

High-Speed Calculation of Least-Squares Best Half-Wave Potentials and Slopes of Polarographic Waves Using an Electronic Computer

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The fundamental equation which describes the polarographic wave (1) for the reversible reduction of a hydrated metal ion to a soluble, dilute amalgam is

$$E_{\text{dme}} = E_{1/2} + \frac{RT}{nF} \ln \frac{i_a - i}{i}$$

where E_{dme} refers to the potential of the dropping mercury electrode at some point on the wave at which the current is i , and i_a as the diffusion limited current. The half-wave potential, $E_{1/2}$, is a constant of thermodynamic significance and is independent of concentration.

In most electrochemical research involving polarography, the half-wave potentials and slopes of the waves are desired experimental quantities and various techniques have been used to obtain these quantities. Approximate values of half-wave potentials and slopes may be obtained by the simple technique of drawing a line along the residual current portion of the wave, drawing another line parallel to this one along the diffusion portion of the curve and then dividing the distance between these two lines to obtain the half-wave point. The potential at this point is the $E_{1/2}$. The potential difference between the $1/4$ and $3/4$ points on the wave is equal to $0.954(0.0591/n)$, from which the usual slope can be calculated.

A mathematically more precise procedure of obtaining the half-wave potential is to plot E_{dme} vs. $\log (i_a - i)/i$ using values of E_{dme} and i from the rising portion of the polarographic wave. This plot theoretically should be a straight line from which the $E_{1/2}$ can be read off at the point where the $\log (i_a - i)/i$ term is zero, i.e., the zero intercept. The slope of this line has significance because it is equal to $0.0591/n$ at 25°C , where n is the number of electrons involved in a polarographically reversible reduction.

The statistically best method is to fit the E_{dme} and $\log (i_a - i)/i$ data to a straight line of the type $y = a_1 + a_2x$ by the method of least-squares. The constant a_1 is the zero intercept, i.e., the half-wave potential, and a_2 is the slope of the best straight line. To do this calculation completely on a desk calculator would probably take at least 30 minutes apiece. To prepare the graph even on semi-log graph paper requires about ten minutes apiece. For optimum efficiency and accuracy, the least-squares best half-wave potential and slope can be calculated on a high-speed electronic computer. In our case an IBM 650 Magnetic

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Drum Calculator and 'Bell Labs Code' were used in making such calculations. (The calculator is located at the Research Computing Center at Indiana University.)

The overall time necessary to transfer the data from the polarogram to special mimeographed sheets (designed to increase the speed and accuracy of punching the IBM data cards), then punch the cards, perform the machine calculation and tabulate the answers, amounts to four minutes per polarogram. Of these four minutes only 15 seconds are used by the electronic computer for each calculation. One other important feature of the program is that both the half-wave potential and slope are corrected for the resistance of the set-up.

Procedure for Tabulation of Data

This program has been designed for polarograms recorded by the Sargent Model XXI Visible Recording Polarograph, but with only a few obvious and minor changes this program can be adapted to other manually and automatically recorded polarograms.

During the process of actually recording the polarogram, the investigator should record (preferably directly onto the polarogram) the sensitivity setting of the polarograph ($\mu\text{a}/\text{mm.}$); the cell resistance as measured with a resistance bridge (ohms); the resistance of the measuring resistor at the given sensitivity (ohms)¹; two calibrating voltages measured with a potentiometer, one measured before the wave and one after the wave (volts); and finally the polarogram number.

The following method of obtaining the remaining data from the curve is recommended for convenience:

(1). Draw a straight line along the top of the residual current curve.

(2). Draw a straight line parallel to this along the top of the diffusion current curve.

(3). Number consecutively 5,6,7 or 8 d.m.e. pips in the middle part of the rising portion of the polarogram. It makes no difference whether these pips are numbered starting from the bottom or the top. (The program was set up to use up to a maximum of eight current-voltage points in making the calculations.)

After these steps have been performed, all the necessary data may be tabulated on special mimeographed sheets. The general form of this sheet is shown in Table 1. All numbers must be recorded in 'floating decimal' form. The number occupies the first eight digits of a ten-digit word and the exponent occupies the last two. The exponent is simply 50 plus the exponent of base 10. For example, $543.21 = 5.4321 \times 10^2$ and hence is written 5432100052; $0.00543 = 5.43 \times 10^{-3}$ and is written 5430000047. (Zero is given a zero exponent, hence all ten digits are zero.)

¹ Since reasonably precise calculations are being made, the half-wave potential must be corrected for the total resistance through which the current passes. This resistance is the resistance of the cell (measured with a resistance bridge) plus the resistance of the measuring resistor of the sensitivity unit. This resistance is different for each sensitivity setting and can be obtained from the manufacturer's instrument manual.

If less than eight points are used, the data must be tabulated starting from the top of the data sheet and the unused data positions must be filled with numbers of some sort (usually zeros) for the entire routine to operate correctly.

The E_{dme} terms are tabulated not as voltage, but in % divisions starting from the initial voltage point. The program converts % divisions into applied voltage.

The i terms are tabulated not in units of current, but are recorded in units of mm. distance from the residual current line. Again, it is not necessary to convert to current since the program performs the necessary conversions.

The constants are tabulated thus: the diffusion current in mm., the sensitivity in amps./mm. (not in μ amps./mm.), the total resistance in ohms (which is the sum of the cell resistance and the resistance of the measuring resistor at the sensitivity used), the two calibrating voltages in volts, the number of voltage divisions between the initial and final voltage in % and the number of d.m.e. pips used, expressed in two different forms. (One form of this number is in the form of an instruction with only the last three digits actually to be used in the program i.e., 0 000 000 00j. The second form is written in floating decimal form as j000000050, which is used in the least-squares portion of the routine as the number of points used.)

The polarogram number follows each group of data so that the number is on each data card. A test routine in the program checks these numbers to be sure that all the data it is using for each calculation are from the same polarogram.

TABLE 1

Data Sheet for Polarographic Data

Data Locations	Voltages	Currents	Constants	
100	E_1	i_1	i_a	Pol. No.
104	E_2	i_2	sens.	Pol. No.
108	E_3	i_3	resistance	Pol. No.
112	E_4	i_4	init. E	Pol. No.
116	E_5	i_5	final E	Pol. No.
120	E_6	i_6	voltage div.	Pol. No.
124	E_7	i_7	no. of data	Pol. No.
128	E_8	i_8	no. of data	Pol. No.

Block Diagram of the Program

Any mathematical program designed for an electronic computer is based on two fundamental types of processes. One process involves the use of the ordinary mathematical calculations (add, subtract, multiply and divide, and computation of logarithms, sines, etc.), the other involves the use of logical operations, i.e., having the machine read and store the program and data, set-up certain instructions, punch out the results, etc. In general, the mathematical operations are located in

the middle of the program with the logical operations both preceding and following the mathematical operations.

This half-wave potential program is written in 'Bell Labs Code'. This code is a Complete Floating-Decimal Interpretive System which transforms the IBM 650 into a three-address, floating-decimal, general-purpose computer. The system is complete in the sense that all mathematical, logical and input-output operations normally called for in such calculations can be performed within the system, i.e., without reference to the basic operation codes of the IBM 650.

The magnetic drum which is the heart of the machine has 2,000 locations which have location addresses numbering from 0000 to 1999. The Bell Labs interpretive routine requires the use of the last 1,000 locations for its operations; this leaves the locations from 0000 to 0999 available for computing purposes. Either instructions or data can be stored in any of these latter locations.

The half-wave potential program can be summarized conveniently in the following block diagram form:

READ DATA

The machine reads the eight data cards and stores the information into consecutive drum locations from 100 to 131.

MOVE DATA

The data are then moved to "more convenient" locations for ease in programming the calculations. For example, the i values are moved to consecutive locations so that the LOOP BOX can be used. A LOOP is any series of calculations involving a repetition of a mathematical procedure, but which uses different numerical values each time the mathematical procedure is repeated. For example, the term $\log(i_a - i)/i$ has to be calculated for each value of i . The calculation is done with the first value of i , then the LOOP BOX has the computer to repeat the calculation using the next value of i . This is repeated until all the values of i are used.

SET LOOPS

In this step the LOOP instructions have to be set for the number of times these calculations are to be performed. Since a variety of the number of d.m.e. pips are used in the calculations, the LOOP orders have to be modified to loop just as many times as there are d.m.e. pips. This is the portion of the program where that "number of data" in the form of an instruction is used.

TEST POLAROGRAM NO.

This routine checks the polarogram number from each card to be sure the data are from the same polarogram. (This is accomplished by subtracting the second number from the first number. If the answer is *not* zero the machine will stop and the cards have to be corrected. If the

answer is zero, the routine continues by subtracting the third number from the second number, etc.)

iR AND INIT. E CORRECTIONS

The voltage terms, which are actually in units of chart divisions, have to be converted to voltage using the initial and final voltages and the chart divisions between these two points. Next, the initial voltage is added to each voltage term. These voltages are then corrected for iR drop by adding on the iR correction.

LOG($i_a - i$)/ i CALCULATION

The other set of coordinates needed for the least-squares calculation is the series of $\log(i_a - i)/i$ terms. These are calculated for each value of i and then the results are used in the least-squares calculations along with the appropriate E_{dme} values.

LEAST-SQUARES CALCULATION

The least-squares procedure calculates the two statistically best constants of the linear equation

$$E_{dme} = E_{i/2} + (0.0591/n) \log(i_a - i)/i.$$

The rest of the program involves performing this least-squares calculation.

PUNCH ANSWERS

The final step of the procedure is the punching-out of the answers.

The computer automatically punches out the results on IBM cards. These tabulated results include the polarogram number, half-wave potential and slope, all on one card, the corrected E values (in volts) on two cards and the $\log(i_a - i)/i$ terms for each value of i on the last two cards. These latter two sets of data are punched-out so that if it is desired the half-wave potential and slope can be checked by plotting these data manually.

In summary, the high-speed calculation of the least-squares best half-wave potentials and slopes of polarographic waves using an electronic computer can be accomplished very efficiently to give useful and accurate results.

Literature Cited

1. KOLTHOFF I. M. and JAMES J. LINGANE. 1952. Polarography, second edition. Interscience Publishers, New York.