    XMAT1(Q1%, QK%) = 1: QJ% = Q1% + 1: NEXT QK%: GOTO 3030
3020 QNTC% = NR% + NCC%
3030 IF QNTC% <= NR% THEN 3200
3040 FOR QI% = 1 TO NR%: QTTEMP = 0!: FOR QI% = QI% TO QNTC%: IF QI% = 1
THEN 3060
3050 QKX% = 1: FOR QK% = 1 TO QI% - 1: XMAT1(QI%, QJ%) = XMAT1(QI%, QJ%) - XMAT1(QK%, QKX%) * XMAT1(QK%, QI%): QKX% = QKX% + 1: NEXT QK%
3060 IF QI% > NR% THEN 3090
3070 IF ABS(XMAT1(QI%, QJ%)) <= QTEMP THEN 3090
3080 QTEMP = ABS(XMAT1(QI%, QJ%)): QNX% = QI%
3090 NEXT QI%: IF QI% = NR% THEN 3120
3100 IF QNX% = QI% THEN 3120
3110 QTEMP% = LP(QNX%): LP(QNX%) = LP(QI%): LP(QI%) = QTEMP%:
QLPIS% = QNX%: FOR QK% = 1 TO NR%: QTEMP = XMAT1(QK%, QI%): XMAT1(QK%, QI%) = XMAT1(QK%, QLPIS%): XMAT1(QK%, QLPIS%) = QTEMP: NEXT QK%: DT = -DT
3120 DT = DT * XMAT1(QI%, QI%): IF ZMCH% - ABS(XMAT1(QI%, QI%)) > 0 THEN 3210
3130 FOR QI% = QI% + 1 TO QNTC%: XMAT1(QI%, QJ%) = XMAT1(QI%, QJ%) / XMAT1(QI%, QI%): NEXT QI%: IF QI% = 1 THEN 3160
3140 IF QI% = NR% THEN 3160
3150 FOR QM% = QI% + 1 TO NR%: QKX% = 1: FOR QKY% = 1 TO QI% - 1:
XMAT1(QM%, QI%) = XMAT1(QM%, QI%) - XMAT1(QM%, QKX%): XMAT1(QKY%, QI%) = QKX% + 1: NEXT QKY%: NEXT QM%
3160 NEXT QI%: FOR QI% = 1 TO NR% - 1: QREV% = NR% - QI%: QKRS% = NR% + 1 - QI%: FOR QRCT% = NR% + 1 TO QNTC%: QKCS% = QREV% + 1: FOR QK% = QKRS% TO NR%: XMAT1(QREV%, QRCT%) = XMAT1(QREV%, QRCT%) - XMAT1(QKCS%, QRCT%) * XMAT1(QREV%, QK%): QKCS% = QKCS% + 1: NEXT QK%: NEXT QRCT%: NEXT QI%: FOR QI% = 1 TO NR% - 1
3170 IF LP(QI%) = QI% THEN 3190
3180 QNX% = LP(QI%): LP(QI%) = LP(QNX%): LP(QNX%) = QNX%: QIXS% = QI%: QIXY% = QNX%: FOR QIX% = NR% + 1 TO QNTC%: QTEMP = XMAT1(QIXS%, QIX%): XMAT1(QIXS%, QIX%) = XMAT1(QIXY%, QIX%): XMAT1(QIXY%, QIX%) = QTEMP: NEXT QIX%: GO TO 3170
3190 NEXT QI%: GO TO 3220
3200 IERR = 2: DT = 999999999#: GO TO 3220
3210 IERR = 1: GO TO 3220
3220 END SUB

DEFDBL I, J, M
SUB fpa (f$, pp(), e#, i#, num%, ntran%)
DIM real#(300), imag#(300), 1x#(300), 1y#(300)
p# = 3.1415926536#
ntrano% = 1
bf# = (i#(num%) - i#(1)) / num%
g# = 0
FOR j% = 2 TO num%
i#(j%) = i#(j%) - i#(1) - bf# * (j% - 1)
g# = g# + i#(j%)
NEXT j%
real#(0) = g# / num%
7110 IF ntrano% <= ntrano% THEN 7120
FOR k% = ntrano% TO ntrano% - 1
sum# = 0
sumi# = 0
FOR j% = 2 TO num% - 1
S# = SIN(2 * pi# * (j% - 1) * k% / num%)
NEXT j%
c# = COS(2 * pi# * (j% - 1) * k% / num%)  
sumn# = sumn# + i#(j%) * c#  
sumi# = sumi# + i#(j%) * S#
NEXT j%
real#(k%) = sumn# / num%  
imag#(k%) = -sumi# / num%  
lx#(k%) = k%  
ly#(k%) = real#(k%) ^ 2 + imag#(k%) ^ 2
NEXT k%
CALL plot(0$, pp$, 1, lx#, ly$, ntran$, ntran - 1)  
IF ntran > ntran THEN ntran = ntran
7120 f1# = 0: f2# = 0
FOR k% = 1 TO ntran - 1  
f1# = f1# + real#(k%)  
f2# = f2# + k% ^ 2 + real#(k%)  
f0# = 1 - k% ^ 2 / (ntran * ntran)  
real#(k%) = f0# * real#(k%)  
imag#(k%) = f0# * imag#(k%)  
NEXT k%
i#(1) = i#(1) + real#(0) + 2 * (f1# - f2# / (ntran * ntran))
FOR j% = 2 TO num%  
sum# = 0  
FOR k% = 1 TO ntran - 1  
S# = SIN(2 * pi# * k% * (j% - 1) / num%)  
c# = COS(2 * pi# * k% * (j% - 1) / num%)  
sum# = sum# + real#(k%) * c# - imag#(k%) * S#
NEXT k%
i#(j%) = i#(1) + (j% - 1) * bf# + real#(0) + 2 * sum#
NEXT j%
END SUB

SUB noise (i#, num%, wr)
DIM ni%(300)
kint% = 100
FOR j% = 1 TO num% \2  
IF i#(j%) > imax THEN imax = i#(j%)  
NEXT j%
PRINT "method of noise"
PRINT " 1. Oldham noise"
PRINT " 2. Computer noise"
INPUT "choice": c%
ON c% GOTO 11110, 11120
11110 pi# = 3.1415926536#
k% = 0
mu = 0
bn# = 199017
S# = 2 * (wr * imax# / 100) ^ 2
j% = 2 * num%  
n# = 2 * num%  
11100 n# = 24298 * n# + 99991  
n# = 1 + n# - bn# * INT(n# / bn#)
ni% = 1 + INT(n# / bn# * kint%)  
ni%(ni%) = ni%(ni%) + 1  
j% = j% - 1  
IF j% \2 = j% / 2! THEN 11200
x# = (S# * LOG(bn# / n#)) ^ (1 / 2)
GOTO 11100
11200 x# = mu + x# * COS(2 * pi# * n# / bn#)
k% = k% + 1
i#(k%) = i#(k%) + x#
IF j% > 0 THEN 11100 ELSE 11300
11120 FOR j% = 1 TO num%
x# = (RND(1) - .5) * imax# * sqrt / 100
i#(j%) = i#(j%) + x#
NEXT j%
11300 FOR j% = 1 TO kint%
snsq# = snsq# + (ni%(j%) - 2 * num% / kint%) ^ 2 / (2 * num% / kint%)
NEXT j%
chisq# = snsq#
PRINT chisq#, kint%
DO
LOOP UNTIL INKEYS <> ""
END SUB

SUB pfit (fl$( ), px#( ), py#( ), jl%, jh%, a#, b#, c#, rsq#)
DIM pny#(1500), pp(4)
20000 FOR j% = jl% TO jh%
IF fl$(j%) = "n" THEN 20100
smx = smx + px#(j%) 
smu = smu + px#(j%) ^ 2
smy = smy + py#(j%) 
smysq = smysq + py#(j%) ^ 2
smxu = smxu + px#(j%) ^ 3
smusq = smusq + px#(j%) ^ 4
smxy = smxy + py#(j%) * px#(j%) 
smuy = smuy + py#(j%) * px#(j%) ^ 2
pnum% = pnum% + 1
20100 NEXT j%
A1 = smu - smx ^ 2 / pnum%
B1 = smxu - smx * smu / pnum%
B2 = smusq - smu ^ 2 / pnum%
A3 = smxy - smx * smy / pnum%
B3 = smuy - smu * smy / pnum%
A2 = B1
c = (A3 - A1 * b) / A2
a = (smy - b * smx - c * smu) / pnum%
sy = smysq - smy ^ 2 / pnum%
FOR j% = jl% TO jh%
IF fl$(j%) = "n" THEN 20010
pny#(j%) = a + b * px#(j%) + c * px#(j%) ^ 2
spny = spny + pny#(j%)
spnysq = spnysq + pny#(j%) ^ 2
20010 NEXT j%
syd = spnysq - spny ^ 2 / pnum%
rsq = syd / sy
CALL plot(fl$( ), pp( ), 1, px#( ), py#( ), jl%, jh%)
PRINT a, b, c, rsq
CALL plot(fl$( ), pp( ), 0, px#( ), pny#( ), jl%, jh%)
END SUB
SUB plot (fl$(i), pp(), clr%, lx#, ly#, pln%, phn%)
REM clr%= (0:nc,p) (1:x,p) (2:nc,pp) (3:nc,np)
IF clr% = 0 OR clr% = 3 THEN 999
CLS
IF fl$(pln%) = "n" THEN DO: pln% = pln% + 1: LOOP UNTIL fl$(pln%) <> "n"
pp(2) = lx#(pln%): pp(1) = lx#(pln%)
pp(4) = ly#(pln%): pp(3) = ly#(pln%)
FOR j% = pln% TO phn%
IF fl$(j%) = "n" THEN 30010
IF lx#(j%) >= pp(1) THEN pp(1) = lx#(j%)
IF lx#(j%) <= pp(2) THEN pp(2) = lx#(j%)
IF ly#(j%) >= pp(3) THEN pp(3) = ly#(j%)
IF ly#(j%) <= pp(4) THEN pp(4) = ly#(j%)
NEXT j%
30010 NEXT j%
999 SCREEN 2
IF pp(3) = pp(4) THEN pp(3) = pp(3) * 1.1
WINDOW (0, 0)-(pp(1) - pp(2), 2.2 * (pp(3) - pp(4)))
FOR j% = pln% TO phn%
IF fl$(j%) <> "n" THEN PSET (lx#(j%) - pp(2), 11 * (pp(3) - pp(4)) + ly#(j%) - pp(4))
NEXT j%
NEXT j% 
IF clr% = 1 OR clr% = 2 THEN PRINT USING "****", pp(2); pp(4); PRINT "<" ; PRINT USING "****" ; pp(1); pp(3)
IF clr% = 2 OR clr% = 3 THEN 9999
DO
q$ = INKEY$
LOOP WHILE q$ = ""
IF q$ <> "f" AND q$ <> "F" THEN 9999
sign = 1
INPUT "filename": o$
INPUT "change sign of x-axis": q$
IF q$ = "Y" OR q$ = "y" THEN sign = -1
OPEN o$ FOR OUTPUT AS #1
FOR j% = pln% TO phn%
IF fl$(j%) <> "n" THEN x! = sign * lx#(j%): y! = ly#(j%): PRINT #1, x!, y!
NEXT j%
NEXT j%
CLOSE #1
99999 END SUB

DEFNG A-Z
SUB potpair (e#, i#, num%, switch%)
DIM Eq(#(1500), io(#(1500)
e# = e#(1)
e# = e#(switch%)
inc# = ABS(e#(2) - e#(1))
nswtch% = switch%
PRINT switch%
FOR j% = 1 TO num%
Eo#(j%) = e#(j%)
io#(j%) = i#(j%)
NEXT j%
PRINT "THE POTENTIAL INCREMENT ON THE FORWARD SWEEP IS="; inc#
INPUT "DO YOU WISH TO CHANGE THE INCREMENT (YN)"; o$
IF o$ = "y" OR o$ = "Y" THEN INPUT "NEW INCREMENT"; inc#: nswtch% = ABS(e# - ch#) / inc# + 1
num% = 2 * nswch% - 1
j1% = 1
FOR i% = 1 TO nswch% + 1
e# = ei# - (i% - 1) * inc#
e#(i%) = e#
FOR j% = j1% TO switch%
IF e# < Eo#(j%) AND e# > Eo#(j% + 1) THEN j#(j%) = io#(j%) + (io#(j% + 1) - i
o#(j%)) * (e# - Eo#(j%)) / (Eo#(j% + 1) - Eo#(j%)): j1% = j%: j% = switch%
NEXT j%
NEXT i%

d1% = switch% + 1
FOR i% = nswch% + 1 TO num%
e# = eh# + (1% - nswch%) * inc#
e#(i%) = e#
FOR j% = j1% TO num%
IF e# > Eo#(j%) AND e# < Eo#(j% + 1) THEN i#(i%) = io#(j%) + (io#(j% + 1) - i
o#(j%)) * (e# - Eo#(j%)) / (Eo#(j% + 1) - Eo#(j%)): j1% = j%: j% = num%
NEXT j%
NEXT i%
PRINT num%
um% = num%
switch% = nswch%
END SUB

DEFDBL A-Z
SUB pwlfit (fl$, wmd%, px#(), py#(), w#(), jl%, jh%, a#, b#, c#, rsq#)
DIM pny#(1500), pp(4)
IF wmd% = 1 THEN 30000
FOR j% = j1% TO jh%
w#(j%) = 1
NEXT j%
30000 FOR j% = j1% TO jh%
IF fl$(j%) = "n" THEN 30100
swmx# = swmx# + w#(j%) * px#(j%)
swmu# = swmu# + w#(j%) * px#(j%) ^ 2
swmy# = swmy# + w#(j%) * py#(j%)
swmysq# = swmysq# + w#(j%) * py#(j%) ^ 2
swmxu# = swmxu# + w#(j%) * px#(j%) ^ 3
swmusq# = swmusq# + w#(j%) * px#(j%) ^ 4
swmxy# = swmxy# + w#(j%) * py#(j%) * px#(j%)
swmyu# = swmyu# + w#(j%) * py#(j%) * px#(j%) ^ 2
sw# = sw# + w#(j%)
num% = num% + 1
30100 NEXT j%
NR1% = 3: MC1% = 3: NCC1% = 1: ZMCH% = 0: IRHS% = NR1% + NCC1%
XMAT1(1, 1) = swmu#
XMAT1(1, 2) = swmx#
XMAT1(1, 3) = sw#
XMAT1(1, IRHS%) = swmy#
XMAT1(2, 1) = swmxu#
XMAT1(2, 2) = swmu#
XMAT1(2, 3) = swmx#
XMAT1(2, IRHS%) = swmxy#
XMAT1(3, 1) = swmusq#
XMAT1(3, 2) = swmxu#
XMAT1(3, 3) = swmu#
XMAT1(3, IRHS%) = swmuy#
CALL CROUT(NR1%, MC1%, NCC1%, ZMCH%)  
c# = XMAT1(1, IRHS%)  
b# = XMAT1(2, IRHS%)  
a# = XMAT1(3, IRHS%)  
sy# = swmysq# - swmy# ^ 2 / sw#  
FOR j% = j1% TO jh%  
IF fl$(j%) = "n" THEN 30200  
pny#(j%) = a# + b# * px#(j%) + c# * px#(j%) ^ 2  
spny# = spny# + w%(j%) * pny#(j%)  
spnysq# = spnysq# + w%(j%) * pny#(j%) ^ 2  
30200 NEXT j%  
syd# = spnysq# - spny# ^ 2 / sw#  
rsq# = syd# / sy#  
CALL plot(fl$(0), pp(), 1, px#(), py#(), j1%, jh%)  
PRINT a#, b#, c#, rsq#  
CALL plot(fl$(0), pp() + 1, px#(), py#(), j1%, jh%)  
END SUB

SUB weight(fl$(0), pp(), c#, i#, imax#, num%, w#, chalf#)  
FOR j% = 1 TO num%  
w%(j%) = (imax# - i#(j%)) ^ 2 * i#(j%) ^ 2  
IF w%(j%) > wmax THEN wmax = w%(j%); wj% = j%  
NEXT j%  
CALL plot(fl$(0), pp(), 2, c#, w(), 1, num%)  
PRINT "E\(w(i)\)max\)="; c#(wj%)  
DO  
LOOP UNTIL INKEY$ <> ""  
END SUB

SUB wls(fl$(0), pp(), wmd%, w#, lx#, ly#, j1%, jh%, m#, c#, rsq#)  
DIM ply#(1500)  
IF wmd% = 1 THEN 100  
FOR j% = j1% TO jh%  
w%(j%) = 1  
NEXT j%  
100 sx# = 0; sy# = 0; sxy# = 0; ssxsq# = 0; ssysq# = 0; sw# = 0  
FOR j% = j1% TO jh%  
IF fl$(j%) = "n" THEN CALL plot(fl$(0), pp(), 1, lx#, ly#, j1%, jh%)  
FOR j% = j1% TO jh%  
IF wmd% <> -1 THEN CALL plot(fl$(0), pp(), 1, lx#, ly#, j1%, jh%)  
FOR j% = j1% TO jh%  
if fl$(j%) <> "n" THEN ply#(j%) = m# * lx#(j%) + c#  
NEXT j%  
rsq# = (sw# * sxy# - sx# * sy#) ^ 2 / ((sw# * ssxsq# - sx# ^ 2) * (sw# * ssysq# - sy# ^ 2))
PRINT m#, c#, rsq#
IF wmd% <> -1 THEN CALL plot(fi$,(), pp(), 0, lx#(), ply#(), j1%, jh%)
END SUB

SUB xwcight (fi$,(), pp(), c#(), i#(), imax#, num%, w#(), ehalf#, tomes)
xff = -32.063 * tomes + 3.83
IF xff < 0 THEN xff = .05
FOR j% = 1 TO num%
w#(j%) = (imax# - i#(j%)) ^ 2 * i#(j%) ^ 2 * EXP(-xff * f * ABS(e#(j%) - ehalf#)) / (rg *
t))
IF w#(j%) > wmax THEN wmax = w#(j%): wj% = j%
NEXT j%
CALL plot(fi$,(), pp(), 2, e#(), w#(), 1, num%)
PRINT "E(w(i)max)=": e#(wj%)
DO
LOOP UNTIL INKEY$ <> ""
END SUB
PROGRAM FSTSCN.BAS FOR THE SCALING AND ANALYSIS OF FAST SCAN CYCLIC VOLTAMMGRAMS
WRITTEN BY PETER J. MAHON

REM FUNCTIONS AND SUBROUTINES FOR FOURIER TRANSFORM PROCEDURES
DECLARE SUB sg9smooth (i#, num%)
DECLARE SUB powerspectrumcalc (xreal#, yimag#, numdat%, delta#)
DECLARE SUB fftcalc (xreal#, yimag#, numdat%)
DECLARE SUB ffitinvcalc (xreal#, yimag#, numdat%)
DECLARE FUNCTION Parzen! (n%, j%)
DECLARE FUNCTION Hanning! (n%, j%)
DECLARE FUNCTION Hamming! (n%, j%)
DECLARE FUNCTION ExactBlackman! (n%, j%)
DECLARE FUNCTION Welch! (n%, j%)
DECLARE SUB FFTSolve (xreal#, yimag#, numdat%, flag%)
DECLARE FUNCTION SquareAndSum! (a#, b#)

CONST pi = 3.141592653589793#, maxv% = 1024

DECLARE SUB adjcc (c#, i#, ch#, num%, perip!)
DECLARE SUB pfit (fl$, pp#, py#, j1%, jh%, a, b, c)
DECLARE SUB fpa (fl$, pp#, c#, i#, num%, ntran%)
DECLARE SUB plot (fl$, pp#, clr%, lx#, ly#, pln%, phn%)
DECLARE SUB weight (fl$, pp#, c#, i#, sm#, ii#, ms#, num%, dt#, pi#, wi#, wm#)
DECLARE SUB wls (fl$, pp#, wmod%, w#&, lx#, ly#, j1%, jh%, m#, c#)
DECLARE SUB noise (i#, num%, vr)
DECLARE SUB potpair (e#, i#, num%, switch%)
DECLARE SUB deriv (x#, d#, dt#, npt%, num%)
COMMON SHARED dcr#, fl$, pp#, i#, c#, eo#, xreal#, yimag#, lx#, ly#, f#, px#, py#, w#

GOSUB 1
GOTO 10

1 REM INITIALIZE
f = 96484.6
rg = 8.31441
size% = 1200
DIM der%(size%), fl$[2 * size%), ppt(4), i%(2 * size%), e%(2 * size%), eo%(2 * size%) DIM xreal%(2 * size%), yimag%(2 * size%), lx%(2 * size%), ly%(2 * size%), fl%(2 * size%) DIM px%(size%), py%(size%), w%(size%), i%(size%) wmod% = 0 RETURN

10 REM SCREEN MENU
CLS : SCREEN 0
PRINT : PRINT " FAST SCAN CV PROCESSING"
PRINT " -------------------": PRINT
PRINT " 1, READ RAW FILE"
PRINT " 2, READ SCALED DATA WITH EXPT. PARAMETERS"
PRINT "  3, ADJUST EXPT. PARAMETERS"
PRINT "  4, PERFORM FOURIER ANALYSIS"
PRINT "  5, SAVE SCALED DATA WITH PRESENT EXPT. PARAMETERS"
PRINT "  6, APPLY iR CORRECTION FOR SINGLE CYCLE"
PRINT "  7, APPLY SMOOTHING"
PRINT "  8, APPLY CHARGING CURRENT CORRECTION"
PRINT "  9, READ SIMULATED DATA (mV,mA)"
PRINT " 10, ADD RANDOM NOISE"
PRINT " 11, SAVE OUTPUT DATA"
PRINT " 12, MEASURE CAPACITANCE AND RESISTANCE"
PRINT " 13, FIND PEAKS"
PRINT " 14, APPLY iR CORRECTION FOR CONTINUOUS CYCLING"
PRINT " 15, SCALE BANDWIDTH DATA"
PRINT " 16, EXIT"
PRINT : INPUT "  INPUT OPTION (1-16): "; qq
main = 1
IF qq < 1 OR qq > 16 THEN 10
ON qq GOTO 1000, 2000, 3000, 4000, 5000, 6000, 7000, 8000, 9000, 10000, 11000, 12000, 13000, 14000, 15000, 16000
GOTO 10

1000 REM READ RAW DATA FILE
CLS
INPUT "current file": c$
INPUT "potential file": p$
OPEN c$ FOR INPUT AS #1
j% = 0
DO WHILE NOT EOF(1)
  j% = j% + 1
  INPUT #1, i#(j%)
LOOP
CLOSE #1
OPEN p$ FOR INPUT AS #1
j% = 0
DO WHILE NOT EOF(1)
  j% = j% + 1
  INPUT #1, e#(j%)
  lx#(j%) = j%
LOOP
CLOSE #1
num% = j% - 2
CALL plot(fl$(), pp(), 1, lx#, e#, 1, num%)
CALL plot(fl$(), pp(), 1, lx#, i#, 1, num%)
CALL plot(fl$(), pp(), 1, e#, i#, 1, num%)
SCREEN 0
INPUT "DO YOU WISH TO INVERT POTENTIAL SCALE"; a$
IF a$ = "Y" OR a$ = "y" THEN FOR j% = 1 TO num%; i#(j%) = -i#(j%); NEXT j%
INPUT "DO YOU WISH TO INVERT CURRENT SCALE"; a$
IF a$ = "Y" OR a$ = "y" THEN FOR j% = 1 TO num%; e#(j%) = -e#(j%); NEXT j%
INPUT "DO YOU WISH TO ZERO CURRENT SCALE"; cc$
IF cc$ = "N" OR cc$ = "n" THEN 1050
1025 INPUT "WHAT IS LOWER LIMIT FOR ZERO REGION"; jl%
INPUT "WHAT IS UPPER LIMIT FOR ZERO REGION"; jh%
FOR j% = jl% TO jh%
  lx#(j%) = j%
ly#:j% = i#:j%
NEXT j%
CALL wls(fls(), pp(), 2, w#(), ly#(), jl%, jh%, m#, c#)
INPUT "REASSESS THE ZERO LIMITS"; a$
IF a$ = "Y" OR a$ = "y" THEN 1025
izer# = m# * jl% + c#
FOR j% = 1 TO num%: i#:j% = i#:j% - izer#: NEXT j%
1050 INPUT "INITIAL POTENTIAL (V)"; ei#
INPUT "SWITCHING POTENTIAL (V)"; ch#
INPUT "INPUT POTENTIOSTAT SCALE (mA/V)"; scp
INPUT "INPUT C.R.O. SCALE (mV/DIV)"; scc
scale = scp * scc / 1000000
emax# = -99999
emin# = 99999
FOR j% = 1 TO num%
IF e#:j% > emax# THEN emax# = e#:j%; thigh% = j%
NEXT j%
FOR j% = 1 TO thigh%
IF e#:j% < emin# THEN emin# = e#:j%;
NEXT j%
sum = 0: shigh = 0
FOR j% = 1 TO num%
IF e#:j% = emax# THEN shigh = shigh + j%; sum = sum + 1
NEXT j%
switch% = INT(shigh / sum)
j% = switch%
DO
j% = j% - 1
LOOP UNTIL j% = 1 OR e#:j% = emin#
ptb% = j% * j% FOR single : 1 FOR cycle
j% = switch%
DO
j% = j% + 1
LOOP UNTIL e#:j% <= emin# OR j% = num%
ptc% = j% * j% FOR single : num% FOR cycle
num% = ptc% - ptb% + 1
delt = emax# - emin#
FOR j% = ptb% TO ptc%
' skip next two lines for cycle
IF j% <= switch% THEN e#:j% = (j% - ptb%) * delt / (switch% - ptb%) + emin#
IF j% > switch% THEN e#:j% = (ptc% - j%) * delt / (ptc% - switch%) + emin#
e#:j% = (e#:j% - ptb% + 1) = (((ch# - ei#) * (e#:j% - emin#)) / delt) + ei#
i#:j% = i#:j% + 1 = i#:j% * scale * .0346
NEXT j%
CALL plot(fil$(), pp(), 1, e#, i#, 1, num%)
PRINT ptb%, ptc%, num%, switch%
IF ptc% - switch% <> switch% - ptb% THEN switch% = switch% - ptb% + 1: CALL
potpair(e#(), i#, num%, switch%)
CALL plot(fil$(), pp(), 1, e#, i#, 1, num%)
IF cc$ = "y" OR cc$ = "Y" THEN 1100
j% = 1: jh% = num% \ 10
FOR j% = jl% TO jh%
ix#:j% = j%
ly#:j% = i#
NEXT j%
CALL wls(fl$(0), pp(), 2, w#(), 1x#(), 1y#(), j1%, j1#, m#, c#)
ibeg = m# + c#
FOR j% = 1 TO num%
i#(j%) = i#(j%) - ibeg
NEXT j%
CALL plot(fl$(0), pp(), 1, e#(), i#(), 1, num%)
1100 GOTO 10

2000 REM READ SCALED DATA
CLEAR
GOSUB 1
INPUT "filename": o$
OPEN o$ FOR INPUT AS #1
INPUT #1, title$
INPUT #1, num%, t, n, sr, d, ssa, ei#, eh#, cb
FOR j% = 1 TO num%
INPUT #1, e#(j%), i#(j%)
NEXT j%
CLOSE #1
CALL plot(fl$(0), pp(), 2, e#(), i#(), 1, num%)
rad# = (ssa / (4 * pi#)) ^ (1 / 2)
PRINT title$, "SPHERICITY="; spher; "%"
DO
LOOP UNTIL INKEY$ <> ""
GOTO 10

3000 REM ADJUST EXPT. PARAMETERS
CLS : SCREEN 0
PRINT : PRINT : PRINT : PRINT " CURRENT EXPT. PARAMETERS": PRINT
PRINT " 1, TEMPERATURE (K) " ; t
PRINT " 2, DIFFUSION CO-EFFICIENT (CM^2/SEC) " ; d * 10000
PRINT " 3, SCAN RATE (V/SEC) " ; sr
PRINT " 4, SURFACE AREA OF SPHERE (CM^2) " ; ssa * 10000
PRINT " 5, NUMBER OF ELECTRONS " ; n
PRINT " 6, CONCENTRATION (MOLAR) " ; cb / 1000
PRINT " 7, EXIT"
PRINT : PRINT : PRINT : INPUT " INPUT SELECTION"; qq
SELECT CASE qq
CASE IS = 1
INPUT "NEW TEMPERATURE (K)" ; t
CASE IS = 2
INPUT "NEW DIFFUSION CO-EFFICIENT (CM^2/SEC)" ; d
d = d / 10000
CASE IS = 3
INPUT "NEW SCAN RATE (V/S)" ; sr
CASE IS = 4
INPUT "NEW SURFACE AREA (CM^2/SEC)" ; ssa
ssa = ssa / 10000
CASE IS = 5
INPUT "NEW NUMBER OF ELECTRONS" ; n
CASE IS = 6
INPUT "NEW CONCENTRATION (MOLAR)" ; cb
cb = cb * 1000
CASE IS = 7
GOTO 10
CASE ELSE
END SELECT
GOTO 3000

4000 REM FFT
CALL plot(fl$, pp$, 1, e#(), i#(), 1, num%)  
INPUT "freq response file"; a$
IF a$ = "" THEN 4010
OPEN a$ FOR INPUT AS 1
i% = 0
DO
i% = i% + 1
INPUT #1, px#(i%), py#(i%)
LOOP UNTIL EOF(1)
frnum% = i%
4010 dt# = 2 * (eh# - ci#) / (sr * num%)
FOR i% = 1 TO 1024
xreal#(i%) = i#(i%)
IF i% > num% THEN xreal#(i%) = (1024 - i%) * xreal#(num%) / (1024 - num%)
yimag#(i%) = 0
f#(i%) = i% / (1024 * dt#)
NEXT i%
CALL powerspectrumcalc(xreal#(), yimag#(), 1024, dt#)
CALL plot(fl$, pp$, 1, f#(), xreal#(), 1, 1024 / 8)
INPUT "filename"; o$
OPEN o$ FOR OUTPUT AS 1
FOR i% = 1 TO 1024
p = xreal#(i%); f = f#(i%)
PRINT #1, f, p
NEXT i%
CLOSE #1
FOR i% = 1 TO 1024
xreal#(i%) = i#(i%)
IF i% > num% THEN xreal#(i%) = 0
yimag#(i%) = 0
f#(i%) = i% / (1024 * dt#)
NEXT i%
CALL fftcalc(xreal#(), yimag#(), 1024)
CALL plot(fl$, pp$, 1, f#(), xreal#(), 1, 1024 / 2)
CALL plot(fl$, pp$, 1, f#(), yimag#(), 1, 1024 / 2)
IF a$ = "" THEN 4020
i% = 1
FOR j% = 1 TO 1024
IF f#(i%) > px#(frnum%) THEN 4015
FOR i% = 1 TO frnum%
IF f#(i%) > px#(i%) AND f#(j%) < px#(i% + 1) THEN gain# = py#(i%) + (py#(i% + 1) - py#(i%)) * ((f#(j%) - px#(i%)) / (px#(i% + 1) - px#(i%)))
NEXT i%
norm# = 1 / EXP(LOG(10) * gain# / 20)
xreal#(j%) = xreal#(i%) * norm#
yimag#(j%) = yimag#(i%) * norm#
4015 NEXT j%
4020 CALL fftinvcalc(xreal#(), yimag#(), 1024)
CALL plot(fl$, pp$, 1, e#(), xreal#(), 1, num%)
CALL plot(fl$, pp(), 1, e#(), yimag#(), 1, num%)  
FOR j% = 1 TO 1024  
i#(j%) = xreal#(j%)  
NEXT j%  
CALL plot(fl$, pp(), 1, e#(), i#(), 1, num%)  
GOTO 10  

5000 REM SAVE SCALED DATA FILE  
CLS  
INPUT "filename"; o$  
INPUT "title"; title$  
OPEN o$ FOR OUTPUT AS #1  
PRINT #1, title$  
PRINT #1, num%; t, n, sr, d, ssa, ci#, eh#, cb  
FOR j% = 1 TO num%  
e = e#(j%); i = i#(j%)  
PRINT #1, e, i  
NEXT j%  
CLOSE #1  
GOTO 10  

6000 REM I/R CORRECTION  
6010 INPUT " USE REAL BACKGROUND CURRENT"; a$  
IF a$ = "y" OR a$ = "Y" THEN 6100  
GOTO 6200  
6100 INPUT " BACKGROUND CURRENT FILENAME"; o$  
OPEN o$ FOR INPUT AS #1  
INPUT #1, title$  
INPUT #1, ccnum%; t, n, sr, d, ssa, ci#, eh#, cb  
FOR j% = 1 TO ccnum%  
INPUT #1, px#(j%), py#(j%)  
NEXT j%  
CLOSE #1  
CALL plot(fl$, pp(), 2, px#(), py#(), 1, ccnum%)  
INPUT "Apply smoothing"; b$  
IF b$ <> "Y" AND b$ <> "y" THEN 6200  
CALL sg9smooth(py#(), ccnum%)  
CALL plot(fl$, pp(), 0, px#(), py#(), 1, ccnum%)  
6200 INPUT " INPUT UNCOMPENSATED RESISTANCE (OHMS)"; ru  
INPUT " INPUT CHARGING CURRENT (pF)"; cd: cd = cd * 1E-12  
nnum% = .95 * num%  
sign = 1: IF ei# > eh# THEN sign = -1  
s/dir = 1  
dt# = ABS(2 * (eh# - ei#) / (sr * num%))  
ei# = e#(1)  
emax# = eh#  
eh# = e#(1)  
i1% = 1  
nsg% = 3: IF ru * cd >= nsg% * dt# THEN nsg% = 1 + ru * cd / dt#  
IF a$ <> "Y" AND a$ <> "y" THEN 6220  
CALL deriv(e#(), der#(), dt#, 5, num%)  
i% = 0  
FOR j% = 1 TO num%  
loop$ = ""
IF der#(j%) < 0 THEN 6210
WHILE der#(j%) > 0 AND loop$ <> "end"
i% = i% + 1: IF i% > num% THEN i% = i1% - 20
IF e#(j%) >= px#(i%) AND ef#(j%) <= px#(i% + 1) THEN f#(j%) = py#(i%) + (py#(i% + 1) - py#(i%)) * (ef#(j%) - px#(i%)) / (px#(i% + 1) - px#(i%)): loop$ = "end": i1% = i%
WEND
GOTO 6215
6210 WHILE der#(j%) < 0 AND loop$ <> "end"
i% = i% + 1: IF i% > num% THEN i% = i1% - 20
IF e#(j%) <= px#(i%) AND ef#(j%) >= px#(i% + 1) THEN f#(j%) = py#(i%) + (py#(i% + 1) - py#(i%)) * (ef#(j%) - px#(i%)) / (px#(i% + 1) - px#(i%)): loop$ = "end": i1% = i%
WEND
6215 NEXT j%
6220 scdir = 1
FOR j% = 1 TO num%
lx#(j%) = ef#(j%): ly#(j%) = i#(j%)
IF j% > nsg% + 1 AND j% < num% - nsg% THEN norm = 0: di# = 0: FOR npt% = 1 TO nsg%: di# = di# + (-i#(j% - npt%) - f#(j% - npt%) + i#(j% + npt%) + f#(j% + npt%)) * npt%: norm = norm + 2 * npt% ^ 2: NEXT npt%: did# = di# / (norm * di#)
IF a$ = "y" OR a$ = "Y" THEN 6230
IF ef#(j%) = emax# THEN scdir = -1: PRINT scdir
itot# = i#(j%) + scdir * cd * sr: GOTO 6240
6230 itot# = i#(j%) + f#(j%)
6240 eo#(j%) = e#(j%): itot# * ru * sign
if#(j%) = i#(j%) + cd * ru * did#:
i#(j%) = if#(j%) + f#(j%): sr * ru * did#
IF ABS(eo#(j%)) > ABS(ci#) THEN ci# = eo#(j%)
IF ABS(eo#(j%)) > ABS(ch#) THEN eh# = eo#(j%)
NEXT j%
PRINT ci#, ch#
INPUT "Save file of total current": zi$
IF zi$ = "Y" OR zi$ = "y" THEN INPUT "filename": z$: OPEN z$ FOR OUTPUT AS #1
FOR j% = 1 TO num%
f#(j%) = i#(j%) + f#(j%)
IF zi$ = "y" OR zi$ = "Y" THEN PRINT #1, e#(j%), f#(j%)
NEXT j%
IF zi$ = "Y" OR zi$ = "y" THEN CLOSE #1
CALL plot(f$(), pp(), 1, e#(), f#(), 1, num%)
CALL plot(f$(), pp(), 2, eo#(), i#(), 1, num%)
'scdir = 1
'FOR j% = 4 TO num% - 3
'IF eo#(j%) = eh# THEN scdir = 1: PRINT scdir
'enorm = 0: de# = 0: FOR npt% = 1 TO 3: de# = de# + (-eo#(j% - npt%) + eo#(j% + npt%)) * npt%: enorm = norm + 2 * npt% ^ 2: NEXT npt%: ded# = de# / (norm * di#)
i#(j%) = i#(j%) + cd * (sr * scdir - ded#)
NEXT j%
CALL sg9smooth(eo#(), num%)
FOR i% = 1 TO num%
f#(i%) = i%
NEXT i%
CALL plot(f$, pp(), 1, f#, eo#, 1, num%
CALL plot(f$, pp(), 2, eo#, i#, 1, num%
CALL plot(f$, pp(), 3, eo#, i#, 1, num%
INPUT "Choose between (L)inear and (B)ackground capacitance"; c$
IF c$ = "$B" OR c$ = "$b" THEN FOR j% = 1 TO num%; i#(j%) = i#(j%); NEXT j%
inc# = ABS((ch# - ci#) * 2 / num%
j1% = 1
FOR i% = 1 TO num% \ 2
f#(i%) = 0
c# = ci# + i% * inc# * sign
c#(i%) = c#
6250 FOR j% = j1% TO 3 * num% / 5
IF ABS(c#) > ABS(co#(j%)) AND ABS(c#) <= ABS(co#(j% + 1)) THEN f#(i%) =
   i#(j%) + (i#(j% + 1) - i#(j%)) * (c# - co#(j%)) / (co#(j% + 1) - co#(j%)); j1% =
   j% - 50; j% = 3 * num% / 5
IF j1% < 1 THEN j1% = 1
NEXT j%
NEXT i%
j1% = num% \ 2 + 1
FOR i% = num% \ 2 TO num%
f#(i%) = 0
c# = ch# - (i% - num% \ 2) * inc# * sign
c#(i%) = c#
FOR j% = j1% TO num%
IF ABS(c#) < ABS(co#(j%)) AND ABS(c#) >= ABS(co#(j% + 1)) THEN f#(i%) =
   i#(j%) + (i#(j% + 1) - i#(j%)) * (c# - co#(j%)) / (co#(j% + 1) - co#(j%)); j1% =
   j%: j% = num%
NEXT j%
NEXT i%
FOR i% = 1 TO num%
i#(i%) = f#(i%)
NEXT i%
CALL plot(f$, pp(), 0, e#, i#, 1, num%
CALL plot(f$, pp(), 2, lx#, ly#, 1, num%
CALL plot(f$, pp(), 0, e#, i#, 1, num%
um% = num%
GOTO 10

7000 REM SMOOTHING
CLS : SCREEN 0
PRINT "CHOOSE MODE OF SMOOTHING"
PRINT " 1, 3-POINT TRIANGULAR WINDOW SMOOTHING"
PRINT " 2, FOURIER SMOOTHING"
PRINT " 3, 9-POINT LEAST SQUARES WINDOW SMOOTHING"
PRINT " 4, EXIT"
PRINT : INPUT "MODE OF SMOOTHING"; i%
FOR j% = 1 TO num%
eo#(j%) = i#(j%)
NEXT j%
ON i% GOTO 7010, 7020, 7030, 7040
7010 CALL plot(f$, pp(), 2, e#, i#, 1, num%
FOR j% = 2 TO num% - 1
i#(j%) = eo#(j%) / 2 + (eo#(j% - 1) + eo#(j% + 1)) / 4
NEXT j%
CALL plot(f$, pp(), 0, e#, i#, 1, num%)

GOTO 7040
7020 INPUT "NUMBER OF TRANSFORMATIONS": ntran%
CALL plot(fl$(0), pp(), 2, e#(), i#(), 1, num%)
CALL ftp(fl$(0), pp(), e#(), i#(), num%, ntran%)
CALL plot(fl$(0), pp(), 1, e#(), i#(), 1, num%)
GOTO 7040
7030 CALL plot(fl$(0), pp(), 2, e#(), i#(), 1, num%)
CALL sg9smooth(i#(), num%)
CALL plot(fl$(0), pp(), 0, e#(), i#(), 1, num%)
7040 GOTO 10

8000 REM ADJUST CHARGING CURRENT
INPUT "DO YOU WISH TO (Z)ERO CURRENT SCALE OR ADJUST (C)HARGING CURRENT": cc$
IF cc$ = "C" OR cc$ = "c" THEN 8050
IF cc$ = "Z" OR cc$ = "z" THEN 8025
GOTO 10
8025 INPUT "WHAT IS LOWER LIMIT FOR ZERO REGION": jl%
INPUT "WHAT IS UPPER LIMIT FOR ZERO REGION": jh%
FOR j% = jl% TO jh%
lx%(j%) = j%
ly%(j%) = i#(j%)
NEXT j%
CALL wls(fl$(0), pp(), 2, w#(), lx#(), ly#(), jl%, jh%, m#, c#)
INPUT "REASSESS THE ZERO LIMITS": a$
IF a$ = "Y" OR a$ = "y" THEN 8025
izero# = m# * jl% + c#
FOR j% = 1 TO num%
i#(j%) = i#(j%): izero#: NEXT j%
GOTO 8100
8050 INPUT "CHARGING CURRENT CORRECTION AS A % OF ip": perip
CALL adjcc(e#(), i#(), ch#, num%, perip)
8100 CALL plot(fl$(0), pp(), 1, e#(), i#(), 1, num%)
GOTO 10

9000 REM READ SIMULATED DATA (mV, mA)
CLEAR
GOSUB 1
CLS
INPUT "filename": o$
OPEN o$ FOR INPUT AS #1
INPUT #1, title$
INPUT #1, num%
INPUT #1, t, n, sr, d
INPUT #1, ssa, ei#, eh#, cb
num% = num% - 1
d = d / 10000
ssa = ssa / 10000
cb = cb * 1000
FOR j% = 0 TO num%
INPUT #1, e#(j%), i#(j%)
e#(j%) = -e#(j%): e#(j%) = e#(j%): i#(j%) = i#(j%): i#(j%) = i#(j%): i#(j%) = i#(j%): i#(j%)
NEXT j%
CLOSE #1
CALL plot(f1$, pp0, 2, c#, i#, 0, 1, num%)
ci# = (c#(1) + c#(num%)) / 2
rad# = (ssa / (4 * pi#)) ^ (1 / 2)
isp = .7516 * n * f * ssa * d * cb / rad#
ipl = .4463 * n * f * ssa * d ^ (1 / 2) * sr ^ (1 / 2) * cb * (n * f / (rg * t)) ^ (1 / 2) + isp
spher = isp * 100 / ipl
PRINT title$; " SPHERICITY="; spher; "%"; " Epc="; e#(maxi%); " Epn="; e#(mini%)
DO
LOOP UNTIL INKEYS$ <> ""
GOTO 10

10000 REM ADD RANDOM NOISE
CLS
INPUT "VARIANCE AS % OF ip"; vr
CALL noise(i#, num%, vr)
CALL plot(f1$, pp0, 1, c#, i#, 0, 1, num%)
PRINT vr
GOTO 10

11000 REM SAVE OUTPUT DATA
CLS
jlo% = 1
jho% = num% \ 2
INPUT "FILENAME OF OUTPUT FILE"; o$
INPUT "OUTPUT DENSITY"; dd%
PRINT "i=",; j%"; " jh = ";; jh%; "; total number="; num% \ 2
INPUT "LOWER DATA LIMIT"; jlo%
INPUT "UPPER DATA LIMIT"; jho%
OPEN o$ FOR OUTPUT AS #1
PRINT #1, title$
PRINT #1, num%, t, n, sr, d, ssa, ci#, ch#, cb
PRINT #1, "E(Y)--> i(A)--> mu*->"
PRINT #1, "E(Y)<-- i(A)<-- mu*<"
FOR j% = jlo% TO jho% STEP dd%
PRINT #1, c#(i%), i#(j%)
PRINT #1, c#(num% - j% + 1), i#(num% - j% + 1)
NEXT j%
CLOSE #1
GOTO 10

12000 CLS
INPUT "Estimate from simulation method"; a$
IF a$ <> "Y" OR a$ <> "Y" THEN 13100
j% = 0
INPUT "capacitance"; c
INPUT "scan rate"; sr
ei% = ei# * 1000
eh% = eh# * 1000
FOR r = 10000 TO 60000 STEP 10000
FOR i% = ei% TO eh%
  j% = j% + 1
  lx#(j%) = i% / 1000
  ly#(j%) = -c * sr * (2 * EXP(-(lx#(j%) - ei#) / (r * c * sr)) - 1)
NEXT i%
NEXT r

NEXT i%
FOR i% = ei% TO eh%
j% = j% + 1
lx#(j%) = i% / 1000
ly#(j%) = c% * sr% * (2 * EXP(-(eh% - lx#(j%)) / (r% * c% * sr%)) - 1)
NEXT i%
NEXT r
CALL plot(fl$, pp(), 2, lx#(), ly#(), 1, j%)
CALL plot(fl$, pp(), 0, el#, i#(), 1, num%)
GOTO 10
12100 PRINT : PRINT : INPUT "DO YOU WISH TO ADJUST FOR ZERO I": a$
IF a$ = "N" OR a$ = "n" THEN 12005
FOR j% = 1 TO 50
ly#(j%) = i#(j%)
lx#(j%) = j%
NEXT j%
CALL wls(fl$, pp(), 0, w#, lx#(), ly#(), 1, 50, m#, c#)
c1# = c#
NEXT j%
FOR j% = num% TO num% - 50 STEP -1
ly#(j%) = num% + 51 = i#(j%)
lx#(j%) = num% + 51 = j% - num% + 51
NEXT j%
CALL wls(fl$, pp(), 0, w#, lx#(), ly#(), 1, 50, m#, c#)
i#(j%) = (c1# + c#) / 2
FOR j% = 1 TO num%
i#(j%) = i#(j%) - i0#
NEXT j%
12005 CALL plot(fl$, pp(), 1, el#, i#(), 1, num%)
PRINT : PRINT : INPUT "USE DATA FROM THE (F)ORWARD OR (B)ACKWARD SWEEP": a$
INPUT "capacitance": cap#
j1% = 1: INPUT "NUMBER OF POINTS": rng%. jh% = rng%
IF a$ = "F" OR a$ = "f" THEN 12010
ehigh# = e#(1): FOR i% = num% \ 2 - 20 TO num% \ 2 + 20: IF e#(i%) > ehigh# THEN ehigh# = e#(i%): j1% = i%: jh% = i% + rng%
NEXT i%
12010 FOR j% = j1% TO jh%
fl$(j%) = "n"
IF a$ = "f" AND cap# * sr > ABS(i#(j%)) THEN ly#(j%) = LOG(ABS(i#(j%)) + cap# * sr): fl$(j%) = ""
IF a$ = "b" AND cap# * sr > ABS(i#(j%)) THEN ly#(j%) = LOG(i#(j%) + cap# * sr): fl$(j%) = ""
sl# = 2 * (eh# - el#) / (sr * num%) * (j% - j1%)
lx#(j%) = -sl#
NEXT j%
CALL plot(fl$, pp(), 1, el#, i#, j1%, jh%)
CALL wls(fl$, pp(), 0, w#, lx#(), ly#(), j1%, jh%, m#, c#)
rn# = 1 / (m# * cap#)
PRINT cap#, rn#
FOR j% = 1 TO num%: fl$(j%) = "": NEXT j%
DO
LOOP WHILE INKEY$ = ""
GOTO 10
13000 REM PEAK FINDING ROUTINE
CLS : PRINT : PRINT : PRINT : PRINT " FINDING THE PEAKS"

dt# = ABS(2 * (eh# - ei#) / (sr * num%))
npt% = ABS(.005 * num% / (eh# - ei#))
CALL deriv(i#, der#, dt#, npt%, num%)
imax# = -99999: imin# = 99999
FOR j% = 1 TO num%
  IF i%(j%) > imax# THEN imax# = i%(j%)
  IF i%(j%) < imin# THEN imin# = i%(j%)
NEXT j%
sume# = 0: i% = 0
PRINT "maximum current = "; imax#
FOR j% = 4 TO num% - 3
  IF dcr%(j% - 3) > 0 AND dcr%(j% + 3) < 0 AND i%(j%) > imax# / 20 THEN PRINT
e%(j%), i%(j%): i% = i% + 1: sume# = sume# + e%(j%)
  IF i% = 6 THEN PRINT "Average = "; sume# / 6: DO: LOOP WHILE INKEY$ = "": i%
   = 0: sume# = 0
NEXT j%
sume# = 0: i% = 0
PRINT "minimum current = "; imin#
FOR j% = 4 TO num% - 3
  IF dcr%(j% - 3) < 0 AND dcr%(j% + 3) > 0 AND i%(j%) < imin# / 5 THEN PRINT
e%(j%), i%(j%): i% = i% + 1: sume# = sume# + e%(j%)
  IF i% = 6 THEN PRINT "Average = "; sume# / 6: DO: LOOP WHILE INKEY$ = "": i%
   = 0: sume# = 0
NEXT j%
PRINT "end"
DO
  LOOP WHILE INKEY$ = ""
GOTO 10

14000 REM iR CORRECTION
CLS : PRINT : PRINT : PRINT : PRINT : PRINT
INPUT " USE REAL BACKGROUND CURRENT"; a$
IF a$ = "y" OR a$ = "Y" THEN 15100
GOTO 14200
14100 INPUT " BACKGROUND CURRENT FILENAME"; c$
OPEN c$ FOR INPUT AS #1
INPUT #1, title$
INPUT #1, ccnum%, t, n, sr, d, ssa, ei#, ch#, cb
FOR j% = 1 TO ccnum%
  INPUT #1, px%(j%), py%(j%)
NEXT j%
CLOSE #1
CALL plot(fl$(a), pp(), 2, px#(), py#(), 1, num%)
INPUT "Apply smoothing"; b$
IF b$ <> "Y" AND b$ <> "y" THEN 15200
CALL sg9smooth(py#(), num%)
CALL plot(fl$(a), pp(), 0, px#(), py#(), 1, num%)
14200 INPUT " INPUT UNCOMPENSATED RESISTANCE (OHMS)"; ru
INPUT " INPUT CHARGING CURRENT (PF)"; cd: cd = cd * 1E-12
num% = .95 * num%
sign = 1: IF ei# > eh# THEN sign = -1
scdir = 1
INPUT "TIMEBASE (sec)"; tb: dt# = tb / 100
IF tb = 0 THEN dt# = 2 * (eh# - ei#) / (sr * num%)
ei# = c#(1)
emax# = ch#
ch# = c#(1)
i1% = 1
nsg% = 3: IF ru * cd >= nsg% * dt# THEN nsg% = 1 + ru * cd / dt#
IF a$ <> "Y" AND a$ <> "y" THEN 15220
14220 scdir = 1
FOR j% = 1 TO num%
lx##(j%) = e#(j%): ly##(j%) = n#(j%)
IF j% > nsg% + 1 AND j% < num% - nsg% THEN norm = 0: di# = 0: FOR npt% = 1
TO nsg%: di# = di# + (-1#(j% - npt%) + f##(j% - npt%) + n#(j% + npt%) + f##(j% +
npt%)) * npt%: norm = norm + 2 * npt% ^ 2: NEXT npt%: didt# = di# / (norm *
dt#)
IF a$ = "y" OR a$ = "Y" THEN 14230
IF e#(j%) = emax# THEN scdir = -1: PRINT scdir
14320 itot# = i#(j%) + scdir * cd * sr: GOTO 14240
14420 eo#(j%) = e#(j%) - itot# * ru * sign
iff#(j%) = i#(j%) + cd * ru * didt#
IF co#(j%) < ci# * sign THEN ei# = co#(j%)
IF co#(j%) > ch# * sign THEN ch# = co#(j%)
NEXT j%
CALL plot(fil$(0, pp(), 2, eo#(), i#(), 1, num%)
CALL deriv(e#(), doc#(), dt#, 4, num%)
FOR j% = 4 TO num% - 3
scdir = 1
IF doc#() < 0 THEN scdir = -1
enorm = 0: de# = 0: FOR npt% = 1 TO 4: de# = de# + (-eo#(j% - npt%) + eo#(j% +
npt%)) * npt%: enorm = enorm + 2 * npt% ^ 2: NEXT npt%: dedt# = de# /
(enorm * dt#)
i#(j%) = i#(j%) + cd * (sr * scdir - dedt#)
NEXT j%
FOR j% = 1 TO num%
e#(j%) = eo#(j%)
NEXT j%
CALL plot(fil$(0, pp(), 2, lx(), ly(), 1, num%)
CALL plot(fil$(0, pp(), 0, e#(), i#(), 1, num%)
DO
LOOP WHILE INKEY$ = ""
GOTO 10

15000 CLS
INPUT "FREQUENCY RESPONSE file": r$
INPUT "FREQUENCY PROFLE file": f$
OPEN r$ FOR INPUT AS #1
j% = 0
DO WHILE NOT EOF(1)
j% = j% + 1
INPUT #1, i#(j%)
LOOP
CLOSE #1
OPEN f$ FOR INPUT AS #1
j% = 0
DO WHILE NOT EOF(1)
j% = j% + 1
INPUT #1, e#(j%)  
ix#(j%) = j%  
LOOP  
CLOSE #1  
num% = j% - 2  
CALL plot(fl#(0, pp0, 1, ix#(0, e#(0), 1, num%))  
CALL plot(fl#(0, pp0, 1, ix#(0, i#(0), 1, num%))  
CALL plot(fl#(0, pp0, 1, e#(0, i#(0), 1, num%))  
SCREEN 0  
INPUT "spectrum analyzer scale (mV/DIV)"; sa  
INPUT "oscilloscope scale (mV/DIV)"; os  
INPUT "starting frequency"; fstart  
scale = os * sa / (250! * 1000!) result in Volts  
FOR j% = 1 TO num%  
IF c#(j%) > ch# THEN ch# = c#(j%): jh% = j%  
IF c#(j%) < ci# THEN ci# = c#(j%): ji% = j%  
IF i#(j%) > ih# THEN ih# = i#(j%)  
IF i#(j%) < ih# THEN ih# = i#(j%)  
NEXT j%  
FOR j% = 1 TO num%  
e#(j%) = (ci#(j%) - ci#) / (eh# - ei#) * 100000 + fstart  
i#(j%) = i#(j%) * scale * .0346  
NEXT j%  
CALL plot(fl#(0, pp0, 1, e#(0, i#(0, ji%, jh%))  
CLS  
INPUT "Save the scaled data"; o$  
IF o$ <> "Y" OR o$ <> "y" THEN 10  
PRINT "filename"; o$  
OPEN o$ FOR OUTPUT AS #1  
FOR j% = ji% TO jh%  
PRINT #1, e#(j%), i#(j%)  
NEXT j%  
CLOSE #1  
DO  
LOOP WHILE INKEY$ = ""  
GOTO 10  
16000 END  
SUB adjcc (e#(), i#(), ch#, num%, perip)  
emax# = -99999  
FOR j% = 1 TO num%  
IF e#(j%) > emax# THEN emax# = e#(j%): swtch% = j%  
NEXT j%  
imax = 0  
FOR j% = 1 TO swtch%  
IF i#(j%) > imax THEN imax = i#(j%)  
NEXT j%  
FOR j% = swtch% + 1 TO num%  
i#(j%) = i#(j%) + perip * imax / 100  
NEXT j%  
END SUB  
SUB deriv (x#(), dcr#, dt#, npt%, num%)  
FOR j% = 1 TO num%  

IF j% > npt% + 1 AND j% < num% - npt% THEN norm = 0: dx# = 0: FOR nsg% = 1 
TO npt%: dx# = dx# + (x#(j% - nsg%) + x#(j% + nsg%)) * nsg%: norm = norm + 2 * nsg% ^ 2: NEXT nsg%: dcr#(j%) = dx# / (norm * dt#)
NEXT j%
END SUB

FUNCTION ExactBlackman (n%, j%) = .42 - .5 * COS(2! * pi * j% / n%) + .08 * COS(4! * pi * j% / n%)
END FUNCTION

SUB fftcalc (xreal#(), yimag#(), numdat%)
CALL FFTSolve(xreal#(), yimag#(), numdat%, 0)
END SUB

SUB fftinvcalc (xreal#(), yimag#(), numdat%)
CALL FFTSolve(xreal#(), yimag#(), numdat%, 1)
END SUB

SUB FFTSolve (xreal#(), yimag#(), numdat%, flag%)

DIM cosary(0 TO maxv%)
DIM sinary(0 TO maxv%)
DIM harm, prodreal, prodimag, sign
DIM maxpower AS INTEGER, cnt AS INTEGER, arg AS INTEGER
DIM pnt0 AS INTEGER, pnt1 AS INTEGER

j% = 0
IF flag% <> 0 THEN
    sign = 1!
    FOR i% = 0 TO numdat% - 1
        xreal#(i%) = xreal#(i%) / numdat%
        yimag#(i%) = yimag#(i%) / numdat%
    NEXT i%
    sign = -1!
ELSE
    END IF
    FOR i% = 0 TO numdat% - 2
    IF i% < j% THEN
        SWAP xreal#(i%), xreal#(j%)
        SWAP yimag#(i%), yimag#(j%)
    END IF
    k% = numdat% \
    WHILE k% <= j%
        j% = j% - k%
        k% = k% \
    WEND
    j% = j% + k%
    NEXT i%
    maxpower% = 0
    i% = numdat%
    WHILE i% <= 1
        maxpower% = maxpower% + 1
        i% = i% \
    WEND
harm = 2 * pi / numdat
FOR i% = 0 TO numdat - 1
    sinary(i%) = sign * SIN(harm * i%)
    cosary(i%) = COS(harm * i%)
NEXT i%

a% = 2
b% = 1
FOR cnt% = 1 TO maxpower
    pnt0% = numdat\a%
    pnt1% = 0
    FOR k% = 0 TO b% - 1
        i% = k%
        WHILE i% < numdat
            arg% = i% + b%
            IF k% = 0 THEN
                prodreal = xreal#(arg%)
                prodimag = yimag#(arg%)
            ELSE
                prodreal = xreal#(arg%) * cosary(pnt1%) - yimag#(arg%) * sinary(pnt1%)
                prodimag = xreal#(arg%) * sinary(pnt1%) + yimag#(arg%) * cosary(pnt1%)
            END IF
            xreal#(arg%) = xreal#(i%) - prodreal
            yimag#(arg%) = yimag#(i%) - prodimag
        NEXT i%
        pnt1% = pnt1% + pnt0%
    NEXT k%
NEXT cnt%

SUB fpa (fl$(0), pp(), e$(0), i$(0), num%, ntran%)
    DIM real#(300), imag#(300), lx#(300), ly#(300)
    ntran% = 1
    bf# = (i#(num%) - i#(1)) / num%
    g# = 0
    FOR j% = 2 TO num%
        i#(j%) = i#(j%) - i#(1) - bf# * (j% - 1)
        g# = g# + i#(j%)
    NEXT j%
    real#(0) = g# / num%
    7110 IF ntran% <= ntran% THEN 7120
    FOR k% = ntran% TO ntran% - 1
        sumr# = 0
        sumi# = 0
        FOR j% = 2 TO num% - 1
            s# = SIN(2 * pi# * (j% - 1) * k% / num%)
            c# = COS(2 * pi# * (j% - 1) * k% / num%)
            sumr# = sumr# + i#(j%) * c#
            sumi# = sumi# + i#(j%) * s#
        NEXT j%
    END IF
    NEXT k%
real#(k%) = sumr# / num%
imag#(k%) = -sumi# / num%
lx#(k%) = k%
ly#(k%) = real#(k%) ^ 2 + imag#(k%) ^ 2
NEXT k%
CALL plot(fS(), pp(), 1, lx#(), ly#(), ntran%, ntran% - 1)
IF ntran% > ntran% THEN ntran% = ntran%
7120 f1# = 0: f2# = 0
FOR k% = 1 TO ntran% - 1
  f1# = f1# + real#(k%)
  f2# = f2# + k% ^ 2 * real#(k%)
  f0# = 1 - k% ^ 2 / (ntran% * ntran%)
  real#(k%) = f0# * real#(k%)
  imag#(k%) = f0# * imag#(k%)
NEXT k%
i#(1) = i#(1) + real#(0) + 2 * (f1# - f2# / (ntran% * ntran%))
FOR j% = 2 TO num%
  sum# = 0
  FOR k% = 1 TO ntran% - 1
    s# = SIN(2 * pi% * k% * (j% - 1) / num%)
    c# = COS(2 * pi% * k% * (j% - 1) / num%)
    sum# = sum# + real#(k%) * c# - imag#(k%) * s#
  NEXT k%
i#(j%) = i#(1) + (j% - 1) * bf# + real#(0) + 2 * sum#
NEXT j%
END SUB

FUNCTION Hamming (n%, j%)
  Hamming = .54 - .46 * COS(2! * pi% * j% / n%)
END FUNCTION

FUNCTION Hanning (n%, j%)
  Hanning = .5 * (1 - COS(2! * pi% * j% / n%))
END FUNCTION

SUB noise (i#, num%, vr)
  DIM mi%(500)
  kint% = 100
  FOR j% = 1 TO num% \ 2
    IF i#(j%) > imax# THEN imax# = i#(j%)
  NEXT j%
  PRINT "method of noise"
  PRINT " 1, Oldham noise"
  PRINT " 2, Computer noise"
  INPUT "choice": c%
  ON c% GOTO 11110, 11120
11110 k% = 0
11120 mu = 0
  bn# = 199017
  s# = 2 * (vr * imax# / 100) ^ 2
  j% = 2 * num%
  n# = 2 * num%
  11100 n# = 24298 * n# + 99991
  n# = 1 + n# - bn# * INT(n# / bn#)
  ni% = 1 + INT(n# / bn# * kint%)
 ni% (ni%) = ni% (ni%) + 1
 j% = j% - 1
 IF j% \ 2 = j% / 2! THEN 11200
 x# = (s# * LOG(bn# / n#)) ^ (1 / 2)
 GOTO 11100
 11200 x# = mu + x# * COS(2 * pi# * n# / bn#)
 k% = k% + 1
 i#(k%) = i#(k%) + x#
 IF j% > 10 THEN 11100 ELSE 11300
 11120 FOR j% = 1 TO num%
 x# = (RND(1) - .5) * imax# * vr / 100
 i#(j%) = i#(j%) + x#
 NEXT j%
 11300 FOR j% = 1 TO kint%
 snisq# = snisq# + (ni%(j%) - 2 * num% / kint%) ^ 2 / (2 * num% / kint%)
 NEXT j%
 chisq# = snisq#
 PRINT chisq#, kint%
 DO
 LOOP UNTIL INKEYS <> ""
 END SUB

FUNCTION Parzen (n%, j%)
 Parzen = 1 - ABS((j% - .5 * (n% - 1)) / (.5 * (n% + 1)))
 END FUNCTION

SUB pfit (fl$, px#(), py#(), j1%, jh%, a, b, c)
 DIM px%(1500), pp(4)
 FOR j% = j1% TO jh%
 IF fl$(j%) = "n" THEN 20000
 smx = smx + px%(j%)
 smu = smu + px%(j%) ^ 2
 smy = smy + py%(j%)
 smysq = smysq + py%(j%) ^ 2
 smxu = smxu + px%(j%) ^ 3
 smusu = smusu + px%(j%) ^ 4
 smxy = smxy + py%(j%) * px%(j%)
 smuy = smuy + py%(j%) * px%(j%) ^ 2
 20000 NEXT j%
 pnum% = jh% - j1% + 1
 a1 = smu - smx ^ 2 / pnum%
 b1 = smux - smx * smu / pnum%
 b2 = smusu - smu ^ 2 / pnum%
 a3 = smxy - smx * smy / pnum%
 b3 = smuy - smu * smy / pnum%
 a2 = b1
 b = (a2 * b3 - b2 * a3) / (a2 * b1 - a1 * b2)
 c = (a3 - a1 * b) / a2
 a = (smy - b * smx - c * smu) / pnum%
 sy = smysq - smy ^ 2 / pnum%
 FOR j% = j1% TO jh%
 IF fl$(j%) = "n" THEN 200010
 pny#(j%) = a + b * px#(j%) + c * px#(j%) ^ 2
 spny = spny + pny#(j%)
 spnysq = spnysq + pny#(j%) ^ 2

20010 NEXT J%
syd = spny - spn ^ 2 / pnum%
rsq = syd / sy
CALL plot(fl$, pp(), 1, px(), py(), jl%, jh%) PRINT a, b, c, rsq
CALL plot(fl$, pp(), 0, px(), pny(), jl%, jh%)
END SUB

SUB plot (fl$, pp(), clr%, lx%, ly%, pln%, phn%)
REM clr% = (0:nc,p) (1:cp) (2:cn,p) (3:ncnp)
IF clr% = 0 OR clr% = 3 THEN 999
CLS
f% = pln%
30005 IF fl$(f%) = "n" THEN f% = f% + 1: GOTO 30005
pp(2) = lx%(f%); pp(1) = lx%(f%)
pp(4) = ly%(f%); pp(3) = ly%(f%)
FOR j% = pln% TO phn%
IF fl$(j%) = "n" THEN 30010
IF lx%(j%) >= pp(1) THEN pp(1) = lx%(j%)
IF lx%(j%) <= pp(2) THEN pp(2) = lx%(j%)
IF ly%(j%) >= pp(3) THEN pp(3) = ly%(j%)
IF ly%(j%) <= pp(4) THEN pp(4) = ly%(j%)
30010 NEXT j%
999 SCREEN 2
IF pp(3) = pp(4) THEN pp(3) = pp(3) * 1.1
WINDOW (0, 0) (pp(1) - pp(2), 1.1 * (pp(3) - pp(4)))
FOR j% = pln% TO phn%
IF fl$(j%) <> "n" THEN PSET (lx%(j%) - pp(2), ly%(j%) - pp(4))
NEXT j%
IF clr% = 1 OR clr% = 2 THEN PRINT pp(2); pp(4); "<->": pp(1); pp(3)
IF clr% = 2 OR clr% = 3 THEN 9999
DO LOOP WHILE INKEYS = "" 9999 END SUB

SUB potpair (e#, i#, num%, switch%)
DIM coe(1500), ioe(1500)
e# = e#(1)
chs = e#(switch%)
sign = 1: redn
IF chs > e# THEN sign = -1: oxid
inc# = ABS(e#(2) - e#(1))
nswitch% = switch%
FOR j% = 1 TO num%
coe(j%) = e#(j%)
ioe(j%) = i#(j%)
NEXT j%
PRINT "THE POTENTIAL INCREMENT ON THE FORWARD SWEEP IS="; inc#
INPUT "DO YOU WISH TO CHANGE THE INCREMENT (Y/N)"; o$
IF o$ = "y" OR o$ = "Y" THEN INPUT "NEW INCREMENT"; inc#: nswitch% =
ABS(e# - chs) / inc# + 1
num% = 2 * nswitch% - 1
j1% = 1
FOR i% = 1 TO nswitch% + 1
e# = e# - sign * (i% - 1) * inc#
e#(i%) = e#
FOR j% = j1% TO switch%
IF e# < eo#(j%) AND e# > eo#(j% + 1) THEN
  i#(i%) = io#(j%) + (io#(j% + 1) - io#(j%))/ (eo#(j% + 1) - eo#(j%));
  j1% = j%;
  j% = switch%
NEXT j%
NEXT i%

j1% = switch% + 1
FOR i% = nswtch% + 1 TO nnum%
e# = e# + sign * (i% - nswtch%) * ino#
e#(i%) = e#
FOR j% = j1% TO nnum%
IF e# > eo#(j%) AND e# < eo#(j% + 1) THEN
  i#(i%) = io#(j%) + (io#(j% + 1) - io#(j%))/ (eo#(j% + 1) - eo#(j%));
  j1% = j%;
  j% = num%
NEXT j%
NEXT i%
PRINT num%
um% = nnum%
switch% = nswtch%
END SUB

SUB powerspectrumcalc (xreal#, yimag#, numdat%, delta#)
  DIM numdatr, normal, timespan

  numdatr = numdat% * 1!
normal = 1! / numdatr ^ 2

  CALL FFTSolve(xreal#, yimag#, numdat%, 0)

  xreal#(0) = SquareAndSum(xreal#(0), yimag#(0)) * normal
  FOR i% = 1 TO (numdat% \ 2) - 1
    xreal#(i%) = normal * (SquareAndSum(xreal#(i%), yimag#(i%)) +
                        SquareAndSum(xreal#(numdat% - i%), yimag#(numdat% - i%)))
  NEXT i%
  i% = numdat% \ 2
  xreal#(i%) = SquareAndSum(xreal#(i%), yimag#(i%)) * normal
  timespan = numdat% * delta#
  FOR i% = 0 TO (numdat% \ 2)
    yimag#(i%) = INT(i%) / timespan
  NEXT i%
END SUB

SUB sgsmooth (i#, num%)
  FOR j% = 1 TO num%
    eo#(i%) = i#(j%)
  NEXT j%
  i#(1) = (eo#(1) * 59 + eo#(2) * 54 + eo#(3) * 39 + eo#(4) * 14 + eo#(5) * -21) / 145
  i#(2) = (eo#(2) * 59 + (eo#(1) + eo#(3)) * 54 + eo#(4) * 39 + eo#(5) * 14 + eo#(6) * -21) / 199
  i#(3) = (eo#(3) * 59 + (eo#(2) + eo#(4)) * 54 + (eo#(1) + eo#(5)) * 39 + eo#(6) * 14 +
          eo#(7) * -21) / 238
  i#(4) = (eo#(4) * 59 + (eo#(3) + eo#(5)) * 54 + (eo#(2) + eo#(6)) * 39 + (eo#(1) +
           eo#(7)) * 14 + eo#(8) * -21) / 252
  FOR j% = 5 TO num% - 4
    i#(j%) = eo#(j%) * 59 + (eo#(j% - 1) + eo#(j% + 1)) * 54 + (eo#(j% - 2) + eo#(j% + 2))
\[ 39 + (\text{eo}((\% - 3) + \text{eo}((\% + 3))) \cdot 14 + (\text{eo}((\% - 4) + \text{eo}((\% + 4))) \cdot -21 \]
\[ \text{i}((\%)) = \text{i}((\%)) / 231 \]
\[ \text{NEXT} j\% \]
\[ \text{i}((\% - 3) = (\text{eo}((\% - 3) \cdot 59 + (\text{eo}((\% - 4) + \text{eo}((\% - 2))) \cdot 54 + (\text{eo}((\% - 5) + \text{eo}((\% - 1)))) \cdot 39 + (\text{eo}((\% - 6) + \text{eo}((\%)))) \cdot 14 + \text{eo}((\% - 7) \cdot -21) \cdot 252 \]
\[ \text{i}((\% - 2) = (\text{eo}((\% - 2) \cdot 59 + (\text{eo}((\% - 3) + \text{eo}((\% - 1)))) \cdot 54 + (\text{eo}((\% - 4) + \text{eo}((\% )))) \cdot 39 + (\text{eo}((\% - 5) \cdot -21)) \cdot 218 \]
\[ \text{i}((\% - 1) = (\text{eo}((\% - 1) \cdot 59 + (\text{eo}((\% - 2) + \text{eo}((\% )))) \cdot 54 + (\text{eo}((\% - 3) \cdot 39 + (\text{eo}((\% - 4) \cdot -21)) \cdot 199 \]
\[ \text{i}((\%)) = (\text{eo}((\% - 3) \cdot 59 + (\text{eo}((\% - 2) + \text{eo}((\% )))) \cdot 54 + (\text{eo}((\% - 3) \cdot 39 + (\text{eo}((\% - 4) \cdot -21)) \cdot 145 \]

FUNCTION SquareAndSum (a\#, b\#)

SquareAndSum = a\# ^ 2 + b\# ^ 2

END FUNCTION

SUB weight (fls\%, pp\%, e\%, i\%, sm\%, ii\%, ms\%, num\%, dt\#, pit\#, wi\%, wmm\%)  

c = 1 

FOR j\% = 1 TO num\% - 2 

b\% = num\% - j\% + 1 

rd = 4 * (dt\# / pit\#) ^ (1/2) / 3 

bot = (sm\%(b\%) - rd * i\%(b\%)) ^ 2 + (sm\%(j\%) - rd * i\%(j\%)) ^ 2 + dt\# * (i\%(j\%) ^ 2 * LOG(2.27 * b\%) + i\%(b\%) ^ 2 * LOG(2.27 * j\%)) / pit\# 

IF i\%(j\%) < 0 THEN wi\%(j\%) = (sm\%(b\%) - sm\%(j\%)) ^ 2 / (cra ^ 2 * dt\# * LOG(180! * j\% * b\%) / pit\# + cta ^ 2 * bot / i\%(j\%) ^ 2) 

IF ms\%(j\%) < 0 THEN wmm\%(j\%) = (sm\%(b\%) * i\%(j\%) - sm\%(j\%) * i\%(b\%)) ^ 2 / (2 * cta ^ 2 + cta ^ 2 * bot / ms\%(j\%) ^ 2) 

IF wi\%(j\%) > wimax THEN wimax = wi\%(j\%): wij% = j\% 

IF wmm\%(j\%) > wmmmax THEN wmmmax = wmm\%(j\%): wmnj% = j\% 

NEXT j\% 

CALL plot(is\%, pp\%, 2, c\#, wi\%, 1, num\% / 2) 

PRINT "E(w(ln i\%)max)="; c\#(wij%)

DO 

LOOP UNTIL INKEYS $ = "" 

CALL.plot(is\%, pp\%, 2, c\#, wmm\%, 1, num\% / 2) 

PRINT "E(w(1/m\%)max)="; c\#(wmn%)

DO 

LOOP UNTIL INKEYS $ = ""

END SUB

FUNCTION Welch (n\%, j\%) 

Welch = 1 - ((j\% - .5 * (n\% - 1)) / (.5 * (n\% + 1))) ^ 2

END FUNCTION

SUB WindowFFTData (xreal\%, yimag\%, numdat\%, wind\%)  

DIM multiplier 

FOR i\% = 0 TO numdat\% - 1 

SELECT CASE wind\% 

CASE 0 

multiplier = 1 

CASE 1 

""
multiplier = Parzen(numdat%, i%)
CASE 2
  multiplier = Hanning(numdat%, i%)
CASE 3
  multiplier = Welch(numdat%, i%)
CASE 4
  multiplier = Hamming(numdat%, i%)
CASE 5
  multiplier = ExactBlackman(numdat%, i%)
CASE ELSE
  multiplier = 1!
END SELECT
xreal#(i%) = multiplier * xreal#(i%)
yimag#(i%) = multiplier * yimag#(i%)
NEXT i%
END SUB

SUB wls (fl$, pp0, wmd%, w#, lx#, ly#, j1, jh, m#, c#)
  IF wmd% = 1 THEN 100
  FOR j% = j1 TO jh
    w#(j%) = 1
    NEXT j%
  100 sx# = 0: sy# = 0: sxy# = 0: sxsq# = 0: sy# = 0: sw# = 0
  FOR j% = j1 TO jh
    sx# = sx# + w#(j%) * lx#(j%)
    sy# = sy# + w#(j%) * ly#(j%)
    sxy# = sxy# + w#(j%) * lx#(j%) * ly#(j%)
    sxsq# = sxsq# + w#(j%) * lx#(j%) * lx#(j%)
    sy# = sy# + w#(j%) * ly#(j%) * ly#(j%)
    sw# = sw# + w#(j%)
  40010 NEXT j%
  m# = (sw# * sxy# - sx# * sy#) / (sw# * sxsq# - sx# * sx#)
  c# = -(sx# * sxy# - sy# * sxsq#) / (sw# * sxsq# - sx# * sx#)
  CALL plot(fl$, pp0, 1, lx#, ly#, j1, jh, m#, c#)
  FOR j% = j1 TO jh
    IF fl$(j%) <> "n" THEN ly#(j%) = m# * lx#(j%) + c#
    NEXT j%
    rsq# = 1
    IF sy# ^ 2 <> sxsq# * sw# THEN rsq# = (sw# * sxy# - sx# * sy#) ^ 2 / (sw# * sxsq# - sxsq# ^ 2) * (sw# * sysq# - sy# ^ 2))
  PRINT m#, c#, rsq#
  CALL plot(fl$, pp0, 0, lx#, ly#, j1, jh)
END SUB
""" PROGRAM MICSQR CR.BAS
""" WRITTEN BY P.J.MAHON

DEFDBL A-Z
DEFINT I-J, M

DECLARE SUB FILEIT (FILE$)
DECLARE SUB SIMULT (NR, MC, NCC, ZMCH)
DECLARE SUB PLOT (PX(), PY(), PP(), IPLN, IPHN, CP)
DECLARE SUB HELP ()
DECLARE SUB INIT ()
DECLARE SUB DISKGRID ()
DECLARE SUB PRINTINPUTDATA ()
DECLARE SUB PROFILE ()
DECLARE SUB WAITFORME ()
COMMON SHARED PX(), PY(), P1X(), P1Y(), YMID0, FAB0(), FDC0(), AREA()
COMMON SHARED DY1(), DY2(), DR1(), DR2(), RMID0, XMAT1(), ZMTMP()
COMMON SHARED ZMAT0(), CO()
COMMON SHARED A11(), A12(), DAI()
COMMON SHARED B11(), B12(), DBI()
COMMON SHARED C11(), C12(), DCI()
COMMON SHARED D11(), D12(), DDI()
COMMON SHARED E0AB, K0ABX, ALPHAB
COMMON SHARED E0DC, K0DCX, ALPHDC
COMMON SHARED KEQBC, KFBCX, KFBC, KBBB, KFCR
COMMON SHARED KEQAD, KFADX, KFAD, KBAD, KBCR
COMMON SHARED D0, IMAX, IMT, MTOUT, MTPROF
COMMON SHARED ESTART, EREV, NHALF
COMMON SHARED ASTART, BSTART, CSTART, DSTART
COMMON SHARED Q$, W$
COMMON SHARED BETAY, BETAY1, BETAR, BETAR1
COMMON SHARED PI, TIME, TMAX, R0, VDT, SPH
COMMON SHARED IYMAX, IRMAX, IYMT, IRMT, IR0, MTMAX, AREASUM
COMMON SHARED IPLN, IPHN, IRDIM, IYDIM, NR, MC, NCC, ZMCH, WE,
FRT, E
DIM SHARED A11(40, 50), A12(40, 50), DAI(40, 50), FAB0(40), FDC0(40),
AREA(40)
DIM SHARED B11(40, 50), B12(40, 50), DBI(40, 50), ZMAT(5, 10), CO(5)
DIM SHARED C11(40, 50), C12(40, 50), DCI(40, 50), P1Y(2000), PP(4)
DIM SHARED D11(40, 50), D12(40, 50), DDI(40, 50)
DIM SHARED DY1(40), DY2(40), DR1(50), DR2(50), YMID(40), RMID(50)
IRDIM = 50
IYDIM = 40

100 CLS
PRINT "Program SQUISIMCR.BAS"
PRINT
PRINT
PRINT "Program to try CV using the Du Fort-Frankel Algorithm as suggested "
PRINT "by da Silva, Avaca and Gonzalez (per review for JEAC 12/2/88)."
PRINT
PRINT "Quasi-reversible CV with square-scheme (with cross reactions)"
PRINT "A + c --> B (EoAB, kAB, alphaAB)"
PRINT "D + c --> C (EoDC, kDC, alphaDC)"
PRINT "B --> C (kBC, KEQBC)"
PRINT "A <-> D  (kfAD, KEQAD)"
PRINT "A + C <-> B + D  (kfCR)"
PRINT "Simulation starts with the assumption that the entire system is in equilibrium at the starting potential."
PRINT "Assume all D's same and that a+b+c+d is constant."
PRINT "Press any KEY to CONTINUE"
PRINT "FRT = 96487.7#/ (8.314399999999999 * 298#)
PI = 3.1415927#
ESTART = -.3
EREV = .2
NHALF = 2
E0AB = 0
E0DC = -.2
OKFAD = .005
OKFBC = .005
OKFCR = 0
KEQBC = .01
OK0AB = 1E+20
OK0DC = 1E+20
ALAB = .5#
ALDC = .5#
OVDT = .001
DORW = .00001
RORW = .01
TEMP = 298
DO
LOOP UNTIL INKEY$ <> ""
PRINT "12, Alpha for AB" ; USING "##.###\ldots"; ALAB
PRINT "13, Alpha for DC" ; USING "##.###\ldots"; ALDC
PRINT "14, Scan Rate (V/s)" ; USING "##.###\ldots"; OVDT
PRINT "15, Diffusion Coefficient (cm^2/s)" ; USING "##.###\ldots"; D0RW
PRINT "16, Disk Radius (cm)" ; USING "##.###\ldots"; R0RW
PRINT "17, Temperature (K)" ; USING "##.###\ldots"; TEMP
PRINT "18, Exit";
PRINT : INPUT "Input Selection"; IN
SELECT CASE IN
CASE IS = 0: GOTO 300
CASE IS = 1: INPUT "New Potential (V)"; ESTART
CASE IS = 2: INPUT "New Potential (V)"; EREV
CASE IS = 3: INPUT "New Number of Half Cycles"; NHALF
CASE IS = 4: INPUT "New Potential (V)"; E0AB
CASE IS = 5: INPUT "New Potential (V)"; E0DC
CASE IS = 6: INPUT "New Rate"; OKFAD
CASE IS = 7: INPUT "New Rate"; OKFBC
CASE IS = 8: INPUT "New Constant"; KEQBC
CASE IS = 9: INPUT "New Rate"; OKFCR
CASE IS = 10: INPUT "New Rate"; OK0AB
CASE IS = 11: INPUT "New Rate"; OK0DC
CASE IS = 12: INPUT "New Alpha"; ALAB
CASE IS = 13: INPUT "New Alpha"; ALDC
CASE IS = 14: INPUT "New Scan Rate"; OVDT
CASE IS = 15: INPUT "New Diffusion Coefficient (cm^2/s)"; D0RW
CASE IS = 16: INPUT "New Disk Radius (cm)"; R0RW
CASE IS = 17: INPUT "New Temperature (K)"; TEMP
CASE IS = 18: END
END SELECT
FRT = 96487.7# / (8.31439999999999# * TEMP)
GOTO 200
300 INUM = 0
DE0 = E0DC - E0AB
K0ABX = OK0AB * R0RW / D0RW
K0DCX = OK0DC * R0RW / D0RW
KFADX = OKFAD * R0RW^2 / D0RW
KFBCX = OKFBC * R0RW^2 / D0RW
KEQAD = KEQBC * EXP(FRT * DE0)
KBBCX = KFBCX / KEQBC
KBADX = KFADX / KEQAD
KFCRX = OKFCR * R0RW^2 / D0RW
KBCRX = KFCRX / EXP(FRT * DE0)
PRINT
PRINT "KEQAD = "; KEQAD; " (computed from KEQBC and E0DC-E0AB)."
KMAX = KFBCX + 9.999999E-21' in case you wanna test it for all k=0
IF KBBGX > KMAX THEN KMAX = KBBGX
IF KFADX > KMAX THEN KMAX = KFADX
IF KBADX > KMAX THEN KMAX = KBADX
IF KBCRX > KMAX THEN KMAX = KBCRX
IF KFCRX > KMAX THEN KMAX = KFCRX
'----------Calculate Simulation Parameters-----------------------------
' Calculate minimum R0 based on kmax:
SPh = D0RW / (FRT * OVDT * R0RW^2)
R0 = SQRT(50 * (KMAX + 9.999999E-21))' Protect for kmax=0
VDT = .001
IF R0 < .25 THEN R0 = .25
  ' Calculate min. R0 or max. vdt based on sphericity and \( D = 0.00001/vdt^2 \)
R01 = SQRT(0.00001 / (FRT * VDT ^ 3 * SPH))
IF R01 < R0 THEN
VDT = (SQRT(0.00001 / (FRT * SPH))) / R01 ^ .666666666#
ELSE
R0 = R01
END IF
  ' Make sure it is done right.
D0 = .00001 / VDT ^ 2
SPHSIM = D0 / (FRT * VDT * R0 ^ 2)
IF ABS(SPHSIM - SPH) / SPH > .000001 THEN PRINT "Screwed up something."
STOP

IF VDT > .0001 GOTO 500
400 PRINT "vdt = "; VDT; ". Too small; Need double precision and that isn't "
PRINT "practical on a PC; also, computation will take too long."
PRINT "To continue type C; to quit restart type R"
Q$ = INPUT$(1)
IF Q$ = "C" OR Q$ = "c" THEN GOTO 500
IF Q$ = "r" OR Q$ = "R" THEN GOTO 100
GOTO 400
500 EOUT = .001
EPROF = .1
K0AB = K0ABX * D0 / R0
K0DC = K0DCX * D0 / R0
KFBC = KFBCX * D0 / R0 ^ 2
KBBC = KBBCX * D0 / R0 ^ 2
KFAD = KFADX * D0 / R0 ^ 2
KBAD = KBADX * D0 / R0 ^ 2
KFCR = KFCRX * D0 / R0 ^ 2
KBCR = KBCRX * D0 / R0 ^ 2
VDT = VDT * ((EREV - ESTART) / ABS(ESTART - EREV))
MTREV = INT(ABS((EREV - ESTART) / VDT))
MT_PLOT = INT(ABS(.001 / VDT) + .01)
MTMAX = NHALF * MTREV
TMAX = MTMAX
MTOUT = INT(ABS(EOUT / VDT) + .01)
MTPROF = INT(ABS(EPROF / VDT) + .01)
MTLAB = 15 * MTOUT
E = ESTART - VDT / 2#
BETAY = .5#
BETAR = .5
BETAY1 = EXP(BETAY) - 1#
BETAR1 = EXP(BETAR) - 1
CALL INIT
CALL DISKGRID
CALL PRINTINPUTDATA
NR1 = 4; MC1 = 4; NCC1 = 1; ZMCH = 0; IRHS = NR1 + NCC1
600 '--------------------------------------Do it-------------------
PRINT " E fnorm(cv) fnorm(ss)"
FOR MT = 1 TO MTMAX
  T = MT
  Q$ = INKEY$
  IF Q$ = "h" OR Q$ = "H" THEN CALL HELP
IF Q$ = "P" OR Q$ = "p" THEN CALL PROFILE: CALL WAITFORME
IF Q$ <> "q" AND Q$ <> "Q" THEN GOTO 700
CALL PRINTINPUTDATA
PRINT "Restart (Y/aok)";
RS = INPUT$1)
IF RS = "y" OR RS = "Y" THEN GOTO 100
PRINT "User Interrupt": END
700 IF Q$ = "I" OR Q$ = "i" THEN CALL PRINTINPUTDATA: CALL WAITFORME
IF MT > 10 AND (MT - 1) / MTREV = INT((MT - 1) / MTREV) THEN E = E + VDT:
VDT = -VDT
E = E + VDT
KEFAB = K0AB * EXP(-ALPHAB * FRT * (E - E0AB))
KEBAB = K0AB * EXP((1 - ALPHAB) * FRT * (E - E0AB))
KEFDC = K0DC * EXP(-ALPHDC * FRT * (E - E0DC))
KEBD = K0DC * EXP((1 - ALPHDC) * FRT * (E - E0DC))
ITYM = INT(LOG6 * BETAY1 * SQR(D0 * T) + 1) / BETAY
IF ITYM > IYMAX - 1 THEN ITYM = IYMAX - 1
IRM = IR0 + INT(LOG6 * BETAR1 * SQR(D0 * T) + 1) / BETAR
IF IRM > IRMAX - 1 THEN IRM = IRMAX - 1
'-------------------------------------------------------------
'-----Solve for changes for iy=1; ir<=ir0- (electroactive part)-----
FOR IR = 1 TO IR0
'----------Compute a coefficients
DENOMW1 = (DY1(1) + KEBAB + KEFAB) / DY1(1)
WF1 = KEFAB / DENOMW1
WB1 = KEBAB / DENOMW1
NUMA = DY2(1) + DR1(IR) + DR2(IR) + WF1 + KFAD + KFCR * CI1(1, IR)
XMAT1(1, 1) = 1# + NUMA
XMAT1(1, 2) = -(WB1 + KBCR * DI1(1, IR))
XMAT1(1, 3) = KFCR * AI1(1, IR)
XMAT1(1, 4) = -(KBAD + KBCR * BI1(1, IR))
XMAT1(1, IRHS) = DY2(1) * AI2(2, IR) + DR2(IR) * AI2(1, IR + 1) + DR1(IR) * AI2(1, IR - 1) + WB1 * BI1(1, IR) + KBAD * DI1(1, IR) - NUMA * AI1(1, IR)
+ KBCR * BI1(1, IR) * DI1(1, IR)
'----------Compute b coefficients
NUMB = DY2(1) + DR1(IR) + DR2(IR) + WB1 + KFBC + KBCR * DI1(1, IR)
XMAT1(2, 1) = -(WF1 + KFCR * CI1(1, IR))
XMAT1(2, 2) = 1# + NUMB
XMAT1(2, 3) = -(KBB + KFCR * AI1(1, IR))
XMAT1(2, 4) = -KBCR * AI1(1, IR)
XMAT1(2, IRHS) = DY2(1) * BI2(2, IR) + DR2(IR) * BI2(1, IR + 1) + DR1(IR) * BI2(1, IR - 1) + WF1 * AI1(1, IR) + KBB + CI1(1, IR) - NUMB * BI1(1, IR)
+ KFCR * AI1(1, IR) * CI1(1, IR)
'----------Compute c coefficients
DENOMW2 = (DY1(1) + KEBDC + KEFDC) / DY1(1)
WF2 = KEFDC / DENOMW2
WB2 = KEBDC / DENOMW2
NUMC = DY2(1) + DR1(IR) + DR2(IR) + WB2 + KBB + KFCR * AI1(1, IR)
XMAT1(3, 1) = KFCR * CI1(1, IR)
XMAT1(3, 2) = -(KFBC + KBCR * DI1(1, IR))
XMAT1(3, 3) = 1# + NUMC
XMAT1(3, 4) = -(WF2 + KBCR * BI1(1, IR))
XMAT1(3, IRHS) = DY2(1) * CI2(2, IR) + DR2(IR) * CI2(1, IR + 1) + DR1(IR) * CI2(1, IR - 1) + WF2 * DI1(1, IR) + KFBC * BI1(1, IR) - NUMC * CI1(1, IR)
+ KBCR * BI1(1, IR) * DI1(1, IR)
Compute d coefficients
NUMD = DY2(1) + DR1(IR) + DR2(IR) + WF2 + KBAD + KBCR * BI1(1, IR)
XMAT1(4, 1) = -(KFAD + KFCR * CI1(1, IR))
XMAT1(4, 2) = KBCR * DI1(1, IR)
XMAT1(4, 3) = -(WB2 + KFCR * AI1(1, IR))
XMAT1(4, 4) = 1 + NUMD
XMAT1(4, IRHS) = DY2(1) * DI2(2, IR) + DR2(IR) * DI2(1, IR + 1) + DR1(IR) *
    DI2(1, IR - 1) + WB2 * CI1(1, IR) + KFAD * AI1(1, IR) - NUMD * DI1(1, IR)
    + KFCR * AI1(1, IR) * CI1(1, IR)
CALL SIMULT(NR1, MC1, NCC1, ZMCH)
DAI(1, IR) = XMAT1(1, IRHS)
DBI(1, IR) = XMAT1(2, IRHS)
DCI(1, IR) = XMAT1(3, IRHS)
DDI(1, IR) = XMAT1(4, IRHS)
FAB0(IR) = -WF1 * (AI1(1, IR) + DAI(1, IR)) + WB1 * (BI1(1, IR) + DBI(1, IR))
FDC0(IR) = -WF2 * (DI1(1, IR) + DDI(1, IR)) + WB2 * (CI1(1, IR) + DCI(1, IR))
NEXT IR

-----------------------------------------------------------------

Solve for changes for i=y=1; ir>ir0- (electroinactive part)
FOR IR = IR0 + 1 TO IRMT
    Compute a coefficients
    NUMA = DY2(1) + DR1(IR) + DR2(IR) + KFAD + KFCR * CI1(1, IR)
    XMAT1(1, 1) = 1 + NUMA
    XMAT1(1, 2) = -KBCR * DI1(1, IR)
    XMAT1(1, 3) = KFCR * AI1(1, IR)
    XMAT1(1, 4) = -(KBAD + KBCR * BI1(1, IR))
    XMAT1(1, IRHS) = DY2(1) * AI1(2, IR) + DR2(IR) * AI2(1, IR + 1) + DR1(IR) *
        AI2(1, IR - 1) + KBAD * DI1(1, IR) - NUMA * AI1(1, IR) + KBCR * BI1(1, IR) * DI1(1, IR)
    XMAT1(2, IRHS) = DY2(1) + DR1(IR) + DR2(IR) + KFBC + KBAD * DI1(1, IR)
    XMAT1(2, 1) = -KFCR * CI1(1, IR)
    XMAT1(2, 2) = 1 + NUMB
    XMAT1(2, 3) = -(KBBC + KFCR * AI1(1, IR))
    XMAT1(2, 4) = KBCR * BI1(1, IR)
    XMAT1(2, IRHS) = DY2(1) * BI2(2, IR) + DR2(IR) * BI2(1, IR + 1) + DR1(IR) *
        BI2(1, IR - 1) + KBBC * CI1(1, IR) - NUMB * BI1(1, IR) + KFCR * AI1(1, IR) * CI1(1, IR)
    XMAT1(3, IRHS) = DY2(1) + DR1(IR) + DR2(IR) + KBBC + KFCR * AI1(1, IR)
    XMAT1(3, 1) = KFCR * CI1(1, IR)
    XMAT1(3, 2) = -(KBBC + KFCR * DI1(1, IR))
    XMAT1(3, 3) = 1 + NUMC
    XMAT1(3, 4) = -KBCR * BI1(1, IR)
    XMAT1(3, IRHS) = DY2(1) * CI1(2, IR) + DR2(IR) * CI1(1, IR + 1) + DR1(IR) *
        CI1(1, IR - 1) + KFBC * BI1(1, IR) - NUMC * CI1(1, IR) + KBCR * BI1(1, IR) * DI1(1, IR)
    XMAT1(4, IRHS) = DY2(1) + DR1(IR) + DR2(IR) + KBAD + KBCR * BI1(1, IR)
    XMAT1(4, 1) = -(KFAD + KFCR * CI1(1, IR))
    XMAT1(4, 2) = KBCR * DI1(1, IR)
    XMAT1(4, 3) = -KFCR * AI1(1, IR)
    XMAT1(4, 4) = 1 + NUMD
    XMAT1(4, IRHS) = DY2(1) * DI2(2, IR) + DR2(IR) * DI2(1, IR + 1) + DR1(IR) *
        DI2(1, IR - 1) + KFAD * AI1(1, IR) - NUMD * DI1(1, IR) + KFCR * AI1(1, IR) * DI1(1, IR)
IR) * CI1(I, IR)
CALL SIMULT(NR1, MC1, NCC1, ZMCH)
DA1(I, IR) = XMAT1(1, IRHS)
DB1(I, IR) = XMAT1(2, IRHS)
DC1(I, IR) = XMAT1(3, IRHS)
DD1(I, IR) = XMAT1(4, IRHS)
NEXT IR

'-----Solve for changes for iy>1 and all ir--(DR1(0)=0)---------------------
FOR IY = 2 TO IYMT
FOR IR = 1 TO IRMT

'-----Compute a coefficients
NUMA = DY1(IY) + DY2(IY) + DR1(IR) + DR2(IR) + KFAD * KFCR * CI1(IY, IR)
XMAT1(1, 1) = 1# + NUMA
XMAT1(1, 2) = -KBCR * DI1(IY, IR)
XMAT1(1, 3) = KFCR * AI1(IY, IR)
XMAT1(1, 4) = -(KBAD + KBCR * BI1(IY, IR))
XMAT1(1, IRHS) = DY2(IY) * AI2(IY + 1, IR) + DY1(IY) * AI2(IY - 1, IR) +
                 DR2(IR) * AI2(IY, IR + 1) + DR1(IR) * AI2(IY, IR - 1) + KBAD * DI1(IY, IR)
- NUMA * AI1(IY, IR) + KBCR * BI1(IY, IR) * DI1(IY, IR)

'-----Compute b coefficients
NUMB = DY1(IY) + DY2(IY) + DR1(IR) + DR2(IR) + KFBC + KBCR * DI1(IY, IR)
XMAT1(2, 1) = -KFCR * CI1(IY, IR)
XMAT1(2, 2) = 1# + NUMB
XMAT1(2, 3) = -(KFCR + KFCR * AI1(IY, IR))
XMAT1(2, 4) = KBCR * BI1(IY, IR)
XMAT1(2, IRHS) = DY2(IY) * BI2(IY + 1, IR) + DY1(IY) * BI2(IY - 1, IR) +
                 DR2(IR) * BI2(IY, IR + 1) + DR1(IR) * BI2(IY, IR - 1) + KBBC * CI1(IY, IR)
- NUMB * BI1(IY, IR) + KFCR * AI1(IY, IR) * CI1(IY, IR)

'-----Compute c coefficients
NUMC = DY1(IY) + DY2(IY) + DR1(IR) + DR2(IR) + KBBC + KFCR * AI1(IY, IR)
XMAT1(3, 1) = KFCR * CI1(IY, IR)
XMAT1(3, 2) = -(KFBC + KBCR * DI1(IY, IR))
XMAT1(3, 3) = 1# + NUMC
XMAT1(3, 4) = -KBCR * BI1(IY, IR)
XMAT1(3, IRHS) = DY2(IY) * CI2(IY + 1, IR) + DY1(IY) * CI2(IY - 1, IR) +
                 DR2(IR) * CI2(IY, IR + 1) + DR1(IR) * CI2(IY, IR - 1) + KFBC * BI1(IY, IR)
- NUMC * CI1(IY, IR) + KBCR * BI1(IY, IR) * DI1(IY, IR)

'-----Compute d coefficients
NUMD = DY1(IY) + DY2(IY) + DR1(IR) + DR2(IR) + KBAD + KBCR * BI1(IY, IR)
XMAT1(4, 1) = -(KFAD + KFCR * CI1(IY, IR))
XMAT1(4, 2) = KBCR * DI1(IY, IR)
XMAT1(4, 3) = -KFCR * AI1(IY, IR)
XMAT1(4, 4) = 1# + NUMD
XMAT1(4, IRHS) = DY2(IY) * DI2(IY + 1, IR) + DY1(IY) * DI2(IY - 1, IR) +
                 DR2(IR) * DI2(IY, IR + 1) + DR1(IR) * DI2(IY, IR - 1) + KFAD * AI1(IY, IR)
- NUMD * DI1(IY, IR) + KFCR * AI1(IY, IR) * CI1(IY, IR)
CALL SIMULT(NR1, MC1, NCC1, ZMCH)
DA1(IY, IR) = XMAT1(1, IRHS)
DB1(IY, IR) = XMAT1(2, IRHS)
DC1(IY, IR) = XMAT1(3, IRHS)
DD1(IY, IR) = XMAT1(4, IRHS)
NEXT IR
NEXT IY

'-----------------------------------Reset-----------------------------------

FOR IY = 1 TO IYMT
FOR IR = 1 TO IRMT
   A13 = A11(IY, IR) + 2# * DA1(IY, IR): A11(IY, IR) = A12(IY, IR): A12(IY, IR) =
   A13
   B13 = B11(IY, IR) + 2# * DB1(IY, IR): B11(IY, IR) = B12(IY, IR): B12(IY, IR) =
   B13
   C13 = C11(IY, IR) + 2# * DC1(IY, IR): C11(IY, IR) = C12(IY, IR): C12(IY, IR) =
   C13
   D13 = D11(IY, IR) + 2# * DD1(IY, IR): D11(IY, IR) = D12(IY, IR): D12(IY, IR) =
   D13
NEXT IR
NEXT IY

'-----------------------------------Output-----------------------------------

IF MT / MTOUT <> INT(MT / MTOUT) THEN 900
F0SUM = 0
FOR IR = 1 TO IR0
   F0SUM = F0SUM + (FAB0(IR) + FDC0(IR)) * AREA(IR)
NEXT IR
F0NORMCV = F0SUM / SQR(D0 * FRT * ABS(VDT))
F0NORMD = F0SUM / ((4 / PI) * D0 / R0)
INUM = INUM + 1
P1X(INUM) = E
P1Y(INUM) = F0NORMD
IF MT / MTLAB <> INT(MT / MTLAB) THEN GOTO 800
PRINT
   PRINT " E    fnorm(cv)   fnorm(ss)"
800 PRINT USING "#.####
   ; E, F0NORMCV, F0NORMD
900 IF MT / MTPROF <> INT(MT / MTPROF) THEN GOTO 1000
PRINT " x     a       b       c       d       sum-1"
   SUM = 0
FOR IY = 1 TO IYMT
   FOR IR = 1 TO IRMT
      SUM = A12(IY, IR) + B12(IY, IR) + C12(IY, IR) + D12(IY, IR)
      IF IR = 1 THEN PRINT USING "###.####
         ; YMID(IY), A12(IY, 1), B12(IY, 1), C12(IY, 1), D12(IY, 1), SUM - 1
NEXT IR
NEXT IY
PRINT
1000 NEXT MT

20000 INPUT " COMPARE WITH EXPERIMENTAL CURVE"; A$
   IF A$ = "N" OR A$ = "n" THEN CALL PLOT(P1X(), P1Y(), PP(), 1, INUM, 0): GOTO 1100
INPUT "FILENAME"; OS$
OPEN OS$ FOR INPUT AS #1
INPUT #1, TITLE$
INPUT #1, IDAT, Z, Z, Z, Z, Z, Z,
FOR I = 1 TO IDAT
   INPUT #1, PX(I), PY(I)
NEXT I
CLOSE #1
CLS
CALL PLOT(P1X(), P1Y(), PP(), 1, INUM, 0)
CALL PLOT(PX0, PY0, PP0, 1, IDAT, 1)
1100 PRINT " $fBC=";
PRINT USING "##.#####`````````; OKFBC,
PRINT " $eqBC=";
PRINT USING "##.#####`````````; KEQBC
PRINT " $fAD=";
PRINT USING "##.#####`````````; OKFAD,
PRINT " $eqAD=";
PRINT USING "##.#####`````````; KEQAD
PRINT O$
DO
LOOP UNTIL INKEY$ <> ""
INPUT "OUTPUT DATA TO FILE"; A$
IF A$ = "y" OR A$ = "Y" THEN 200
INPUT "OUTPUT AS CURRENT DATA"; O$
CFACT = 1
IF O$ = "Y" OR O$ = "y" THEN INPUT "BULK CONCENTRATION (M)";
CBULK: CFACT = 4 * 1 * 96487.7 * CBULK * D0RW * R0RW / 1000
INPUT "FILENAME"; A$
INPUT "TITLE"; TITLE$
OPEN A$ FOR OUTPUT AS 1
PRINT #1, TITLE$
PRINT #1, INUM, TEMP, 1, OVDT, D0RW, R0RW, ESTART, EREV, CBULK
FOR I = 1 TO INUM
PRINT #1, P1X(I), P1Y(I) * CFACT
NEXT I
CLOSE 1
GOTO 200
END

SUB DISKGRID STATIC
' Compute operative DY1(IY) and DY2(IY) for diffusion normal to disk.
FOR IY = 1 TO IYMAX
    DY2(IY) = D0 * EXP(2 * BETAY * (.75 - IY))
    DY1(IY) = D0 * EXP(2 * BETAY * (1.25 - IY))
    YMID(IY) = (EXP(BETAY * (IY - .5)) - 1) / BETAY1
    IF IY = 1 THEN DY1(IY) = D0 / YMID(1)
NEXT IY
' Compute operative DR1(IR) and DR2(IR) for radial cylindrical diffusion.
' First, for r>r0:
FOR IR = IR0 + 1 TO IRMAX
    I = IR - IR0
    DR = EXP(BETAR * (I - 1))
    R2 = R0 + (EXP(BETAR * I) - 1) / BETAR1
    R1 = R2 - DR
    DRBAR2 = EXP(BETAR * (I - .5))
    DRBAR1 = EXP(BETAR * (I - 1.5))
    RRMD = (EXP(BETAR * (I - .5)) - 1) / BETAR1
    RMD(IR) = R0 + RRMD
    DR2(IR) = D0 / (DRBAR2 * (DR - .5 * DR ^ 2 / R2))
    DR1(IR) = D0 / (DRBAR1 * (DR + .5 * DR ^ 2 / R1))
    IF I = 1 THEN DR1(IR) = D0 / (2 * RRMD * (DR + .5 * DR ^ 2 / R0))^mid ir0+1
    to mid ir0
NEXT IR
' Then, for r<r0

FOR IR = 2 TO IR0
    I = IR0 + 1 - IR
    DR = EXP(BETAR * (I - 1))
    R2 = R0 - (EXP(BETAR * (I - 1)) - 1) / BETAR1
    R1 = R2 - DR
    AREA(IR) = (R2^2 - R1^2) / R0^2
    RRMD = (EXP(BETAR * (I - .5)) - 1) / BETAR1
    RMID(IR) = R0 - RRMD
    DRBAR2 = EXP(BETAR * (I - 1.5))
    DRBAR1 = EXP(BETAR * (I - .5))
    DR2(IR) = D0 / (DRBAR2 * (DR - .5 * DR^2 / R2))
    DR1(IR) = D0 / (DRBAR1 * (DR + .5 * DR^2 / R1))
    IF I = 1 THEN DR2(IR) = D0 / (2 * RMID * (DR - .5 * DR^2 / R0))
    IF IR = 2 THEN DR1(IR) = D0 / (RMID(IR) * (DR + .5 * DR^2 / R1))
NEXT IR
    DR1(1) = 0
    R2 = R0 - (EXP(BETAR * (IR0 - 1)) - 1) / BETAR1
    AREA(1) = (R2 / R0)^2
    DR2(1) = D0 / (RMID(2) * .5 * R2)
END SUB

'----------------- Subroutine FILEIT(FILE$)-----------------'

SUB FILEIT (FILE$) STATIC
    OPEN FILES FOR OUTPUT AS #1
    PRINT #1, "Simulator values:");
    PRINT #1, " D0 = ");
    PRINT #1, USING "#####"; D0
    PRINT #1, " Beta = ");
    PRINT #1, USING "#####"; BETA
    PRINT #1, " VDT = ");
    PRINT #1, USING "#####"; VDT
    PRINT #1, " MDTMAX = ");
    PRINT #1, USING "#####"; MDTMAX
    PRINT #1, " IMAX = ");
    PRINT #1, USING "#####"; IMAX
    PRINT #1, "");
    PRINT #1, " Electron transfer parameters for the A/B couple:");
    PRINT #1, " E0AB = ");
    PRINT #1, USING "#####"; E0AB
    PRINT #1, " k0AB = ");
    PRINT #1, USING "#####"; k0AB
    PRINT #1, " k0ABX = ");
    PRINT #1, USING "#####"; k0ABX
    PRINT #1, " alphAB = ");
    PRINT #1, USING "#####"; alphAB
    PRINT #1, " ALPHAB = ");
    PRINT #1, USING "#####"; ALPHAB
    PRINT #1, "");
    PRINT #1, " Electron transfer parameters for the D/C couple:");
    PRINT #1, " E0DC = ");
    PRINT #1, USING "#####"; E0DC
    PRINT #1, " k0DC = ");
    PRINT #1, USING "#####"; k0DC
    PRINT #1, " k0DCX = ");
    PRINT #1, USING "#####"; k0DCX
    PRINT #1, " alphDC = ");
    PRINT #1, USING "#####"; alphDC
    PRINT #1, " ALPHDC = ");
    PRINT #1, "");
    PRINT #1, " Homogeneous kinetic parameters:");
    PRINT #1, " kfBC = ");
    PRINT #1, USING "#####"; kfBC
    PRINT #1, " KFBCX = ");

PRINT #1, " KcqBC = ";
PRINT #1, USING "####

PRINT #1, " kfBC = ";
PRINT #1, USING "####

PRINT #1, " kbBC = ";
PRINT #1, USING "####

PRINT #1, " KFADX = ";
PRINT #1, USING "####

PRINT #1, " KEQAD = ";
PRINT #1, USING "####

PRINT #1, " KEQAD = ";
PRINT #1, USING "####

PRINT #1, " CV control parameters:
PRINT #1, " Estart = ";
PRINT #1, USING "####

PRINT #1, " Erev = ";
PRINT #1, USING "####

PRINT #1, " nhalf = ";
PRINT #1, USING "####

PRINT #1, " Starting concentrations:
PRINT #1, " astart = ";
PRINT #1, USING "####

PRINT #1, " bstart = ";
PRINT #1, USING "####

PRINT #1, " cstart = ";
PRINT #1, USING "####

PRINT #1, " dstart = ";
PRINT #1, USING "####

PRINT #1, " NOW WE BEGIN
END SUB

SUB HELP STATIC
-----------Subroutine HELP----------
PRINT "This program has a number of useful interrupts:
PRINT PRINT "Type"
PRINT "-----------------------------------------------"
PRINT "H Summons this HELP routine.
PRINT "I Gives a listing of all parameters (some of this stuff"
PRINT "will be simulation junk that is of no interest to most).
PRINT PRINT "P Gives Some concentration and flux profiles."
PRINT PRINT "Q Exit Program"
PRINT PRINT "Hit any key to continue."
Q$ = INPUT$(1)
PRINT "-----------------------------------------------"
END SUB
SUB INIT STATIC
  IYMAX = LOG(6 * BETAY1 * SQR(D0 * TMAX) + 1) / BETAY
  IYMAXSS = LOG(1000 * BETAY1 * R0 + 1) / BETAY
  IF IYMAX > IYMAXSS THEN IYMAX = IYMAXSS
  IR0 = 1 + INT(LOG(R0 * BETAR1 + 1) / BETAR)
  IRMAX = IR0 + LOG(6 * BETAR1 * SQR(D0 * TMAX) + 1) / BETAR
  IRMAXSS = IR0 + LOG(1000 * BETAR1 * R0 + 1) / BETAR
  IF IRMAX > IRMAXSS THEN IRMAX = IRMAXSS
  IF IRMAX < IRDIM THEN 2000
  PRINT "irmax ("; IRMAX; "); exceed dimension ("; IRDIM; "); change something."
  STOP
  2000 IF IYMAX < IYDIM THEN 2100
  PRINT "iyamx ("; IYMAX; "); exceed dimension ("; IYDIM; "); change something."
  STOP

2100 '---------------------Initialization-------------------------------
  WAB = EXP(FRT * (E - E0AB))
  WDC = EXP(FRT * (E - E0DC))
  ASTART = 1/#(1/# + 1/# / WAB + KEQBC / WAB + KEQAD)
  BSTART = ASTART / WAB
  CSTART = BSTART * KEQBC
  DSTART = BSTART * KEQAD
  PRINT " astart = ";
  PRINT USING "#.####"; ASTART
  PRINT " bstart = ";
  PRINT USING "#.####"; BSTART
  PRINT " cstart = ";
  PRINT USING "#.####"; CSTART
  PRINT " dstart = ";
  PRINT USING "#.####"; DSTART
  IF ABS(ASTART + BSTART + CSTART + DSTART - 1#) > .000001 THEN
    PRINT " Error in computation of starting concentrations- check it out!": END
  CALL WAITFORME
  FOR IY = 1 TO IYMAX
    FOR IR = 1 TO IRMAX
      A11(IY, IR) = ASTART: B11(IY, IR) = BSTART: C11(IY, IR) = CSTART: D11(IY, IR) = DSTART
      A12(IY, IR) = ASTART: B12(IY, IR) = BSTART: C12(IY, IR) = CSTART: D12(IY, IR) = DSTART
      DAI(IY, IR) = 0#: DBI(IY, IR) = 0#: DCI(IY, IR) = 0#: DDI(IY, IR) = 0#
      NEXT IR
    NEXT IY
  END SUB

SUB PLOT (PX(), PY(), PP(), IPLN, IPHN, CP)
  PP(3) = PY(1): PP(4) = PY(1)
  IF CP = 1 THEN 5000
  PP(1) = PX(1): PP(2) = PX(1)
  5000 FOR J = IPLN TO IPHN
    IF PY(J) >= PP(3) THEN PP(3) = PY(J)
    IF PY(J) <= PP(4) THEN PP(4) = PY(J)
    IF CP = 1 THEN 5100
    IF PX(J) >= PP(1) THEN PP(1) = PX(J)
IF PX(J) <= PP(2) THEN PP(2) = PX(J)
5100 NEXT J
SCREEN 2
WINDOW (0, -55)-(PP(1) - PP(2), 1.1)
FOR J = IPLN TO IPHN
PSET (PX(J) - PP(2), PY(J) / PP(3))
NEXT J
PRINT USING "###.#######"; PP(2);
PRINT ",
PRINT USING "#.#######"; PP(4);
PRINT "<-> ";
PRINT USING "#.#######"; PP(1);
PRINT ",
PRINT USING "#.#######"; PP(3)
END SUB

'------------------------Subroutine PRINTINPUTDATA--------------------------
SUB PRINTINPUTDATA STATIC
PRINT "Critical Input Parameters:"
PRINT "sph = ";
PRINT USING "#.####### "; SPH
PRINT "Simulation stuff:"
PRINT "DO = "; DO
PRINT "betay = "; BETAY
PRINT "betar = "; BETAR
PRINT "r0 = ";
PRINT USING "#.####### "; R0
PRINT "vdt = "; VDT
PRINT "mtmax = "; MTMAX
PRINT "tmax = ";
PRINT USING "#.####### "; TMAX
PRINT "iymax = "; IYMAX
PRINT "irmax = "; IRMAX
PRINT "ir0 = "; IR0
PRINT
CALL WAITFORME
PRINT "Electron transfer parameters for the A/B couple:"
PRINT "E0AB = ";
PRINT USING "#.####### "; E0AB
PRINT "k0AB* = ";
PRINT USING "#.####### "; K0ABX
PRINT "alphAB = ";
PRINT USING "#.####### "; ALPHAB
PRINT
PRINT "Electron transfer parameters for the D/C couple:"
PRINT "E0DC = ";
PRINT USING "#.####### "; E0DC
PRINT "k0DC* = ";
PRINT USING "#.####### "; K0DCX
PRINT "alphDC = ";
PRINT USING "#.####### "; ALPHDC
PRINT
PRINT "More to come!"
CALL WAITFORME
PRINT
PRINT "Homogeneous kinetic parameters:"
PRINT " kBC* = ";
PRINT USING "#.#####^### "; KFBCX
PRINT " KeqBC = ";
PRINT USING "#.#####^### "; KEQBC
PRINT " kBC = ";
PRINT USING "#.#####^### "; KFB
PRINT " kbBC = ";
PRINT USING "#.#####^### "; KBBC
PRINT
PRINT " kfAD* = ";
PRINT USING "#.#####^### "; KFADX
PRINT " KeqAD = ";
PRINT USING "#.#####^### "; KEQAD
PRINT " kfAD = ";
PRINT USING "#.#####^### "; KFAD
PRINT " kbAD = ";
PRINT USING "#.#####^### "; KBAD
PRINT
PRINT "CV control parameters:"
PRINT " Estart = ";
PRINT USING "#.#####^###": ESTART
PRINT " Erev = ";
PRINT USING "#.#####^###": EREV
PRINT " nhalf = ";
PRINT USING "#.#####^###": NHALF
PRINT
CALL WAITFORME
END SUB

SUB PROFILE STATIC
'----------------------Subroutine PROFILE---------------------'
PRINT
IR = 1
PRINT " y b(y,1) b(y,iro) b(y,irmax)"
FOR IY = 1 TO IYMT - 1
  PRINT USING "#.#####^###": YMID(IY), B12(IY, 1), B12(IY, IR0), B12(IY, IRMAX)
NEXT IY
CALL WAITFORME
PRINT : PRINT
PRINT " ir f(ir) area(ir) f(ir)*area(ir)"
AREASUM = 0: F0SUM = 0
FOR IR = 1 TO IR0
  F0SUM = F0SUM + (FAB0(IR) + FDC0(IR)) * AREA(IR)
NEXT IR
FOR IR = 1 TO IR0
  AREAUM = AREASUM + AREA(IR)
  PRINT USING "#.#####^###": IR, FAB0(IR) + FDC0(IR), AREA(IR),
  (FAB0(IR) + FDC0) * AREA(IR) / F0SUM
NEXT IR
PRINT "areasum = "; AREASUM
PRINT : PRINT
END SUB
'----------------- Subroutine SIMULT(NR, MC, NCC, ZMCH) -----------------

SUB SIMULT (NR, MC, NCC, ZMCH) STATIC
FOR I = 1 TO 4: FOR J = 1 TO 4
ZMAT(I, J) = XMAT1(I, J)
NEXT J: NEXT I
GOSUB 3000
D1 = DET
FOR K = 1 TO 4: FOR I = 1 TO 4: FOR J = 1 TO 4
ZMAT(I, J) = XMAT1(I, J)
ZMAT(I, K) = XMAT1(I, 5)
NEXT J: NEXT I
GOSUB 3000
D2 = DET
CO(K) = D2 / D1
NEXT K
FOR I = 1 TO 4
XMAT1(I, 5) = CO(I)
NEXT I
GOTO 3100

3000 N = 4
DET = 1
3010 IF N = 2 THEN DET = DET * (ZMAT(1, 1) * ZMAT(2, 2) - ZMAT(2, 1) * ZMAT(1, 2)): RETURN
IF ZMAT(1, 1) = 0 THEN 3050
3015 N = N - 1
DET = DET / (ZMAT(1, 1) ^ (N - 1))
FOR J = 1 TO N: FOR I = 1 TO N
ZMTMP(I, J) = ZMAT(1, 1) * ZMAT(I + 1, J + 1) - ZMAT(I + 1, 1) * ZMAT(1, J + 1)
NEXT I: NEXT J
FOR J = 1 TO N: FOR I = 1 TO N
ZMAT(I, J) = ZMTMP(I, J)
NEXT I: NEXT J
GOTO 3010

3050 FOR J = 2 TO N
IF ZMAT(1, J) = 0 THEN 3060
FOR I = 1 TO N
ZMAT(I, 1) = ZMAT(I, J)
NEXT I
DET = -DET
GOTO 3015

3060 NEXT J
DET = 0
RETURN

3100 END SUB

SUB WAITFORME STATIC
PRINT
PRINT "Hit Q to quit; any other key to continue."
DO
WS = INKEY$ LOOP WHILE WS = ""
IF WS = "q" OR WS = "Q" THEN PRINT #1, 0#, 0#: CLOSE : END
PRINT : PRINT
END SUB
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