Electrochemist Manual

Print-Ready Edition

<!DOCTYPE HTML PUBLIC "-//IETF//DTD HTML//EN">

Electrochemistry Software ELECTROCHEMIST.com 5.8

Electrochemical simulation and data analysis

DrHuang.com

226 Anzac Pde, Kensington, Sydney, NSW 2032, Australia

Mobile Phone: +61413008019

Fax: (61 2) 9662 0516

DrHuang@DrHuang.com

www.electrochemist.com

www.DrHuang.com

www.electrochemistrySoftware.com

December 6, 2025

Contents

<big>Chapter 1

Introduction</big>

Software ELECTROCHEMIST.com (former Polar and Polarograph) is virtual electrochemist who can analyse and simulate electrochemical experiments. It simulates

1. analytically and digitally
2. voltammetry and chronoamperometry
3. on virtually **any mechanism**
4. in 4 models (finite and semi-infinite diffusions, convection and adsorption)
5. at over 10 electrode geometries (planar, spherical, semi-spherical, cylindrical, semi-cylindrical, microdisc, and thin film electrodes, and their rotating electrodes)
6. by virtually **any waveform** techniques (e.g. linear sweep, CV, DC, normal pulse, differential pulse, square wave, additive square wave, staircase voltammetry, **user-defined waveform** chronoamperometry and voltammetry).

It also simulates the effects to change over 30 parameters, e.g. charge current, resistance, noise, preconcentration time and potential, convection, pH, the reactant and product numbers, etc. This software provides five ways to check accuracy of simulation. It calculates over 1000 types of theoretical peak values.

It plots and analyses any x-y data for peak location, peak height, peak width, semi-derivative, semi-integral, derivative, integral, convolution, deconvolution, curve fitting, and separating overlapped peaks and background current.

It shows tip when the user put mouse cursor over a label. The program can separate overlapped voltammograms into individuals, and extract real peak from voltammogram with noise and baseline. It outputs the theoretical peak values, the peak current and potential and current-potential data, which can be imported into other program (e.g. Spreadsheet). Users can copy-and-paste the voltammogram into his document.

It has been successfully applied to fit experimental polarograms (voltammograms) of In(III), Cd(II), Pb(II), Tl(I), Cr(III), Zn(II), and binuclear copper complex in aqueous and non-aqueous media at mercury, solid metal and non-metal electrodes (specifically the dropping mercury, hanging mercury drop, gold, platinum and glassy carbon electrodes) by various electrochemical techniques (differential pulse, square wave, and pseudo-derivative normal pulse polarographies) [1-5].

It is available from the author or my Web site. If you have any question, please read FAQ in its document. For tutorial, please read the course practices in the rmit.htm file.

It is assumed that you agree the Shareware license that you should register by $10 to author in 20 days or you should delete it.

<big>Chapter 2

Polarography and Voltammetry</big>

2.1 Introduction

Modern electrochemical methods offer the analytical chemist a wide variety of techniques to solve analytical problems. Voltammetry is one such method, in which the current is measured as a function of applied potential. Polarography is another method, which differs from voltammetry in that it employs a dropping mercury electrode (DME) to continuously renew the electrode surface.

In this chapter, the fundamental principles of popular electrochemical techniques, e.g. direct current polarography (DCP), alternating current polarography (ACP), square wave polarography (SWP), normal pulse polarography (NPP), differential pulse polarography (DPP), pseudo-derivative normal pulse polarography (PDNPP), Linear sweep voltammetry (LSV) and stripping voltammetry (SV), are reviewed. Much of this theory is also applicable to voltammetry. If you are familiar with polarography and voltammetry, they can move directly to the next chapter.

Beside techniques, theoretical equations also depend on mechanism and electrode geometry. E.g. for 8 techniques, 15 mechanisms and 10 electrode geometries, we need 8x15x10=1200 theoretical equations. There are more than 1000 theoretical equations for analytical simulation and theoretical peak current and potential in this software. You can calculate the peak (or limiting) current and potential from the theoretical equations by clicking on the **Theoretical Peak** submenu.

2.2 Direct Current Polarography

Heyrovsky invented the original polarographic method, conventional direct current polarography (DCP), and Heyrovsky and Shikata constructed the first polarograph in 1925 [6]. DCP involves the measurement of current flowing through the dropping mercury electrode (DME) as a function of applied potential. Under the influence of gravity, mercury drops grow from the end of a fine glass capillary until they detach. Then the process is allowed to repeat itself. Drops may be allowed to fall naturally or may be dislodged after a specified interval with the aid of a mechanical device. A major advantage of the DME is that a constantly renewed electrode surface is exposed to the test solution so that problems of electrode blockage are avoided. Another advantage of the DME is that it allows a number of electrode reduction processes to be monitored, which would otherwise be inaccessible, because a wide negative potential region is available on account of the high overpotential for water reduction.

If an electroactive species is capable of undergoing a redox process at the DME, then an S-shaped current-potential relation is usually observed. This is called a polarographic wave. Figure 1.1 illustrates the response obtained from a reduction reaction where the current (i) increases over a particular potential (E) range until it reaches a limiting value. The limiting current is the diffusion-controlled limiting current (i_d). This i_d is of interest in analytical measurements as it is proportional to the concentration of reactant. For a charge reaction

$A + ne = B$

Ilkovic [4] first put the measurement of this current on a theoretical basis, and his equation is [4-6]

$$i_d = (7/3)^{1/2} (36 \pi)^{1/6} \rho^{2/3} nF D^{1/2} m^{2/3} t_d^{1/6} C \qquad (2.1)$$

where ρ is the density of mercury, n is the number of electrons, F is Faraday's constant, D is the diffusion coefficient, m is the flow rate of mercury, t_d is the drop time, and C is the concentration of the electroactive species in the bulk solution.

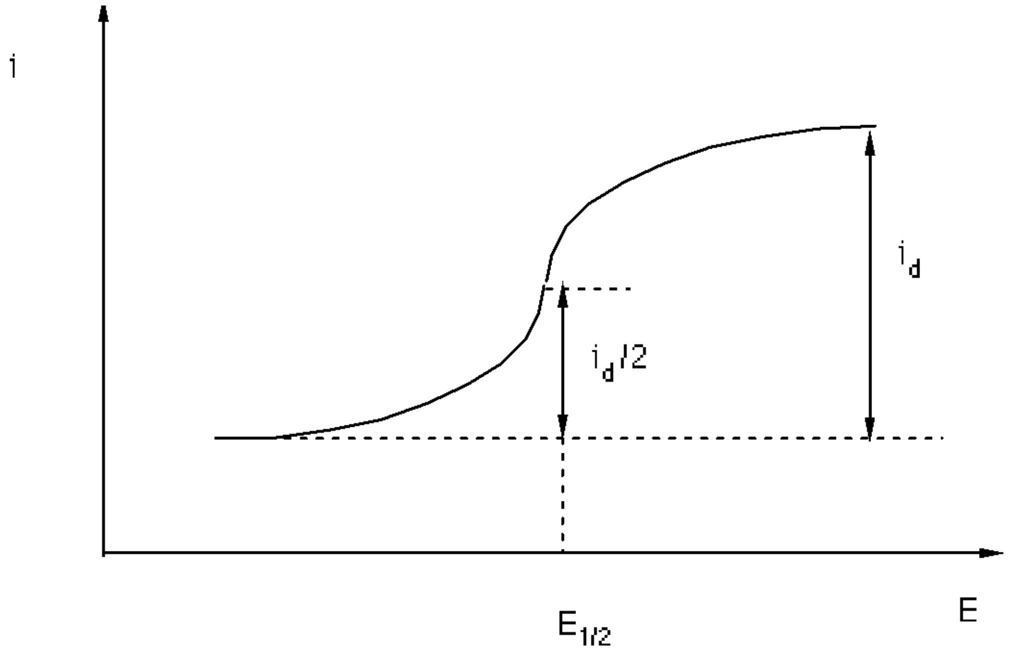

Figure 1.1 Diagram of a DC polarogram

For a planar electrode,

$$i_d = nFAD^{1/2} C / (\pi t_d)^{1/2} \qquad (2.2)$$

For a spherical electrode with radius r,

$$i_d = i_d(\text{planar}) + nFADC / r = nFAD^{1/2} C/(\pi t_d)^{1/2} (1+ (\pi t_d D)^{1/2} / r) \qquad (2.3)$$

For a microelectrode, a steady-state current is

$$i_d = GnFA^{1/2} DC \qquad (2.4)$$

where G is an electrode geometry constant, only depending on electrode geometry.

For a microdisc electrode, $G=4/(\pi)^{½}$

$i_d = 4/(\pi)^{½} nFA^{1/2} DC = 4nFDC\ r$

For a microsphere electrode, $G=2\pi^{½}$

$i_d = 2\pi^{½} nFA^{1/2} DC = 4\pi nFDC\ r$

For a microhemisphere electrode, $G=\pi^{½}$

$i_d = \pi^{½} nFA^{1/2} DC = 2\pi nFDC\ r$

The half-wave potential $E_{1/2}$ is another important parameter of the DC polarogram. This is the potential at which the current reaches half of its limiting value (Figure 1.1). The value of half-wave potential is usually independent of concentration and is characteristic of the electroactive species. Therefore it can be used for qualitative characterization of the species, and is the foundation of qualitative analysis.

The shape of the DC polarogram is also very important to the overall characterization of the electrode process. If the reduction reaction is reversible and controlled by diffusion, the potential (E) is related to the concentrations of reactant and product by the Nernst equation [7]:

$$E = E° + (RT/nF) \ln(C_O(0)/C_R(0)) \quad (2.5)$$

where E° is the standard redox potential, R is a gas constant, T is temperature, $C_O(0)$ and $C_R(0)$ are the surface concentrations of species Ox and Red, respectively. The shape of the DC polarographic wave is then derived by combining the Nernst and Ilkovic equations as follows [8, 9]

$$E = E_{1/2} + (RT/nF) \ln((i_d - i)/i)$$

or

$$i = i_d / [1 + \exp((nF/RT) (E - E_{1/2}))] \quad (2.6)$$

where

$$E_{1/2} = E° + (RT/2nF) \ln(D_R/D_O) \quad (2.7)$$

Since the diffusion coefficients of oxidized and reduced forms, D_O and D_R, are often almost equal, then $E_{1/2} = E°$. When $i = i_d/2$, then $E = E_{1/2}$.

Equation (2.6) is the Heyrovsky-Ilkovic equation, and is often used in investigations into the nature of electrode processes. However, an experimental DC polarogram also shows the oscillatory behavior of the current due to the growth and fall of the mercury drop, and this is superimposed on the DC behaviour. This invariably causes problems in the measurement of wave heights and/or half-wave potentials, and of course has deleterious effects on measures of analytical performance, especially sensitivity and resolution. Despite these problems, the DME remains popular because of its constantly renewed surface.

2.3 Linear Sweep Voltammetry and Cyclic Voltammetry

Linear sweep voltammetry (LSV) is performed by applying a linear potential ramp in the same manner as DCP. However, with LSV the potential scan rate is usually much faster than with DCP. When the reduction potential of the analyte is approached, the current begins to flow. The current increases in response to the increasing potential. However, as the reduction proceeds, a diffusion layer is formed and the rate of the electrode reduction becomes diffusion limited. At this point the current slowly declines. The result is the asymmetric peak-shaped I-E curve, as in Figure 1.3.

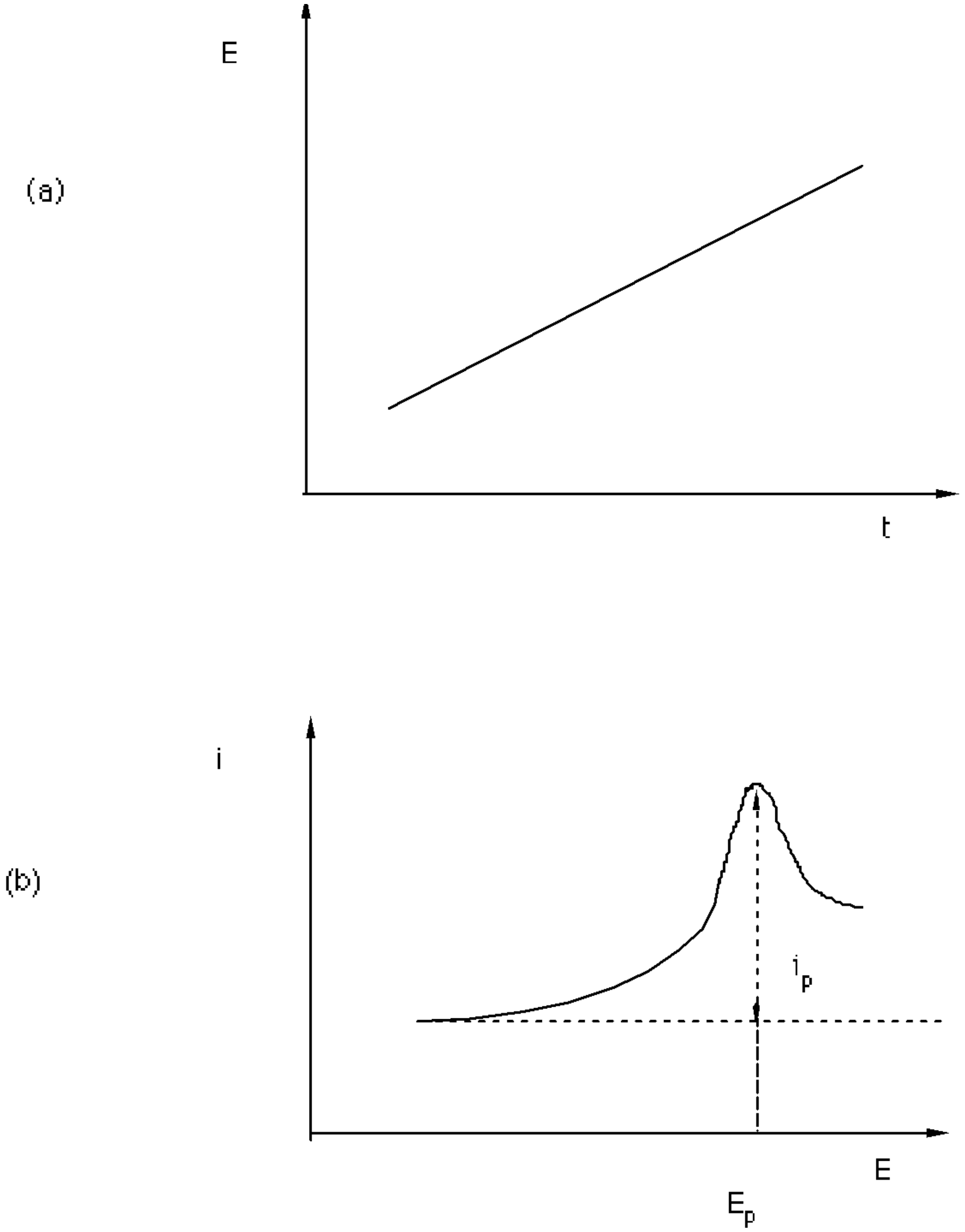

Figure 1.3 The linear sweep experiment.
(a) potential waveform (b) linear sweep voltammogram

For a reversible reaction at a planar electrode, the peak current is

$I_p = 0.4463\ AC\ (nF)^{3/2}\ (vD/(RT))^{1/2}$ (2.8)

The peak potential is

$E_p = E_{1/2} - 1.109\ RT/(nF) = E_{1/2} - 28.5/n$ (mV) at 25 °C (2.9)

The half-peak potential is

$E_{p/2} = E_{1/2} + 1.09\ RT/(nF)$ (2.10)

The difference between peak potential and half-peak potential, similar to the half-peak width, is

$| E_p - E_{p/2} | = 2.2\ RT/(nF) = 56.5/n$ (mV) at 25 °C (2.11)

Cyclic voltammetry is similar to linear sweep voltammetry except for the potential scans from the starting potential to the end potential, then reverse from the end potential back to the starting potential. Cyclic voltammetry is perhaps the most widely used electrochemical technique, and is frequently used for the characterization of a redox system. It can provide information about the number of redox states, as well as qualitative information about the stability of these oxidation states and the electron transfer kinetics. There are also simple models that can be used to calculate the rate of electron transfer (represented by k_s) and the rate of chemical reactions coupled to the electron transfer for simple systems (those where the cyclic voltammetric behavior is controlled by only one of these parameters). However, these simple models cannot be used for more complicated systems, since the effects of, for example, slow electron transfer kinetics and a coupled chemical reaction cannot be readily separated. This simulation software can help quantitative studies (e.g., mechanistic investigations) in cyclic voltammetry, so it can be useful for investigating the electrochemical mechanisms of real redox systems. The difference between two peak potentials is

$\Delta E_p = | E_{pa} - E_{pc} | = 2.3\ RT/(nF) = 58/n$ (mV) at 25 °C (2.12)

$E_{1/2} = (E_{pa} + E_{pc})/2$

For a non-reversible reaction, ΔE_p becomes larger.

For a microdisk electrode, its steady-state current is the same as the eq. (2.4). Cyclic voltammetric responses at a disk microelectrode can be approximated in simulation by using a hemispherical electrode of the appropriate radius $r_h=2r_d/\pi$, where r_d is the radius of the disk microelectrode; the CV responses at a band electrode can be approximated using a hemicylindrical electrode of the appropriate radius $r_h=w/4$, where *w* is width of the band electrode.

The rotating-disk electrode was developed following the mathematical solution given by Levich of the hydrodynamic equations describing the rate of transfer of substance in solution to a rotating disk surface, in terms of the angular velocity of rotation ω ($\omega = 2\pi N$, N in rps), the diffusion coefficient D, the concentration C^0 of the substance and the kinematical viscosity *v* of the solution. For the case when the reaction is relatively fast and the current is determined by mass transport, the corresponding equation for the limiting current density j_l , developed by Levich, is:

$$j_l = 0.62nFD^{2/3}\nu^{-1/6}\omega^{1/2}C^0$$

where j_1 is in A/cm^2, D in cm^2/s, v in cm^2/s , ω in rad/s and C^0 in mol/cm^3. In such a case the limiting current is independent of potential over a wide range. This range of potential is limited at one end by the reversible potential and a small overpotential needed to drive even a very fast reaction to mass-transport limitation and at the other end by another reaction which may take place, usually the evolution or oxygen or hydrogen in aqueous solutions.

2.4 Staircase Voltammetry

Staircase Voltammetry (SV) is similar to linear scan voltammetry. It scans by staircase potentials, instead of linear potential. When a potential step is very small, it is the almost same as linear scan voltammetry. But you have choice to change the sampling time.

2.5 Differential Staircase Voltammetry

Differential Staircase Voltammetry (DSV) is similar to staircase voltammetry. Two currents are sampled at the beginning and the end of the staircase. When the difference between the two current samples is plotted as a function of the applied ramp voltage, a peak-shaped current response is shown.

2.6 Alternating Current Voltammetry

A number of modifications to DCP have improved its analytical performance. One of them is alternating current voltammetry (ACV). It is the result of superimposing a small amplitude sinusoidal potential (ΔE) with a fixed frequency (ω) on a slowly scanning DC ramp, as (c) in Figure 1.2. The applied potential is then given by summing the AC and DC components. Finally, the alternating current (AC) is measured as a function of DC potential. In particular, the amplitude of the AC current vs. the DC potential is plotted, as (g) in Figure 1.2. The current-potential (I-E) curve for a reversible reaction follows the equation [6]

$$I = n^2F^2\ AC\ \Delta E\ (\omega D)^{1/2}\ \mathrm{sech}^2\ [(nF/2RT)(E - E_{1/2})]\ /(4RT) \qquad (2.13)$$

At a peak, sech()=1, then the above equation reduces to

$$I_p = n^2F^2\ AC\ \Delta E\ (\omega D)^{1/2}/(4RT) \qquad (2.14)$$

It may be deduced from this equation that the amplitude of the AC component of the Faradic current (I) is peak-shaped. Moreover, the peak current is a linear function of concentration and therefore may be used in analytical applications. Like the half-wave potential $E_{1/2}$ in DCP, the peak potential E_p in ACP is characteristic of the electroactive species. Also, the half-peak width (i.e. the width of the peak at half its height, $W_{1/2}$) is [6]

$$W_{1/2} = 3.52\ RT/(nF) = 90/n \text{ mV at } 25\ °C. \qquad (2.15)$$

2.7 Square Wave Voltammetry

Square wave voltammetry (SWV) uses a small amplitude square wave voltage in place of the sinusoidal one used in ACP. Its potential waveform is shown in (d) of Figure 1.2. The current is sampled near the end of each square wave half cycle, to minimize double-layer charging effects, and the I-E response is obtained by plotting the differences in current between successive half cycles. For reversible electrode processes, the I-E curve for SWP is similar to that in ACP [6], so its properties, including the half-peak width $W_{1/2}$ and resolution, are obviously akin to ACP.

2.8 Additive Square Wave Voltammetry

Additive square wave polarography (ASWP) uses a small amplitude square wave voltage in the same as one used in SWP, but its total current is sum of the positive and negative pulses currents, instead of difference of the positive and negative pulses currents. Because its two charge currents by the positive and negative pulses are opposite, it is possible to select suitable sample time to make its charge currents offset to zero. A charge current by a positive pulse is

$I_c(t1) = (E_{j-1} – E_j)\exp(-t1/RC) = -(Es+Ep)\exp(-t1/RC)$

where t1 is a sampling time at a positive pulse, R is resistance, C is double layer capacitance, Es is potential step, Ep is pulse potential.

A charge current by a negative pulse is

$I_c(t2) = (E_j – E_{j+1})\exp(-t2/RC) = Ep \exp(-t2/RC)$

Total charge current is

$I_c = I_c (t1) + I_c (t2)$

By setting $I_c = 0$, a solution for the sampling time is

$t2 = t1 - RC \ln(Es/Ep+1)$

It can show in dimensionless sampling time by division of the pulse time tp:

$T2 = T1 – RC/tp \ln(Es/Ep+1)$

According to this equation, select sampling time t2 different from t1 to offset charge current to zero.

2.9 Normal Pulse Voltammetry

The pulse voltammetry including normal pulse voltammetry (NPV) and differential pulse voltammetry (DPV) stem from Barker's original work on square wave voltammetry [6]. The increased sensitivity of these techniques over DCP arises from their ability to discriminate against the charging current by measuring the total current after the charging current has decayed to values substantially less than the Faradic current.

The potential-time waveform used in NPP is presented as (a) in Figure 1.2. At the beginning of the potential sweep, the electrode is held at an initial potential where no Faradic current flows. Potential pulses of increasing amplitude are then applied to the electrode at regular intervals. The potential pulses are about 50 ms in duration and the current is measured at a time near the end of each pulse. A potential pulse is ended by a return to the initial potential and the drop is dislodged. The whole process is repeated except a few millivolts are added to the potential pulse in next cycle. A normal pulse polarogram is shown as (e) of Figure 1.2. The shape of the normal pulse polarogram is sigmoidal, looking similar to the shape of a DC polarogram, and indeed it can be described by a current-potential equation similar to that in DCP [6].

For a planar electrode, its limiting current is similar to one of DCV:

$$i_d = nFAD^{1/2}\ C / (\pi\ t_p)^{1/2} \qquad (2.16)$$

For a spherical electrode with radius *r*,

$$i_d = i_d(\text{planar}) + nFADC / r = nFAD^{1/2}\ C\ (1/ (\pi\ t_p)^{1/2} + D^{1/2} /r\ ) \qquad (2.17)$$

2.10 Reverse Pulse Voltammetry

Reverse Pulse Voltammetry is similar to normal pulse voltammetry, but its start potential is negative and its pulse is positive as opposite to normal pulse voltammetry.

2.11 Differential Pulse Voltammetry

Normal pulse voltammetry gives improved sensitivity by avoiding most of the charging current by sampling the total current as late as possible after the application of each potential pulse. However, there still is the charging current to some extent. Another defect of NPP is poor resolution between neighbouring wave because of drawn-out sigmoidal I-E response. Differential pulse polarography (DPP) was designed to overcome these problems by arranging a charging current of smaller magnitude, and by producing a peak-shaped I-E curve.

The potential-time waveform used in DPV is shown as (b) of Figure 1.2. A voltage ramp is applied to the electrode as in the DCP, and a small amplitude potential pulse (DE) is added to the voltage towards the end of each drop's life. Two currents are measured before applying the pulse and at the end of the pulse. When the difference between the two current samples is plotted as a function of the applied ramp voltage, a peak-shaped current response is shown.

The peak-shaped I-E curve allows polarographic responses in close proximity to each other to be more clearly resolved than in either DCP or NPV. The I-E curve for all values of the pulse amplitude is described by [6]

$$I = nFAC\ (D/ \pi\ t_p)^{1/2}\ P\ (\sigma^2-1)/[(\sigma+P)(1+P\sigma)] \qquad (2.18)$$

where

$$\sigma = \exp(nF\Delta E/(2RT)) \qquad (2.19)$$

$P = \exp[(nF/(RT))(E - E_{1/2} + \Delta E/2)]$ (2.20)

At a peak, P=1, then the current equation reduces to
$I_p = nFAC (D/ \pi t_p)^{1/2} (\sigma -1)/(1+\sigma)$ (2.21)
$E_p = E_{1/2} - \Delta E/2$ (2.22)

The half-peak width is a very important parameter in resolution. The half-peak width $W_{1/2}$ is a function of the pulse amplitude as follows [6]

$W_{1/2} = 2RT/(nF) \cosh^{-1}[2 + \cosh(nF\Delta E/(2RT))]$ (2.23)

For large values of $|\Delta E|$ (say $|\Delta E| > 200/n$ mV), $W_{1/2}$ approaches to $|\Delta E|$, and for small values of $|\Delta E|$ (e.g. $|\Delta E| < 20/n$ mV), this equation reduces to equation (2.15).

Unfortunately, the above theoretical equations are derived by neglecting the DC effect in DPP, and although this is not a problem when the ratio of the drop time to the pulse time is larger than 50, the resulting distortion makes the theoretical treatment complicated, especially for a non-reversible reaction.

2.12 Pseudo-Derivative Normal Pulse Voltammetry

DPV is a very sensitive electroanalytical technique due to the effective discrimination against the charging current. However, DPV has two problems associated with the slowly increasing DC ramp. As the DC ramp progresses, filming may occur on the surface of the electrode if species form insoluble mercury compounds [6]. Since the characteristics of the electrode are changed by such a film, the current may not correspond to the simple theory. Another problem is that the theory itself is complicated by the effect of the DC ramp. NPP avoids these two problems. But the disadvantage of NPV is its poor resolution because of the sigmoidal wave. To overcome this shortcoming, NPV polarograms can be differentiated to produce peak-shaped responses, and thus combine the best features of both DPV and NPV while avoiding some of their limitations. This pseudo-derivative normal pulse polarography (PDNPV) nevertheless is not sensitive as DPV.

The potential-time waveform in PDNPV is as in NPV, but the current data of PDNPV are displayed in a difference mode. The current is subtracted from those for the following pulses, and the difference is plotted as a function of potential, as in DPV.

The theoretical treatment of PDNPV is simple and easy. The reversible current-potential equation is similar to that of DPV except for the DC term [6]. The half-peak width or resolution is akin to that of DPV.

2.13 Stripping Voltammetry

Stripping voltammetry involves three main steps: electrodeposition (preconcentration), equilibration, and stripping. The first step is to concentrate the analyte from the dilute test solution into or onto the electrode at negative reduction (or positive oxidation) potentials, usually accompanied by stirring. The second step is to leave the solution to settle down. The third step is then to strip the preconcentrated analyte from the electrode back into the solution by using one of the polarographic techniques described above. A major advantage of this method is its extremely sensitivity, in the concentration range of 10^{-6} - 10^{-12} M. This is because the concentration of the analyte on the electrode is 100-1000 times greater than that in the starting solution [6].

<big>Chapter 3

Specification

This software analytically and digitally simulates **voltammetry** and **chronoamperometry** on virtually **any mechanism** in 4 models at over 10 electrode geometries by virtual **any waveform** techniques, calculates their theoretical peak current and potential, retrieve parameters by curve fitting, and separate overlapped peaks and baseline. </big>

- Digital simulation

  Flexible for **any mechanism** up to second-order chemical reaction and **adsorption** by virtual **any waveform** techniques. You can type your mechanism and chemical symbols, and **design or import any waveform**. An implicit finite difference algorithm is used.

- Analytical simulation

  No divergence problem in simulation. No overflow problem in simulation. Fast simulation.

- Design or import any waveform

  Linear sweep, CV, DC, normal pulse, reverse normal pulse, differential pulse, square wave, additive square wave, staircase voltammetry. Multi-cyclic voltammetry, cyclic normal pulse, cyclic differential pulse, cyclic square wave, cyclic additive square wave, cyclic staircase voltammetry, differential staircase voltammetry, chronoamperometry, chronocoulometry, **user-design waveform** chronoamperometry and voltammetry.

- Chemical Reaction Rate up to 10e300

- Surface concentrations

  show what happen each species in the electrode surface, check accuracy of simulation, convert surface concentration to current or current to surface concentration..

- **Conversion between** surface concentration and current

  Convert surface concentration to current or current to surface concentration to check accuracy of simulation.

- Over 1000 type of theoretical peak values

  It calculates theoretical peak values by theoretical equations and compare your data with theoretical peak values to see if your experimental conditions reach upper or lower theoretical limit.

- Over 30 factors

  Simulate over 30 effect factors, e.g. noise, charge current, resistance, preconcentration time and potential, convection, pH, reactant number, product number, electron number, electrode geometries, electrode size, electrode rotating speed, scan rate, concentration, pulse height, pulse width, sampling time, scan direction, scan cycle, diffusion coefficient, drop time, standard redox potentials, rate of electron transfer, transfer coefficient, diffusion coefficient, temperature, electrode area, and experimental parameters, forward and reverse chemical reaction rate constants up to 10e300, etc.

- Separating overlapped peaks

  Manually and auto separates overlapped peaks into individuals, and extract real peak from voltammogram with noise and baseline. So you can exactly determine peaks and check accuracy of simulation.

- Preconcentration

  Change preconcentration conditions for stripping voltammetry.

- Pre-equilibration

  Calculate the concentration at equilibrium.

- Curve fitting

  Manually and auto fits the simulated voltammograms into experimental data, and extracts kinetic parameters from experimental data. Curve fitting to any electrochemical parameter is easy by click to select that parameter.

- Import and export data

  Import parameters, waveform and current data from a text file. Copy-and-paste the simulated voltammogram into your document. Export the simulated data into your favor program (e.g. MS Excel).

- Data Analysis

  Derivative, integral, semi-derivative, semi-integral, convolution, deconvolution, Tafel analysis, convolution analysis. Semi-derivative is useful for CV. It can change a shape of reversible CV into symmetric peak, so easy to determine peak.

- Over 10 electrode geometries

  Planar, spherical, semi-spherical, cylindrical, semi-cylindrical, band, microdisk, thin film, disk, ring electrode, and rotating all these electrodes.

- Check accuracy of simulation

  Provide five ways to check accuracy of simulation.

- Tips

  Show tips for help when you put mouse cursor over a label.

Table 1 Feature

Version	**Shareware**	**Student**	**Teacher**	**Academics**	**Professional**	**Competitor**
Digital simulation	y	y	y	y	y	y
Analytical simulation	y	y	y	y	y	n
Theoretical peak	y	y	y	y	y	n
No. of adsorption reaction	1	2	3	4	5	n
Surface concentration	y	y	y	y	y	n
Convert surface concentration to current	y	y	y	y	y	n
Convert current to surface concentration	y	y	y	y	y	n
Any species symbol	y	y	y	y	y	n
Tips	y	y	y	y	y	n
Open parameter	n	n	y	y	y	n
Open waveform	n	n	y	y	y	n
Open current	n	n	n	y	y	y
Save parameter	n	n	n	y	y	n
Save waveform	n	n	n	n	y	n
Save current	n	n	n	n	y	y
Save graph	y	y	y	y	y	n
Show pulse current	n	n	y	y	y	n
No. Of charge reaction	1	2	3	4	5	y

No. Of chemical reaction	0	2	4	6	9	y
Techniques:						
LSV and CV	y	y	y	y	y	y
DC	n	y	y	y	y	n
Normal pulse	n	n	y	y	y	n
Reverse Pulse	n	n	y	y	y	n
Differential pulse	n	n	y	y	y	n
Cyclic diff. pulse	n	n	y	y	y	n
Square wave	n	n	n	y	y	n
Cyclic square wave	n	n	n	y	y	n
Additive square wave	n	n	n	y	y	n
Staircase	n	n	n	y	y	n
Potential step	n	n	n	n	y	n
Design waveform	n	n	n	n	y	n
Import waveform	n	n	n	n	y	n
Effect:						
Adsorption	y	y	y	y	y	n
Convection	y	y	y	y	y	n
Noise	y	y	y	y	y	n
Charge current	y	y	y	y	y	y
Resistance	y	y	y	y	y	y
Reactant number	y	y	y	y	y	n
Product number	y	y	y	y	y	n

Preconcentration time	y	y	y	y	y	n
Preconcentration potential	y	y	y	y	y	n
Pre-equilibration	y	y	y	y	y	y
pH	y	y	y	y	y	n
Negative electron number	y	y	y	y	y	n
Fractal electron number	y	y	y	y	y	n
Pulse height	n	n	y	y	y	n
Pulse width	n	n	y	y	y	n
First sampling time	n	n	y	y	y	n
Second sampling time	n	n	y	y	y	n
Analysis:						
Differentiate	y	y	y	y	y	n
Integrate	y	y	y	y	y	n
Semi-differentiate	y	y	y	y	y	n
Semi-integrate	y	y	y	y	y	n
Manual fit	n	y	y	y	y	n
Auto fit	n	n	n	y	y	y
Manual separate	n	n	n	n	y	n
Auto separate	n	n	n	n	y	n
Electrode:						
Planar	y	y	y	y	y	y

(Micro) spherical	y	y	y	y	y	y
(Micro) hemispherical	y	y	y	y	y	y
cylindrical	y	y	y	y	y	y
semicylindrical	y	y	y	y	y	n
DME	y	y	y	y	y	n
Microdisc	y	y	y	y	y	n
Band	y	y	y	y	y	n
Thin film	y	y	y	y	y	n
Ring	y	y	y	y	y	n
Rotating all electrodes	y	y	y	y	y	n

Note: y = yes, n = no. Feature may be changed without notice.

<big>Chapter 4 Menu</big>

File menu

- **Open Parameter** submenu

  Open a file of parameters and read parameters back. You can continue your simulation of last time or repeat other people's simulation. The Plot window title will show the file name.

- **Open Waveform** submenu
  Read waveform data from a file and show the waveform. The Plot window title will show the file name. If technique is **9) Design waveform**, then it writes a few design points back to the **Design Waveform** panel.
- **Open Current** submenu
  Read current data from a file and show curves. The Plot window title will show the file name.
- **Save Parameter** submenu
  Save experimental parameters into a text file. You can continue your simulation later by the **Open Parameter** submenu.
- **Save Waveform** submenu
  Save waveform to a file as text file. E.g. if you save data as the .csv file, you can load it into MS

Excel by double-clicking the .csv file. If technique is **9) Design waveform**, then it saves a few design points from the **Design Waveform** panel, otherwise it saves every point of waveform.

- **Save Current** submenu
  Save current data as a text file. E.g. if you save data as the .csv file, you can load it into MS Excel by double-clicking the .csv file.
- **Save Graph** submenu

  Save a graph of current, waveform, and surface concentration to a file as .bmp file. You can use the PAINT program to save it as .gif file to show on Internet.

- **Copy To Clipboard** submenu
  Copy a graph (e.g. current, waveform, surface concentration) into clipboard, so you can paste the graph into your document.

- **Print** submenu
  Print graph (e.g. current, waveform, surface concentration).

- **Exit** submenu

Input menu

- **Technique** submenu

  Open a window to select one of 9 techniques. The default technique is LSV and CV.

- **Instrument** submenu

  Open a window to change instrument parameters. You can click the Reset button to use the default values.

- **Mechanism** submenu

  Open a window to input your mechanism and species symbol in **Digital simulation**, or choose a predefined mechanism in **Analytical simulation**. The default mechanism is Fe^{3+} + e = Fe^{2+}.

- **Kinetics** submenu

  Open a window to change kinetic parameters. You can use the default values without any change.

- **Concentration** submenu

  Open a window to change concentration, diffusion coefficient, adsorption coefficient and maximum adsorption amount of species.

Run menu

- **Simulate** submenu
  Run simulation, and show curves on a **Plot** window. You can click on any point of curve to get the x and y values.

- **Manual Fit** submenu
  Manually fit the simulated curve into experimental curve as you manually change parameter values.

- **Auto Fit** submenu
  Automatically fit the simulated curve into experimental data.

- **Manual Separate** submenu
  Manually separate the overlapped peaks into individuals as you manually change parameter values.

- **Auto Separate** submenu
  Automatically separate the overlapped peaks into individuals.

Plot menu

- **i vs. E** submenu
  Plot current i versus potential E without running simulation.
- **i s vs. E** submenu
  Plot the sampling currents versus potential E without running simulation. It is only available for multi-sampling techniques, e.g. pulse.
- **C0 vs. E** submenu
  Plot surface concentration C0 versus potential E without running simulation.
- **Waveform** submenu
  Plot potential E versus time t, which is imposed to electrodes in a technique.
- **Convert** submenu
  Convert current into the surface concentration or the surface concentration into current.
- **Convert i to C0** submenu
  Convert current into the surface concentration.
- **Convert Co0 and Cr0 to i** submenu
  Convert surface concentrations of both oxidized and reduced species into current.
- **Convert i1 to C0 for E mechanism 1** submenu
  Convert current to surface concentration of oxidized and reduced species for simple charge reaction mechanism 1 in the **Analytical Simulation** panel.
- **Convert Co0 to i1 for E mechanism 1** submenu
  Convert a surface concentration of oxidized species into current for simple charge reaction mechanism 1 in the **Analytical Simulation** panel.
- **Convert Cr0 to i1 for E mechanism 1** submenu
  Convert a surface concentration reduced species into current for simple charge reaction mechanism 1 in the **Analytical Simulation** panel.
- **Convert i8 to C0 for E mechanism 8** submenu

Convert current to surface concentration of oxidized and reduced species for catalytic reaction mechanism 8 in the **Analytical Simulation** panel.

- **Convert Co0 to i8 for E mechanism 8** submenu
  Convert a surface concentration of oxidized species into current for catalytic reaction mechanism 8 in the **Analytical Simulation** panel.
- **Convert Cr0 to i8 for E mechanism 8** submenu
  Convert a surface concentration reduced species into current for catalytic reaction mechanism 8 in the **Analytical Simulation** panel.
- **Semi- dy/dt** submenu

  Semi-differentiate the y data with time t. Semi-differentiation is the same as deconvolution of current with 1/√(πt). Click twice this menu for two time semi-differentiation, i.e. first order differentiation.

- **Semi-integrate** submenu

  Semi-integrate the y data with time t. Semi-integrate is the same as convolution of current with 1/√(πt). Click twice this menu for two time semi-integration, i.e. integration.

- **dy/dt** submenu

  Differentiate the y data with time, dy/dt. Click twice this menu for second order differentiation.

- **Integrate** submenu

  Integrate the y data with time t.

Smooth submenu

Smooth the y data.

Log((i lim 1 - i)/(i – i lim 2)) submenu

Tafel plot. It converts S-shape of curve to a linear line. E.g. it converts DC voltamogram, convolution of CV into linear lines.

- **X Data** submenu
  Operation on all X data of a curve, e.g. X + constant, X * constant.
- **t as X-axis** submenu
  Plot time t as X-axis.
- **E as X-axis** submenu
  Plot potential E as X-axis.
- **0.001X, 0.1X, 10X, 1000X** submenus

  Multiply 0.001, 0.1, 10, or 1000 on X data. If your experimental potential data is not in Volt unit, you should convert to Volt unit by this submenu.

X data reverse submenu

Reverse the order of data.

- **Y Data** submenu

  Operation on all Y data of a curve, e.g. addition and subtraction of curves, Y1 + Y2, Y2 – Y1, Y + constant, Y * constant.

  -Y, 0.001Y, 0.1Y, 10Y, 1000Y submenus
  Multiply –1, 0.001, 0.1, 10, or 1000 on Y data. If your experimental current data is not in Amp unit, you should convert to Amp unit by this submenu.

- **Option** submenu
  Change the plot options, color, line style, etc.

Analyze menu

- **Find Peak** submenu

  Find the peak height, location, left and right sides half peak width, and width of curves of the peak shape. After open a window, you can copy the result by right click mouse.

- **Find Halfwave E** submenu

  Find the half wave potential and limiting current of curves of the S shape.

- **Theoretical Peak** submenu

  Calculate the theoretical peak potential, peak current, left side half peak width, right side half peak width and half peak width from theoretical equations. Select a mechanism from Analytical Simulation in the Mechanism window before you click this menu. This submenu is active for Analytical Simulation only.

- **Curve Number** submenu
  Show current curve number. So you can analyze this curve.
- **Next Curve Number** submenu
  Go to next curve number. So you can analyze this curve.
- **Time** submenu

  Display the simulation time and curve-fitting results.

Help menu

- **Logon** submenu
  Logon to activate menus by input of password.

- **Manual** submenu
  Display this manual.

- **Home Page** submenu

- **About** submenu

  Show version number and ID of this software.

Some menus will be activated only after you click the Simulate submenu or load data because they require data.

<big>Chapter 5

Input Menu

This menu has five submenus.**</big>**

5.1 Techniques Window

Basic Techniques:

1) Linear sweep and cyclic voltammetry and chronoamperometry.
2) DC voltammetry and chronoamperometry.
3) Normal and reverse pulse voltammetry and chronoamperometry.
4) Differential pulse voltammetry and chronoamperometry.
5) Square wave voltammetry and chronoamperometry.
6) Additive square wave voltammetry and chronoamperometry.
7) Staircase voltammetry and chronoamperometry.

8) Potential step chronoamperometry: single, double, and triple steps.
9) Design waveform

10) Import waveform

You can design your waveform in the **Design Waveform** section of the **Instrument** window. You can import your waveform data from a file by the **Open** menu of the **File** menu.

You plot the time t as X-axis for chronoamperometry, and the potential E as X-axis for voltammetry.

By data analysis, you can extend above techniques to more techniques, e.g.
integrating chronoamperometric current leads to chronocoulometry, and
convoluting CV leads to convolution voltammetry.

Extended Techniques:

1. Chronocoulometry: by integrating chronoamperometric current.
2. Convolution voltammetry: by convoluting CV.
3. Differential, semi-differential and semi-integration voltammetry: by differencing, semi-differencing and semi-integrating CV.
4. Anode and cathode stripping voltammetry.
5. Differential staircase voltammetry: produce 2 staircase currents at different sampling times in

the same window with overlap, and then click the **Y2-Y**1 menu of the Y Data menu in the Analyze menu.
6. Multi cyclic voltammetry of all above voltammetry.

You can see their waveform that is applied to electrodes by click on the **Waveform** menu of the **Plot** menu.

5.2 Instrument Window

This **Instrument** window is used to define the parameters of the instrument in experiment as follows:

- The potential range of the experiment (**E start**, and **E end**).
- The scan rate (**v**).
- The number of potential scans: **Cycles.**
- Solution resistance (**R u**) and double layer capacitance (**C d**).
- The electrode **Geometry** (e.g., planar, spherical) and surface **Area.**

5.2.1 Instrumental Parameters panel:

E start: starting potential (V).
E end: ending potential (V).
E step: step potential (V).
v: scan rate (V/s). For square wave voltammetry, $v=E_{step}/t_{pulse}$.
E pulse: pulse potential (V).
T: temperature (°C).
t pulse: pulse time or pulse width for pulse voltammetry (s).
t drop: mercury dropping time or pulse length in pulse voltammetry (s).
Noise: noise signal (A).

ts1: first dimensionless sampling time, value is from 0.1 to 1. For square wave pulse, it is sampled in first pulse during of first half square wave. For different pulse, it is sampled in during before pulse. For normal pulse, it is sampled in pulse during. For staircase, it is sampled in a staircase during. It is not used for LS and CV. For digital simulation, you should set the Time Grid Factor in the **Digital Simulation Model** section to about 10 before you change the sampling time less than 1.

ts2: second dimensionless sampling time, value is from 0.1 to 1. For square wave pulse, it is for second opposite pulse of second half square wave. For different pulse, it is sampled in pulse during. It is not used for other techniques. For digital simulation, you should set the Time Grid Factor in the **Digital Simulation Model** section to about 10 before you change the sampling time less than 1.

Scan:
Single: single scan.
Cycles: cyclic scan, e.g. cyclic voltammetry (CV).
2 Cycles: 2-cycle scan.

3 Cycles: 3-cycle scan.

5.2.2 **Electrode** panel:

1. **Planar:** a planar electrode.
2. **(Micro) Spherical:** a spherical electrode or micro spherical electrode.
3. **(Micro) Hemispherical:** a hemispherical electrode or micro hemispherical electrode.
4. **Microdisk:** a micro disc electrode, radius < 1e-4 cm.

5. **(Micro) Cylindrical:** a cylindrical electrode or micro cylindrical electrode.
6. **(Micro) Hemi cylindrical:** a hemi cylindrical electrode or micro cylindrical electrode.
7. **DME:** a dropping mercury electrode.
8. **Ring-Disc:** ring-disc electrodes.
9. **Thin film:** a thin film electrode, surface modified electrode or thin layer cell, with finite diffusion.
10. **Bond:** a bond electrode.

11. **Ring:** a ring electrode.

All above electrodes can be rotated.

Area: electrode area (cm^2). When you change the value of area, the value of radius is changed automatically. The default value is 0.01.
Radius: electrode radius (cm). When you change the value of radius, the value of area is changed automatically.
Length: electrode length for cylindrical electrode or micro cylindrical electrode (cm).

Ring Radius 2: inner radius of ring electrode (cm).

Ring Radius 3: outer radius of ring electrode (cm).

Thickness: thickness of the polymer or mercury film electrode (cm).

Rotation: electrode rotation rate (rpm). For stationary electrodes, set this value to 0. The default value is 0.

5.2.3 **Preconcentration** panel:

E pre: preconcentration potential (V).
R stir: stirring rate (rpm). Stirring solution.
t pre: preconcentration time (s).

t pre const: preconcentration time constant (/s).

5.2.4 **Baseline** panel:

C dl: double layer capacitance for charge current (F).
R: resistance (Ohm).

I start: a starting current (A).

I end: an ending current (A).

5.2.5 **Digital Simulation Model** panel**:**

Space Grid Factor: space expanding grid factor. Its value is from 0.001 to 0.9. The smaller value it is, the more accuracy simulation is, but the longer computer time. Default value is 0.5.

Time Grid or Step: the time step in second. The smaller value it is, the more accuracy simulation is, but the longer computer time. It depends on techniques. The suggestion value is half pulse width for normal pulse, staircase, differential pulse, and square wave techniques.

This section factors are used for digital simulation only, not for analytical simulation.

The most important three parameters are the Space grid factor**,** the Time Grid and the Potential steps, which specify the resolution of the space and time grids, respectively, that are used in the simulation. Entering lower values for the Expanding grid factor and the Potential steps parameter or higher value for the Time Grid Factor will increase the resolution of the grid, which may increase the accuracy of the simulation. However, there is a point beyond which further increases in resolution will have no effect. Increasing the grid resolution will also increase the time required for the calculation, but this is generally no longer an issue with the speed of PCs now available. There are two occasions when decreasing the Space Expanding grid factor is useful, and these are discussed in later chapter (see **Chapter 7 How Do You Know It is Right?**).

5.2.6 **Design Waveform** panel:

You can design your waveform that is applied to electrodes by setting your time-potential values here. This section is only visible for the Technique **9) Design waveform**.

t0 is the start time, t0=0 second; E0 is the start potential (V).

t1 is the first point of time to change potential; E1 is the first changed potential.

t2 is second point of time to change potential; E2 is the second changed potential

and so on.

You can see its waveform by click on the **Waveform** menu of the **Plot** menu.

Default value is double steps scan.

5.3 Mechanism Window

You can type in your mechanism in the **Digital Simulation** panel with any symbol. Upper case symbol is different from lower case symbol. In order to faster computation, you should type in reactants only without products if chemical reaction is irreversible.

Tick the checkbox under **Adsorb** for adsorption reaction. The adsorptive system assumes that the adsorption obeys Langmuir isotherm and all species can be adsorbed. For non-adsorptive species, set its adsorption coefficient value to 0.

Uncheck the **Digital Simulation** checkbox, you will see the **Analytical Simulation** panel. In the **Analytical Simulation** panel, you choose a predefined mechanism. Although the electron number and reactant and product numbers are inside the **Digital Simulation** panel, they are for both Digital and Analytical Simulations. You can input any value of the electron number (n), e.g. $n = -0.5$.

Some of about 20 predefined mechanisms are as follows:

A+ne = B	charge reaction
A+ne <-> B	reversible charge reaction
A(a)+ne = B(a)	Langmuir adsorption reaction
A(a)+ne <-> B(a)	reversible Langmuir adsorption reaction

5.4 Kinetics Window

It is used to enter thermodynamic and kinetic parameters for the reactions involved in the mechanism. The following must be defined for each (**Heterogeneous**) electron transfer reaction:

1. The redox potential (**E°**).
2. The transfer coefficient (**α**).
3. The electron transfer rate constant (**k_s**).

Heterogeneous Reaction Section:

ks: heterogeneous standard rate constant (cm/s).
α: electron transfer coefficient.
E°: standard electrode potential (V).

Three parameters are required for each chemical (**Homogeneous**) reaction: the equilibrium constant (**Keq**), and the rates of the forward and reverse reaction (**kf** and **kb**). Only two parameters **kf** and **kb** can be defined by the user, since **Keq** = **kf/ kb**.

Homogeneous Reaction Section:

kf: forward chemical reaction rate constant. Its unit is /s for the first order reactions, or /sM for second order reactions. Its value is up to 1e300.
kb: backward chemical reaction rate constant. Its value is up to 1e300
Keq: chemical equilibrium constant, $K_{eq} = k_f / k_b$.

Solution Section:

Electrolyte: electrolyte in solution.

C: concentration of electrolyte (M).

pH: the pH value of solution. The default value is 7.

Vis: viscosity of solution (cm /s).

Vs: volume of solution (ml).

5.5 Concentration Window

The **Species Parameters** are entered in this dialog box. These are the diffusion coefficients (**D**) and concentrations of all the species involved in the redox mechanism. Two concentrations are shown here. The user enter the *analytical* concentrations (**C anal**), which are corresponding to the bulk concentrations that in the solution. The *initial* concentrations (**C init**) are the equilibrium concentrations at the electrode surface, and are determined by **E start**, all **Eo** values, all **Keq** values, and all **C anal** values. It is the **C init** values rather than the **Canal** values that are used in the simulation. The calculation of the **C init** values can be switched off by disabling the **Pre-Equilibration** in its checkbox. If the calculation of **C init** is disabled, the **Canal** values are the same as **C init**.

Species panel:

C anal: analytical concentration (M).
C init: initial concentration at equilibrium (M). This concentration is used for simulation and theoretical calculation.
C fitted: fitted value of concentration (M).
C min: minimum concentration for fitting (M). The minimum value usually is 0.1 time initial value.
C max: maximum concentration for fitting (M). The minimum value usually is 10-time initial value.

D: diffusion coefficient (cm^2/s). The default value is 10^-5.
D fitted: fitted value of diffusion coefficient (cm^2/s).

D min: minimum diffusion coefficient (cm^2/s) for fitting. The minimum value usually is 0.1 time initial value.
D max: maximum diffusion coefficient (cm^2/s) for fitting. The minimum value usually is 10-time initial value.

β: Adsorption coefficient (/M). The default values of all species are 10^4. For non-adsorptive species, set its value to 0.
Γ_m: Maximum adsorption amount (mol/cm^2). The default value is 10^-8.

Pre-equilibration checkbox:

When this option is enabled, it automatically assumes that all the chemical and electrochemical reactions in the vicinity of the electrode surface are in equilibrium as determined by the thermodynamic parameters: chemical equilibrium constant Keq, the standard potential E°, and by the starting electrode potential E_{start}. Then, the entered values of analytical concentrations are not identical to the corresponding initial concentrations.

It is a good idea to keep the pre-equilibration option enabled. When the pre-equilibrated and analytical concentrations are different significantly, the initial condition for the experiment and the simulation may not be what was expected. The degree, to which the pre-equilibrated concentrations may be considered to be the bulk concentrations, will depend upon time of pre-equilibration (i.e., the time between setting the starting potential and initiating the potential scan), the operative kinetics, and the geometry. The value of the initial concentrations will act as if they are the bulk concentrations. A reasonable assumption only if the electrode geometry does not produce steady-state diffusion and if the pre-equilibration time is much longer than the duration of experiment.

When the pre-equilibration is not selected, the pre-equilibrated and analytical concentrations are the same.

<big>Chapter 6

Playing Around</big>

6.1 Simulating over 30 Factors

A simplest way to run simulation is just to click the **Run** menu and then the **Simulate** submenu. It uses the default values to simulate a linear sweep voltammogram. You can change technique under the **Technique** menu, or change mechanism in the **Mechanism** window under the **Mechanism** menu, or change instrumental parameters in the **Instrument** windows under the **Instrument** menu, kinetic parameters in the **Kinetic** window under the **Kinetic** menu, or concentration and coefficients parameters in the **Concentration** window under the **Concentration** menu. You have choice for digital or analytical simulation by clicking the **Digital Simulation** checkbox in the **Mechanism** window. The analytical simulation is fast, and useful for comparison of digital simulation.

Notice that some menu (e.g. the **Plot** menu and the **Analyze** menu) will be activated only after run simulation or load data because they require data.

This software can simulates the effects with changing over 30 factors, e.g. charge current, resistance, noise, preconcentration time, preconcentration potential, convection, pH, the reactant number, and product numbers, standard redox potentials, rate of electron transfer, transfer coefficient, concentration, diffusion coefficient, forward and reverse chemical reaction rate constants, temperature, electrode area, and experimental parameters, etc.

This software can simulate many cases shown in the book: "Electrochemical Methods, Fundamentals and Applications", by AJ Bard [6].

A simple reversible charge reduction reaction at a planar electrode by cyclic linear sweep technique (CV) is assumed here, otherwise stated.

6.1.1 Effect of pH

Click the **Mechanism** menu to open a **Mechanism** window, tick the "**pH effect**" checkbox, change the number of H^+ in the charge reaction, and then click the **OK** button to close the **Mechanism** window. Click the **Kinetics** menu to open a **Kinetics** window, change the pH value in the **Solution** section, and then click the **OK** button to close the window. Run the simulation. You should see the peaks shift when pH is larger or less than 7. As the pH value increases, the peak shifts to more negative potential. For a charge reaction

$a\ \mathrm{A} + h\ \mathrm{H}^+ + ne = b\ \mathrm{B}$

where a is the reactant number, b is the product numbers, h is the number of H^+, and n is the electron number. The relationship of the peak position with the pH value usually is linear:

$E_p = k1 - k2\ \mathrm{pH}$

Where $k1$ and $k2$ are constants. $k2$ depends on the electron number, the number of H^+, the numbers of reactant and product, and temperature. For a=b, it becomes

$E_p = k1 - RTh/nF\ \mathrm{pH}$

For a=b and h=n, it becomes

$E_p = k1 - 0.059\ \mathrm{pH}$

It shows that both peaks in CV shift to 59 mV more negative potential per pH. These agree with the theoretical equation (2.5).

6.1.2 Effect of Hydrogen Ion Number

As the hydrogen ion number h increases from 1 to 2, the peak shift increase from 60 to 120 mV more negative potential per pH. These agree with the above theoretical equation.

6.1.3 Effect of Reactant and Product Numbers

For a charge reaction

a A + ne = b B

where a is the reactant number, b is the product number, and n is the electron number. If you change the reactant and/or product number of charge reactions, you should see the current changes.

As the product number increases, e.g. the reaction A+e=2B, its current becomes lower and broader, the peak shifts about 10 mV more negative.

As the reactant number increases, e.g. the reaction 2A+e=B, its shape is the same as above reaction, and its location and half-peak width are the same as above reaction, but the current height is half.

For the reaction 2A+e=2B, its peak becomes more lower and broader. It is the same as the reaction A+0.5e=B, because the former reaction becomes to the latter reaction by division of the former reaction by 2. Its peak current is 0.5^1.5=0.35 lower than the peak current in the one-electron reaction A+e=B, which agrees with the theoretical value in the eq. (2.8). Its peak potential Ep= $E_{1/2}$ - 0.06 V, which is agree with the theoretical eq. (2.9). This is double of the peak movement to more negative in the one-electron reaction. Its half-peak width $|E_{p/2} - Ep|$=0.11 V, which agrees with the theoretical value in the eq. (2.11). This is double of the half-peak width 0.055 V in the one-electron reaction.

For the charge reaction 2A+2e=2B, its current is the same as the current for the reaction A+e=B. This agrees with the eq. (2.5).

6.1.4 Effect of Electron Number

If you change the electron number of charge reactions in **Digital Simulation** section for both Digital and Analytical Simulation, you should see that peak height increases and peak width decreases as the electron number increases. For LS technique at a planar electrode, its peak current increases, which agrees with the eq. (2.8), its peak potential shifts to more negative, which agrees with the eq. (2.9), and its half peak width decreases, which agrees with the eq. (2.11).

If you change sign of electron number to negative, then reactant *A* becomes a reduced species, product *B* becomes an oxidized species, and the reaction becomes oxidation.

You not only simulate the effect of negative electron number, but also simulate the effect of fraction of electron number. E.g. electron number is 0.5.

Run two simulations for A+0.5e=B and 2A+e=2B. They are the same, which agrees with theory, as reaction A+0.5e=B is the same as 2A+e=2B.

6.1.5 Effect of Electrode

6.1.5.1 Effect of Electrode Geometry

You can simulate the effects of over 10 electrode geometries. Currents at different electrode geometries are different as their diffusion models are different. By keeping the same area of the electrodes, the peak current at the cylindrical electrode is larger than the peak current at the planar electrode. The peak current at the spherical electrode is larger than the peak current at the cylindrical electrode. These agree with theoretical equations.

Note that the planar electrode geometry is not available for microelectrodes. For larger planar electrodes, there is the edge effect, but it has little effect on the over-all performance because the edges are small compared to the area of the plane. As the electrode gets smaller, the relative contribution of the edge becomes more important. A very small electrode, relative to the thickness of the diffusion layer, behaves as if it is all edge.

6.1.5.2 Effect of Microelectrode

Not only the electrode geometry has effects on shape of current, but also the electrode size does. When the electrode size is very small, e.g. electrode radius is 1e-4 cm, its current becomes the S-shape from the peak shape, and steady-state current at the spherical electrode in LS technique is 1.2e-9 A, which agrees with the eq. (2.4). The steady-state current at the micro disc electrode in LS technique is 3.86e-10 A, which agrees with the eq. (2.4).

A shape of linear scan voltammogram at spherical electrodes is changed from peak shape to S-shape. When the products of scan rate and radius, $v\ r > 10^{-5}$, the shape is peak. When $v\ r < 10^{-7}$, the shape is wave. The steady-state current is independence of the time factors, e.g. the scan rate, the electrode-rotating rate, the pulse time, the drop time, or the sampling time.

6.1.5.3 Effect of Electrode Area

The peak current increases linearly with the electrode area for planar electrodes, or with square of the electrode radius for planar disk electrodes. But it increases linearly with square root of the electrode area or with the electrode radius for microelectrodes, regardless of electrode geometry, spherical or disk electrodes. This agrees with theoretical equations.

6.1.5.4 Effect of Electrode Rotating Speed

For the rotating electrodes, current increases as the electrode rotating speed increases, and the limit current increases linearly with square root of the electrode rotating speed, which agree with theoretical equations. When the ratio of rotating speed to scan rate, $\omega/v < 1$, the shape is peak. When high-speed $\omega/v > 10^3$, the shape becomes S-shape wave. If you set the rotation speed to 0, the current should become one without rotation.

6.1.5.5 Effect of Thin Film or Surface Modified Electrode

For a thin film electrode, surface modified electrode or thin layer cell, its current shape is peak-shape as it is finite diffusion. Its behaves are similar to adsorption reaction at plane electrodes. Its peak current increases linearly with scan rate.

6.1.6 Effect of Scan

6.1.6.1 Effect of Scan Rate

For LS and CV techniques at a planar electrode in simple reversible and irreversible charge reactions, the peak current increases linearly as square root of scan rate increases, which agree with the eq. (2.8).

In reversible and irreversible adsorption reactions, the peak current increases linearly with increasing scan rate. So adsorption current increases more rapid than diffusion current. But in quasi-reversible reaction, these relationships are not linear anymore.

In catalytic reaction, the limit current is independent of scan rate.

For reversible charge and adsorption reactions, the peak location and the width at half peak are independent of scan rate. For irreversible charge and adsorption reactions, the widths at half peak are still independent of scan rate, but the peak locations are not. The reduction peak location shifts linearly to more negative potential and the oxidization peak location shifts linearly to more positive potential as log of scan rate increases. Therefore, the separation between the reduction and oxidization peaks becomes larger as scan rate increases. These agree with theoretical equations.

For square wave and additive square wave techniques, the peak current increases linearly as square root of frequency increases.

At a microelectrode, the steady-state currents are independent of the time factors (e.g. the scan rate, the electrode-rotating rate, the drop time, the pulse time, or the sampling time) for all LS, DC, and normal pulse techniques, which agree with the theoretical equations.

6.1.6.2 Effect of Scan Direction

For a reduction reaction, the scan direction is from positive to negative, i.e. the start potential is large than the ending potential, so the current is positive.

For an oxidation reaction, the scan direction is from negative to positive, i.e. the start potential is less than the ending potential, so the current changes to negative.

6.1.6.3 Effect of Scan Cycle

The current in second cycle is different from current in first cycle. But the current in third cycle is close to the current in second cycle. So, third cycle is enough.

6.1.7 Effect of Preconcentration

For anode stripping voltammetry, set the preconcentration potential -0.2/n V more to species' standard electrode potential, the start potential of sweep to –0.3 V and the end potential to 0.3 V.

For cathode stripping voltammetry, set the preconcentration potential 0.2/n V more to species' standard electrode potential, the start potential of sweep to 0.3 V and the end potential to -0.3 V.

Select the **Preconcentration** checkbox in the **Instrument** window.

6.1.7.1 Effect of Preconcentration Time

Change the preconcentration time in the **t pre** field. The preconcentration time usually is a number of minutes. If you increase the preconcentration time, e.g. from 600 second to 1000 second, the peak current increases, but the peak current will have a limit. If you set the preconcentration time to 0, you should see that the current is the same as one without preconcentration. You should enter your mercury film thickness into the **Length** field in the **Electrode** section of the **Instrument** window if you use a planar mercury film electrode.

6.1.7.2 Effect of Preconcentration Potential

Select the **Preconcentration** checkbox in the **Instrument** window. Change the preconcentration potential value in the **E pre** field. If you increase the preconcentration potential, e.g. from 0 to –0.3 V for the standard electrode potential of 0.1 V, the peak current increases, but the peak current will have a limit. It reaches the limit when the preconcentration potential value usually is -0.2/n V to species' standard electrode potential for anode stripping or 0.2/n V for cathode stripping. E.g. you further increase the preconcentration potential, e.g. from –0.3 to –0.4 V, the current will not increase anymore.

6.1.8 Effect of Concentration

For a simple charge reaction, as the bulk concentration of reactant increases, the peak currents increase linearly, but the peak locations do not change, which agrees with the theoretical equations.

But for adsorption reaction, the peak current increases linearly in lower concentration, then increase slowly nonlinearly, finally reach a limit at high concentration, which agrees with the theory because it reaches maximum adsorption.

6.1.9 Effect of Pulse

6.1.9.1 Effect of Pulse Height

In differential pulse and square wave voltammetry, for small pulse, the peak currents increase linearly but resolutions become poor with increasing pulse height, which agrees with the theoretical equations. For large pulse, the increasing of the peak currents is not linear anymore.

But for additive square wave voltammetry, the pulse height has a little effect.

6.1.9.2 Effect of Pulse Width

In pulse voltammetry, as the pulse width increases, the peak or limiting current decreases. This agrees with the theoretical equations.

For normal pulse and different pulse, square wave techniques, the limiting or peak current decreases linearly as square root of pulse time increases, which agrees with the eq. (2.2).

6.1.10 Effect of Sampling Time

As the sampling time decreases, the peak or limiting current increases, but the charge current increases as well. This agrees with the theoretical equations. The sampling time usually is larger than or equal to 0.6. In Staircase voltammetry, the peak potentials shift to positive potential as well. For additive square-wave voltammetry, you can change the first sampling time different from the second sampling time to offset charge current to zero. But the sampling time does not affect steady-state current at the microelectrode.

6.1.11 Effect of Techniques

You can simulate virtually **any waveform** techniques in voltammetry and chronoamperometry. You can design or import your waveform. You see the waveform applied to electrodes by click on the **E vs t** menu of the **Plot** menu.

From current shape point of view, techniques in voltammetry can be divided into three types:

1. The first type is S-shape. E.g. DC and normal pulse voltammograms, steady-state current.

2. The second type is peak shape. E.g. differential pulse and square wave voltammograms. But there is effect of the DC term on differential pulse voltammogram. When you click the **i s vs E** menu, you will see these pulse current and DC current.

3. The third type is the peak tailor shape. E.g. LS, CV, additive square wave, and staircase techniques. Their current shapes usually are the peak tailor shape, but depend on scan rate, electrode geometry, electrode size, reaction mechanism, etc. The pulse currents in square wave technique are the same as the current in the staircase technique when pulses become zero, which agree with theory.

6.1.12 Effect of Diffusion Coefficient

The change in the ratio of diffusion coefficient D_A/D_B leads to the potential shift. It shows that the peak potential shifts to more positive as the ratio increases. This agrees with theoretical equation $dE/d\ln(D_A/D_B) = RT/(2nF)$. However, the height of the reverse peak almost does not change, although a very small change occurs because of the changing relative position of E_{end} and E_{peak}.

When the ratio = 4, the surface concentration of product at end is double of the surface concentration of reactant at the beginning. When the ratio = 1/4, the surface concentration of product at end is half of the surface concentration of reactant at the beginning.

6.1.13 Effect of Catalytic Reaction

For catalytic mechanism

A+e = B, C+B->A

Assume that its charge reaction is reversible, chemical reaction is irreversible, the concentration of species C is much larger than the concentration of species A, and chemical reaction rate is very large.

The currents in LS, CV, staircase, and additive square wave techniques become S-shape from peak-shape.

6.1.13.1 Effect of Catalytic Reaction Rate

The limiting current increases linearly with square root of the chemical reaction rate, but is independence of the time factors, e.g. the scan rate, the electrode rotating rate, the drop time, the pulse time, or the sampling time. It is similar to the steady-state current. This agrees with the theoretical equations. For digital simulation, if you set both chemical reaction rates kf = 0 and kb = 0, it becomes to a simple charge reaction without catalytic mechanism.

6.1.13.2 Effect of Concentration of Catalyst

For above catalytic reaction, the limiting current increases linearly with square root of the concentration of catalyst species *C*. This agrees with theory.

6.1.14 Effect of Drop Time

For DC, NPV and DPV techniques, the limiting or peak currents decrease linearly as square root of the drop time increases, which agrees with the eq. (2.2).

6.1.15 Effect of Chemical Reaction Rate

For EC reactions A+e=B, B=C, a reverse peak decreases as the forward chemical reaction rate k_f increases. But the reverse peak comes back as the backward chemical reaction rate k_b increases to equal to or larger than k_f. You can change the rate up to 10^300.

6.1.16 Effect of Heterogeneous Standard Rate

If the heterogeneous standard rate constant ks is very large, e.g. 10^4, then the charge reaction is reversible, and the heterogeneous standard rate constant has not any effect.

If the heterogeneous standard rate constant is very small, e.g. 10^-4, then the charge reaction is irreversible, and the heterogeneous standard rate constant has effect on the peak position only, as the standard potential. For irreversible charge reaction, the reverse peak is lower than the reduction peak, but for irreversible adsorptive reaction, both peaks are the same height if the value of α is 0.5.

6.1.17 Effect of Adsorption

The adsorptive system assumes that all adsorptions obey Langmuir isotherm and all species can be adsorbed. For non-adsorptive species, set its adsorption coefficient value to 0.

For reversible adsorption reaction, the forward and reverse currents are symmetric peaks in the same location and same height. The reverse current looks like mirror of forward current.

For non-reversible adsorption reduction reaction, the forward and reverse currents are not symmetric peaks in the same location anymore. The forward current peak moves to negative direction, while its reserve current peak moves to positive direction. So the peak separation becomes larger as the rate ks becomes smaller. This agrees with theoretical equations.

Adsorption voltammogram is similar to thin-layer or thin film electrode one as all they are surface reactions. .

In the book by Bard [6]:

Case 1. For the Section 12.5.2 "Cyclic Voltammetry: Only Adsorbed O and R Electroactive - Nernstian Reactions" in page 521 of the book, you just tick on the select box "Adsorb" in the Mechanism window, and click on the RUN menu.

Case 2. For the section 12.5.3 "CV: Irreversible Reaction" in page 523 of the book, it is similar to above Case 1, but you should change kf to very small value, e.g. 1e-3.

Case 3. For section 12.5.4 "CV: Both Dissolved and Adsorbed Species Electroactive" in page 525 of the book, its mechanism can be

A + e = B

O + e = R (adsorption reaction)

A = O, K=1

Parameters are K=1, E1=E2, adsorption coefficients of species A and B are 0.

(a) Product (R) Strongly Adsorbed.

Change the adsorption coefficient of product *R* to 1e6, the adsorption coefficient of reactant *O* to 1e4. You should see CV is similar to the Figure 12.5.4 in the page 527 of the book.

As scan rate increases, adsorption peak becomes higher.

(b) Reactant (O) Strongly Adsorbed.

Change the adsorption coefficient of reactant *O* to 1e6, the adsorption coefficient of product *R* to 1e4,

(c) Reactant (O) Weakly Adsorbed.

Other parameters: adsorption coefficient of species R = 0, adsorption coefficient of species O = 1e3. As scan rate increases, adsorption peak becomes higher.

(d) Product (R) Weakly Adsorbed.

Other parameters: adsorption coefficient of species O = 1e-3, adsorption coefficient of species R = 1e3. As scan rate increases, adsorption peak becomes higher.

6.1.17.1 Effect of Adsorption Coefficient

For reversible adsorption reaction with equal adsorption coefficients of reactant and product, peak location is at the halt-wave potential and half-peak width is 90/n mV. For strong adsorption, the adsorption coefficient affects the peak location, but did not change peak high. When adsorption coefficient of product is larger than adsorption coefficient of reactant, then peaks move to positive direction. When adsorption coefficient of product is smaller than adsorption coefficient of reactant, then peaks move to negative direction.

For irreversible adsorption reduction reaction, adsorption coefficients affect both peak high and location.

You can set its adsorption coefficient value to 0 if species is non-adsorptive.

6.1.17.2 Effect of Concentration

The concentrations do not affect the adsorption peak current when adsorption reaches its maximum.

6.1.17.3 Effect of Scan Rate

The strong adsorption current increases linearly with scan rate. So, the adsorption current increases more than the non-adsorption current with scan rate. But it is not linearly anymore for weak adsorption.

6.1.18 Effect of Electron Transfer Coefficient

The transfer coefficient does not affect on any reversible reaction.

For irreversible charge reactions, as the value of the transfer coefficient increases, the reduction peak is higher and narrower, and the oxidized peak is lower and wider. These agree with theory.

6.1.19 Effect of Frequency

For both square wave voltammetry and additive square wave voltammetry, the currents increase linearly with square root of frequency. These agree with theory.

6.1.20 Effect of Temperature

Current decreases, the positive peak shifts a little bit to negative, and the negative peak shift a little bit to positive as temperature increases. These agree with theory.

6.1.21 Effect of Resistance

As resistance increases, both forward and backward currents in CV decrease and the peak separation increases. These agree with theory.

6.1.22 Effect of Double Layer Capacitance

As the double layer capacitance increases, the baseline current increases. These agree with theory.

The combination of capacitance and resistance lead that baseline is not linear anymore because they induce a non-constant dE/dt.

6.2 Surface Concentration

After run simulation, click the **Plot** menu, and then click the **C0 vs E** submenu to show surface concentrations. The concentrations at the electrode surface are useful for checking accuracy of simulation.

For a reduction reaction A+e=B, the concentration of reactant decreases and the concentration of product increases as potential moves to more negative since scan. The concentration of reactant decreases to zero and the concentration of product increases to the same as initial concentration of reactant at the end of scan. Because all amount of species A becomes the same amount of B at the end of scan. Their concentrations cross at the half wave potential. These agree with the theoretical eq. (2.5).

For a reduction reaction A+e=2B, the concentration of reactant decreases to zero and the concentration of product increases to double of initial concentration of reactant at the end of scan, which agrees with theory because one molecular of species A produces two molecular of species B.

For a reduction reaction 2A+e=B, the concentration of reactant decreases to zero and the concentration of product increases to half of initial concentration of reactant at the end of scan, which agrees with theory because two molecules of species A produce one molecular of species B.

For EE reactions A+e=B, B+e=C, it is interesting to see the maximum surface concentration of the species B is lower than the species A or C.

For EE reactions A+e=2B, B+e=2C, the maximum surface concentration of the species C is double of the species B, and the maximum concentration of the species B is double of the species A, which agrees with theory, because one molecular of species A produces two molecules of species B and two molecules of species B produces four molecules of species C.

For EE reactions 2A+e=B, 2B+e=C, it is opposite to the above reaction.

For effect of diffusion coefficient, see **chapter 6.1.12 Effect of Diffusion Coefficient**.

The surface concentrations look like the same in reversible simple reaction, regardless of scan rate, electrode size, electrode geometry, and techniques if pulse height is zero, digital simulation, and analytical simulation. For NPV and DPV, the surface concentrations move in the pulse potential. For square wave and additive square wave techniques, the surface concentrations move in half the pulse potential.

You also can check accuracy of simulation by converting surface concentration to current or current to surface concentration under the **Convert** submenu of the **Plot** menu.

6.3 Comparing Curves

After run first simulation, click the **Plot** menu, and then the **Option** submenu. Select the **Overlap** checkbox, and then run second simulation. You can change color and line styles for individual curves. This software can compare up to six curves.

6.4 Analyzing Data

This software can analyze the x-y data for peak location, peak height, peak width, convolution, deconvolution, semi-derivative, semi-integral, derivative, integral, curve fitting, and separating overlapped peaks and background current. Semi-derivative is useful for CV. It can change the asymmetric peak shape of CV into the symmetric peak for easy measurement.

6.5 Calculating Theoretical Limiting Current

Click the **Analyze** menu and then the **Theoretical Peak** submenu to calculate the theoretical values of limiting current, peak current, peak location, and peak width of reversible and irreversible reactions. Select a mechanism from the **Analytical Simulation** section in the **Mechanism** window. The theoretical limiting values are good for checking both simulation accuracy and if your experiments reach the theoretical limit or not. The experimental values usually should be between upper limit in reversible reaction and lower limit in irreversible reaction.

6.6 Extracting Parameters by Curve Fitting

The difficult part of a voltammetric experiment is extracting the chemical information from the current-voltage curve. Apart from very simplistic analysis, the measured current cannot be directly interpreted. This software can extract the chemical information from the whole current-voltage curve. It helps to get parameter values and mechanisms. Curve fitting to any electrochemical parameter is easy by click to select that parameter, and then click on the Manual Fit or Auto Fit menu.

6.6.1 Fitting to Simulation Curve

In order to extract kinetic parameters, you can fit a simulation curve to another simulated or experimental curve. It can retrieve any of 30 parameters (e.g. concentration C, standard electrode potential E°, and the heterogeneous standard rate constant ks) from voltammogram by curve fitting. Select parameters that you want to fit, and input the initial, minimum and maximum values of the parameters. The minimum value usually is 0.1time initial value and maximum value usually is 10-time initial value. e.g. after run simulation with all default values, select a concentration, then change the **C** value from 1e-3 to 2e-3 in the Species section, click the **Auto Fit** menu. You will see the fitted value of 0.001 in the ***C fitted*** field next to the ***C*** text field. Notice that when you auto fit, you should not click on the **OK** button on the **Chemicals** window to close the **Chemicals** window, otherwise you will get the “Runtime error 6: overflow”. This bug is fixed since version 4.6.

You should manual fit before auto fit. The manual fit shows how well your initial guesses values work. If it diverged, you should change their initial values and/or minimum and maximum values, and then try again. By the manual fit, you must change the initial values every time of run.

6.6.2 Fitting to Experimental Curve

One of the key functions of this software is a fitting routine that optimizes selected simulation parameters to provide the best fit between the experimental and simulated voltammograms. Data is text file formats without header. There are a number of important points to note:

1. The data must be arranged as potential-current couples.
2. The potential and current values within a data couple must be separated using a comma.
3. The potential step must be constant.

It should also be stressed that the potential step (i.e., the difference between adjacent potential values) must be constant throughout the data set. We have observed that variation of the potential step value can cause considerable problems with the fitting routine.

It is similar to fit the simulated curves. Click the **File** menu, the **Open** submenu, the **Cuurent Data** submenu to select your data file. But you should input your experimental values of $\mathbf{E_{start}}$, $\mathbf{E_{end}}$, $\mathbf{E_{step}}$, etc. into the **Experimental** section. This software requires that data are in SI unit and first peak is positive value. If your experimental data are not, please convert your experimental data to in SI unit. E.g. click the **Analyze** menu, and then the **0.001Y** submenu to convert current from *mA* to *A*. After the experimental data (text) files are selected and loaded into this software, the mechanism and parameter values are then entered, and the parameters to be varied are selected. A parameter of start current in **Baseline** section should be zero. Once these have been done, you can start fitting operation by clicking the **Fit** menu.

It is important to note that any given voltammogram may be accurately simulated by more than one mechanism and/or set of parameter values. Experimental measurements should therefore be made over a wide range of parameter values. The most common variables are scan rate and technique, although variation of concentration and/or temperature can also be used. If one set of parameter values can provide a good match between the experimental and simulated voltammograms measured over a wide range of scan rates (and/or techniques), then this is good evidence that these parameter values are correct. However, it does not *prove* that the correct mechanism and parameter values have been selected. It is up to the user to determine whether the selected mechanism and parameter values are chemically and electrochemically reasonable (i.e., are they consistent with the results of electrochemical studies on similar systems?). The sensitivity of the fit to variations in the parameters values must also be investigated.

It should note that for irreversible charge reactions, you cannot fit both the heterogeneous standard rate constant and the standard electrode potential in the same time because they become dependent each other, and they are coupled.

- For a simple reversible or nearly reversible redox reaction, A + e = B, it is in principle reasonable to evaluate Eo and D (= $D_A = D_B$) from a single CV. Data over a range of scan rates will confirm if it is diffusion control or not.

- If the reaction is quasi reversible it also might be possible to obtain meaningful values for ks and α from a single CV. Here again, wisdom dictates that data from several CVs run over a range of scan rates be used to evaluate ks and α.
- Parameter values may be coupled: Under certain circumstances there may be an infinite number of combinations of values of two (or more) parameters that effect identical (or virtually identical) fits, e.g.:

For a simple charge reaction, A + e = B, the values of Eo and the ratio D_A / D_B are coupled. This is why it allows diffusion coefficient values to be linked during fitting- unlinked there would be an infinite number of combinations of Eo values and D_A / D_B ratios that would effect identical CVs.

For a completely irreversible, A + e -> B, the values of Eo and ks are coupled.

For an EC reaction, A + e = B with an effectively irreversible chemical reaction B -> C by k_f, and RT k_f / F|v| > 1, the values of Eo and k_f are coupled.

The manifestation of coupling can be

- Non-convergence.

- Convergence to vastly different parameter values depending upon the initially guessed values.

- Wide confidence limits on one or more of the coupled parameters.

A seemingly excellent fit of the experimental and simulated data does not warrant high confidence in the value of any given parameter.

Suggestions for experiment:

- Obtain experimental data over a range of scan rates, and vary the starting and reverse potentials.

- Run multiple cycles.

- Alter the chemical conditions, e.g. change of concentrations of reactants, pH.

- Vary the electrode size.

- Use known values for parameters.

Suggestions for simulation:

- Change the initially guessed values of the optimized parameters to confirm that the optimized values remain the same.

- If you suspect that an optimized parameter is playing a minor role, de-select it, and explore the effect of set it at several different values while the remaining parameters are optimized.

- Be aware of sources of systematic error, e.g., uncompensated resistance, capacitance; edge effects; adventitious stirring.

- Attempt to optimize the minimum number of parameters required for a reasonable fit.

6.7 Separating Overlapped Peaks

For multi charge reactions, overlapped peaks are usually observed. There are errors in determination of peak height and position in each reaction as the overlapped peaks. It is necessary to separate overlapped peaks into individual peaks and check accuracy of simulation. If you click the **Manual Separate** submenu under the **Run** menu, you will see individual peaks. Click the **Find Peak** submenu under the **Analyze** menu, and then it will give out individual peak heights and positions.

6.8 Separating Faradic Current From Background Current

Because double layer capacitor and resistance, there is background current such as charge current. This software provides two ways to separate Faradic current from background current.

1. To simulate current with background current, click the **Input** menu, the **Instrument** submenu, change the value of C_d to 0.0001 and the value of resistance R to 10000 in the **Baseline** section, and run simulation. You should see current with baseline. When click the **Manual Separate** menu, you should see third curve for the Faradic current without background current.

2. To simulate background current, click the **Input** menu, the **Instrument** submenu, change the value of C_d to 0.0001, the value of resistance R to 1000 in the **Baseline** section and the value of the concentration C to 0 in the **Concentration** window, and run simulation. You should see background current. Then, select the **Overlap** checkbox in the **Option** window, change the value of the concentration C to 1e-3 in the **Concentration** window, and run simulation. You should see second curve for current with background current. Finally, click the **Plot** menu, the **Y Data** submenu, and the **Y2-Y1** submenu. You should see third curve for the Faradic current without background current.

<big>Chapter 7

How Do You Know It Is Right? </big>

Any simulation procedure has its stability and accuracy limitations. This software provides five ways to check for accuracy of simulation:

1. The first approach is to compare peak values of simulated voltammograms with theoretical values. Uncheck the Digital Simulation checkbox to change to Analytical Simulation, select your mechanism, and then click the Theoretical Peak submenu from the Analyze menu, to calculate the theoretical peak or limiting current and peak potential.

2. The second method is to compare digital simulation voltammograms with analytical simulation voltammograms. E.g. in order to compare digital simulation of adsorptive reversible reaction with analytical simulation of reversible adsorptive reaction and general adsorptive reaction, run digital simulation of adsorptive reaction, click the Overlap checkbox in the Option menu of the Plot menu, uncheck the Digital Simulation checkbox to see the Analytical Simulation, select the mechanism 15, run simulation, select the mechanism 17, run simulation, you will see 3 curves overlap together.

3. The third approach is to change the computational parameters. The exponential time and space grids used by the implicit finite difference computation are characterized by t and x. Although these parameters are not defined explicitly in the user interface, changing the potential steps, and the space expanding grid factor in the Instrument window respectively can alter their values. Decreasing the values of these parameters almost always improves the accuracy of a given simulation, but the computation time is also increased. This software sets default values for these parameters that will produce acceptable accuracy (e.g. better than 0.5%) in most cases. However,

there are instances where the particular set of the used parameter values causes computational problems. Decreasing the values of one or both of these Model Parameters can eliminate this problem. It is possible to obtain a simulated voltammogram that looks reasonable but is still inaccurate. It is good practice to run any simulation using different values for the **expanding grid factor** and the **potential steps** to check for accuracy. A significant difference in the results indicates that the default values are inadequate for accurate simulation. Because the smaller values of the potential step and/or space expanding grid factor will effect a noticeably longer computation time, we should use the possible largest values, which retain acceptable accuracy.

4. The fourth method is to check the concentration at the electrode surface, and to convert surface concentration to current or current to surface concentration. See **Section 2.6 Surface Concentration**.

5. The fifth way is to check the separated individual currents for multi charge reactions by the **Separate** menu.

You can combine any of these five ways to check for accuracy of simulation.

<big></big>Chapter 8

Frequently Asked Questions (FAQ)

Q: How much does registration cost?
A: Its membership is from $10 per year. Shareware version $10 + $10 per function (except $100 for the function of the import experimental data, and auto fit $70) per year per copy. Some functions must be ordered together. Please state what function you want when you order. E.g. for a full package of all functions is $480: Basic (Shareware) version $10 + import data $100 + export data $10 + 10 techniques $100 + manual fit $10 + auto fit $70 + manual separate $10 + auto separate $10 + open parameter file $10 + save parameter file $10 + 5 charge reactions $50 + 9 chemical reactions $90 = $480. It is Australian dollar.

It is recommended that you try shareware version on a computer where you want to work before you buy. You cannot change hard disk drive where it was installed after password is given.

Q: Which platforms can the program run on?
A: Its 32-bit version program runs on IBM PC under Windows 95/98/NT/2000/XP/Vista, while its 16-bit version program runs under Windows 3/3.1/3.11/95/98/NT.

The 32-bit version needs Microsoft Visual Basic 6 runtime DLL files (e.g. msvbvm60.dll, comdlg32.ocx) in the same directory as the program or in the directory \windows\system for Windows 3.11 or 95, or in the directory \winnt\system32 for Windows NT.

The 16-bit version needs Microsoft Visual Basic 4 runtime DLL files (e.g. vb40016.dll and oc25.dll) in the same directory as Polar or in the directory \windows\system for Windows 3.1, or in the directory \winnt\system for Windows NT.

Q: I cannot save a file.

A: You miss the Microsoft Visual Basic 6 runtime DLL file comdlg32.ocx or you did not register.

Q: Where can I download these dll?

A: Microsoft Visual Basic 6 runtime DLL files are from http://www.simtel.net/simtel.net/win95/dll.html, where msvbvm60.dll is inside simvb6-5.zip. Microsoft Visual Basic 4 16-bit runtime DLL files are from http://www.simtel.net/simtel.net/win3/dll.html.

Q: When I click the Simulate menu, I got error: “No data”, or "Run-time error 13”, with the message: "Type mismatch".

A: I guess you are running it under **non-English version of Windows**. Please change language setting to English in the Regional Setting of the Control Panel, and restart Polar. Or try it under English version of Windows. Some non-English versions of Windows have problem to run English version program.

Q: Still have install problem?
A: You should close all programs (include Office, Mail) before install the program. If you still have problem, try to register file msvbvm60.dll by double click or type following command in DOS:

```
Cd \windows\system
Regsvr32 msvbvm60.dll
```

then start Polar.

Q: Why are some menus inactive?
A: Some menus will be activated only after you click the Simulate menu or load data because they need data.

Q: I cannot see any chemical reaction in Shareware version. Is this part of the program not finished yet or is it only available in the registered version?

A: It is only available in the registered versions. You can change chemical reaction rate k_f up to 10^{25}. The registered versions simulate virtually any mechanisms.

Q: Does it include my mechanism?
A: If your mechanism is missing, please send your requirement into author. Author may add your mechanism into new version special for you.

Q: Can it fit data by curve fitting?
A: Yes. Click to select a parameter that you want to fit, and then click the Auto Fit menu.

Q: Can I change graph into other program Spreadsheet Excel?
A: Yes. You export data in text file, and then read data into it.

Q: Some submenus semi-derivative, semi-integral, derivative, and integral, seem to not work sometime. How can I do?
A: You should first click the Next submenu under the Plot menu, then try semi-derivative submenu.

Q: How can I get registered version?
A: You will receive it if you pay author registration fee.

Q: What are differences among Shareware, Student, Teacher, Academics and Professional versions?
A: The Shareware version is for try before you buy, the Student version is for students, the Teacher version is for teachers, the Academic version is for academics, and the Professional version is for professionals. Please see **Table 1 Feature** for details.

Q: When I run the SWV with default conditions, it does not appear to give the correct curve. Why?
Because default conditions are for linear sweep and CV only. For SWV, DC, NPV and DPV, you should change scan rate v to 0.01. For SWV you should calculate correct scan rate by v=E step/t pulse before run digital simulation.

Q: Is it possible to click on a point and then have displayed both the current and potential for the point?

A: Yes, since version 4.7.

Q: How to simulate oxidation reaction?

A: change the scan potential to the E_{start} < the E_{end} in the Instrument window.

Q: When I click on the Auto Fit menu, I got "Runtime error 6: Overflow". Why? How to fix it?

A: Because you close the **Chemicals** window. When you auto fit, you should not click on the OK button on the **Chemicals** window to close the **Chemicals** window, otherwise you will get the "Runtime error 6: overflow". It has been fixed since version 4.6.

Q: What data format can be imported?

A: The x-y pairs of text data. Please see **Chapter 6.6.2 Fitting to Experimental Curve**.

Q: Is it licensed for user or machine?

A: Software is like hardware. If you want to use different PC, you had to buy different machines. Can you just buy a single machine in order to use different PC? Many users can share one machine. It is the same as many users can share one copy of software. Therefore, the software license is for machine, not for user. One copy of software is for one machine. If you want to use software for different PC, you should buy more copies of software, and you will get discount.

Q: What happen when I upgrade machine?

A: When you upgrade the hardware of machine, you can change motherboard, CPU, RAM, add hard disk, but it is suggested that you should keep your old hard disk and never format it, so your software ID does not change, it will still work. You can put old hard disk into external hard disk box with USB connected to new PC. Or you install it in USB disk, not in hard disk.

Q: Can I run a single copy of this software in different PC?

A: Yes, if you install it in USB disk, you can plug the USB disk into any PC, and use the same password to login. It is portable.

Q: How does it compare to competitors?

A: This software has many advantages over competitors (see details on the feature table in **Chapter 2 Features**). Some advantages are as follows:

- Competitor only digitally simulates a single technique CV at 5 electrode geometries, while this software analytically and digitally simulates virtually **any waveform** technique at over 10 electrode geometries.
- Competitor cannot design or import waveform while this software can.
- Competitor cannot simulate **adsorption** while this software can.
- Competitor cannot simulate very fast chemical reaction rate larger than 1e20, while this software can simulate chemical reaction rate up to 1e300.
- Competitor cannot simulate reactions with reactant or product number, e.g. 2A+e=B, while this software can.
- Competitor cannot simulate reactions with fraction of electron number, e.g. A+0.5e=B, while this software can.
- Competitor cannot separate overlapped peaks, while this software can.
- Competitor cannot simulate effect of pH, while this software can, and even simulates over 30 effect factors.
- Competitor cannot calculate any theoretical value, while this software can calculate over 1000 types of theoretical peak values.
- Competitor cannot analyze data, while this software can.
- Competitor cannot check simulation accuracy, while this software can by five ways of checking.
- You download and try this software free.
- This software is more powerful but cheaper.

Q: I still have questions.

A: Please post your questions to Electrochemistry Forum in website www.electrochemistry.net.

<big>Chapter 9

References</big>

1. W. Huang, T. Henderson, A.M. Bond and K.B. Oldham, Curve fitting to resolve overlapping voltammetric peaks: model and examples, Anal. Chim. Acta, 1995, 304, 1-15.

2. W. Huang and B. Hibbert, Computers & Chem., 1995, 19(4), 433.

3. W. Huang and B. Hibbert, Computers & Chem., 1995, 19(4), 435.

4. W. Huang and B. Hibbert, Polar 2.0 for Windows: simulator of voltammogram, Chem. in Aus., 1996, 131.

5. J. Mo, P. Cai, W. Huang and F. Yun, Theory and application on multiple semidifferential electrochemical stripping analysis with thin mercury film formed in situ, Acta Chimica Sinica, 1984, 42(6), 556-561, [CA 101: 162712].

6. A. J. Bard and L. R. Faulkner, Electrochemical Methods, John Wiley & Sons, New York, 1980.

7. D. Britz, Digital Simulation in Electrochemistry, Third Edition, Springer, Berlin, 2005.

8. Roy Lowry, Polar, Physical Science Educational Review, 2002, Nov., 3(2), 26-27, http://www.physsci.ltsn.ac.uk/Publications/Journal/journ3_2.pdf.

9. J. Mo, W. Huang and R.J. Zhang, New Advances in convolution voltammetry (Review), J. Anal. Determining (Fenxiceshi Tongbao), 1985, 4(3), 1-8, CA 105: 163910.