Cyclic Voltammetry

Cyclic voltammetry is often the first experiment performed in an electrochemical study of a compound, biological material, or an electrode surface. The effectiveness of cv results from its capability for rapidly observing the redox behaviour over a wide potential range.

Fundamentals of cyclic voltammetry

CV consists of cycling the potential of an electrode, which is immersed in an unstirred solution, and measuring the resulting current. The potential of this working electrode is controlled versus a reference electrode such as a saturated calomel electrode (SCE) or a silver/silver chloride electrode (Ag/AgCl). The controlling potential which is applied across these two electrodes can he considered an excitation signal. The excitation signal for CV is a linear potential scan with a triangular waveform as shown in Figure 1. This triangular potential excitation signal sweeps the potential of the electrode between two values, sometimes called the switching potentials. The excitation signal in Figure 1 causes the potential first to scan negatively from +0.80 to -0.20 V versus SCE at which point the scan direction is reversed, causing a positive scan back to the original potential of +0.80 V. The scan rate, as reflected by the slope, is 50 mV/s. A second cycle is indicated by the dashed line. Single or multiple cycles can be used. The instrumentation enables switching potentials and scan rates to be easily varied. A cyclic voltammogram is obtained by measuring the current at the working electrode during the potential scan. The current can be considered the response signal to the potential excitation signal. The voltammogram is a display of current (vertical axis) versus potential (horizontal axis). because the potential varies linearly with time, the horizontal axis can also be thought of as a time axis. This is helpful in understanding the fundamentals of the technique.

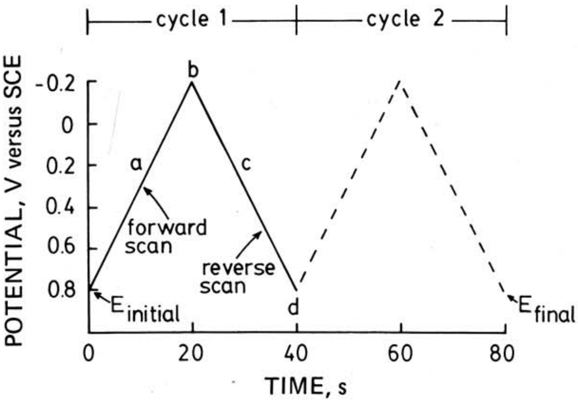


Figure 1. Typical excitation signal for cyclic voltammetry - a triangular potential waveform with switching potentials at 0.8 and –0.2 V versus SCE.

A typical cyclic voltammogram is shown in Figure 2 for a platinum working electrode in a solution containing 6.0 mM $K_3[Fe(CN)_6]$ the electroactive species in 1.0 M KNO_3 in water as the supporting electrolyte. The potential excitation signal used to obtain this voltammogram is that shown in Figure 1, hut with a negative switching potential of -0.15 V. Thus, the vertical axis in Figure 1 is now the horizontal axis for Figure 2. The initial potential (E_i) of 0.80 V applied at (a) is chosen to avoid any electrolysis of $[Fe(CN)_6]^{3-}$ when the electrode is switched on. The potential is then scanned negatively, forward scan, as indicated by the arrow. When the potential is sufficiently negative to reduce $[Fe^{III}(CN)_6]^{3-}$, cathodic current is indicated at (b) due to the electrode process

$$[Fe^{III}(CN)_6]^{3-} + e^{-} \rightarrow [Fe^{II}(CN)_6]^{4-} \qquad (1)$$

The electrode is now a sufficiently strong reductant to reduce $[Fe^{III}(CN)_6]^{3-}$.The cathodic current increases rapidly (b → d) until the concentration of $[Fe^{III}(CN)_6]^{3-}$ at the electrode surface is substantially diminished, causing the current to peak (d). The current then decays (d → g) as the solution surrounding the electrode is depleted of $[Fe^{III}(CN)_6]^{3-}$ due to its electrolytic conversion to $[Fe^{II}(CN)_6]^{4-}$. The scan direction is switched to positive at –0.15 V (f) for the reverse scan. The potential is still sufficiently negative to reduce $[Fe^{III}(CN)_6]^{3-}$, cathodic current continues even though the potential is now scanning in the positive direction. When the electrode becomes a sufficiently strong oxidant, $[Fe^{II}(CN)_6]^{4-}$, which has been accumulating adjacent to the electrode, can now be oxidized by the electrode process

$$[Fe^{II}(CN)_6]^{4-} \rightarrow [Fe^{III}(CN)_6]^{3-} + e^{-} \qquad (2)$$

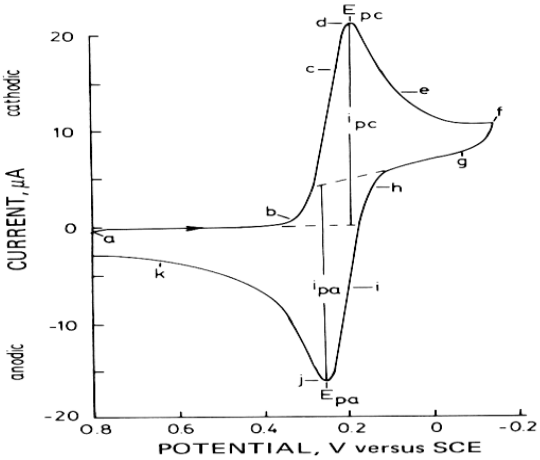


Figure 2. Cyclic voltammogram of 6 mM $K_3[Fe(CN)_6]$ in 1 M KNO_3. Scan initiated at 0.8 V vs. SCE in negative direction at 50 mV/s. Pltainum electrode, area = 2.54 mm^2.

This causes anodic current (i → k). The anodic current rapidly increases until the surface concentration of $[Fe^{II}(CN)_6]^{4-}$ is diminished, causing the current to peak (j). The current then decays (j → k) as the solution surrounding the electrode is depleted of $[Fe^{II}(CN)_6]^{4-}$. The first cycle is completed when the potential reaches +0.80 V. Now that the cyclic voltammogram is obtained, it is apparent that any potential positive of ~ +0.4 V would be suitable as an initial potential in that reduction of $[Fe^{III}(CN)_6]^{3-}$ would not occur when the potential is applied. This procedure avoids inadvertent electrolysis as a result of applying the initial potential. Simply stated, in the forward scan $[\mathrm{Fe^{II}(CN)_6}]^{4-}$ is electrochemically generated from $[\mathrm{Fe^{III}(CN)_6}]^{3-}$ as indicated by the cathodic current. In the reverse scan this $[\mathrm{Fe^{II}(CN)_6}]^{4-}$ is oxidized hack to $[\mathrm{Fe^{III}(CN)_6}]^{3-}$ as indicated by the anodic current. Thus, CV is capable of rapidly generating a new oxidation state during the forward scan and then probing its fate on the reverse scan. This very important aspect of the technique will be illustrated in the section on coupled chemical reactions.

A more detailed understanding can be gained by considering the Nernst equation and the changes in concentration that occur in solution adjacent to the electrode during electrolysis. The potential excitation signal exerts control of the ratio of $[\mathrm{Fe^{III}(CN)_6}]^{3-}/[\mathrm{Fe^{II}(CN)_6}]^{4-}$ at the electrode surface as described by the Nernst equation for a reversible system

$$E = E^0{}_{[\mathrm{Fe^{II}(CN)_6}]^{4-},\,[\mathrm{Fe^{III}(CN)_6}]^{3-}} + \frac{0.059}{1}\log\frac{\left[\mathrm{Fe^{III}(CN)_6}^{3-}\right]}{\left[\mathrm{Fe^{II}(CN)_6}^{4-}\right]} \qquad (3)$$

where E^0 is the formal reduction potential of the couple. An initial value of E which is sufficiently positive of E^0 maintains a ratio in which $[\mathrm{Fe^{III}(CN)_6}]^{3-}$ greatly predominates. Thus, application of +0.80 V as the initial potential causes negligible current. However, as E is scanned negatively, conversion of $[\mathrm{Fe^{III}(CN)_6}]^{3-}$ to $[\mathrm{Fe^{II}(CN)_6}]^{4-}$ by reduction is mandatory for satisfaction of the Nernst equation. The ratios of iron redox states that must exist at the electrode surface at several potentials during the scan are shown on the lower horizontal axis in Figure 2. The logarithmic relationship between E and $[\mathrm{Fe^{III}(CN)_6}]^{3-}/[\mathrm{Fe^{II}(CN)_6}]^{4-}$ is reflected by a rapid rate of change in the region where $E = E^0$, i.e., $[\mathrm{Fe^{III}(CN)_6}]^{3-}/[\mathrm{Fe^{II}(CN)_6}]^{4-} = 1$. This causes the dramatic rise in cathodic current (b → d) during the forward scan.

The physical situation in the solution adjacent to the electrode during the potential scan is illustrated by the concentration-distance profiles (*C*-*x* profiles) in Figure 3 for selected potentials from Figure 2. A *C*-*x* profile is a graphical illustration of how solution concentration (C) varies as a function of distance (x) from the electrode surface.

The *C*-*x* profiles in Figure 3a are for $[\mathrm{Fe^{III}(CN)_6}]^{3-}$ and $[\mathrm{Fe^{II}(CN)_6}]^{4-}$ at the initial potential. Note that the application of E_i does not measurably alter the concentration of $[\mathrm{Fe^{III}(CN)_6}]^{3-}$ at the electrode surface as compared to the solution bulk. As the potential is scanned negatively, the concentration of $[\mathrm{Fe^{III}(CN)_6}]^{3-}$ at the electrode surface decreases in order to establish an $[\mathrm{Fe^{III}(CN)_6}]^{3-}/[\mathrm{Fe^{II}(CN)_6}]^{4-}$ ratio which satisfies the Nernst equation for the applied potential at any particular instant. This is illustrated by profiles c-e. Note that profile (c) (for which the concentration of $[\mathrm{Fe^{III}(CN)_6}]^{3-}$ at the electrode surface exactly equals the concentration of

$[Fe^{II}(CN)_6]^{4-}$ corresponds to an E which equals the formal electrode potential (versus SCE) of the couple.

Profiles (e, g) correspond to potentials sufficiently negative of the formal electrode potential that the concentration of $[Fe^{III}(CN)_6]^{3-}$ is effectively zero at the electrode surface. The conditions for these profiles are analogous to those for chronoamperometry *(1,2)*. Once the potential has reached a value sufficient for a zero reactant-surface-concentration, the potential and its rate of change become immaterial to the diffusion-controlled current. In other words, should the scan be stopped at (el, the current will follow the same time course as if the scan had been continued.

The behaviour of the current during the potential scan can he understood by carefully examining the *C*-*x* profiles in Figure 3. The current is proportional to the slope of the *C*-*x* profile at the electrode surface as described by

$$i = nFAD\left(\frac{\partial C}{\partial x}\right)_{x=0} = K\left(\frac{\partial C}{\partial x}\right)_{x=0} \tag{4}$$

where i is current (A), n is number of electrons transferred per ion (equivalents/mol), A is electrode area (cm^2), D is diffusion coefficient (cm^2/s), C is concentration (mol/cm^3), and x is distance from the electrode (cm). Thus. the current observed at a particular potential for the voltammogram in Figure 2 can be explained by the slope of the corresponding *C*-*x* profile in Figure 3. The slope of profile (a) is zero and current is negligible at that potential. As the potential is then scanned negatively, $(\partial C/\partial x)_{x=0}$ increases for profiles (c-d), and the cathodic current in Figure 2 increases correspondingly. However, when profile (d) is reached, $(\partial C/\partial x)_{x=0}$ decreases as shown by profiles (e) and (g) because of depletion of $[Fe^{III}(CN)_6]^{3-}$ near the electrode. Correspondingly, the current now drops. Thus, the observed current behaviour for the voltammogram is an increase to a peak current at which point the current decays due to depletion of electroactive species near the electrode.

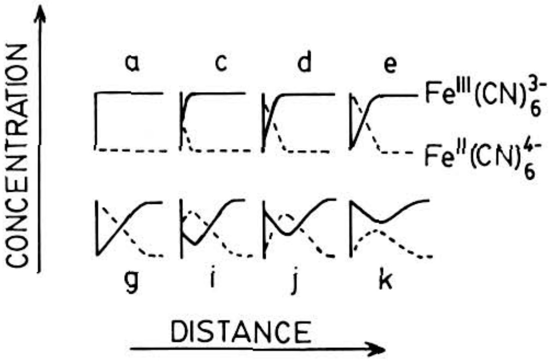


Figure 3. Concentration distance (*C*-*x*) profiles for cyclic voltammogram in Figure 2.

During the negative scan in which $[Fe^{III}(CN)_6]^{3-}$ is reduced to $[Fe^{II}(CN)_6]^{4-}$, the depletion of $[Fe^{III}(CN)_6]^{3-}$ in the vicinity of the electrode is accompanied by an accumulation of $[Fe^{II}(CN)_6]^{4-}$. This can be seen by the *C*-*x* profiles for $[Fe^{II}(CN)_6]^{4-}$. After the direction of potential scan is switched at -0.15 V to a positive scan, reduction continues (as is evident by the cathodic current and the *C*-*x* profile) until the applied potential becomes sufficiently positive to cause oxidation of the accumulated $[Fe^{II}(CN)_6]^{4-}$. Oxidation of $[Fe^{II}(CN)_6]^{4-}$ is signalled by the appearance of anodic current. Once again, the current increases as the potential moves increasingly positive until the concentration of $[Fe^{II}(CN)_6]^{4-}$ becomes depleted at the electrode. At this point the current peaks and then begins to decrease. Thus, the physical phenomena which caused a current peak during the reduction cycle also cause a current peak during the oxidation cycle. This can be seen by comparing the *C*-*x* profiles for the two scans.

The important parameters of a cyclic voltammogram are the magnitudes of the anodic peak current (i_{pa}) and cathodic peak current (i_{pc}), and the anodic peak potential (E_{pa}) and cathodic peak potential (E_{pc}). These parameters are labelled in Figure 2. One method for measuring i_p involves extrapolation of a baseline current as shown in the figure. The establishment of a correct baseline is essential for the accurate measurement of peak currents. This is not always easy, particularly for more complicated systems. A redox couple in which both species rapidly exchange electrons with the working electrode is termed an electrochemically

reversible couple. The half-wave potential ($E_{1/2}$) for a reversible couple is centred between E_{pa} and E_{pc}.

$$E_{1/2} = \frac{E_{pa} + E_{pc}}{2} \tag{5}$$

The formal potential (E^0) can be described with the formula below

$$E^0 = E_{1/2} + E_{ref} \tag{6}$$

where the E_{ref} is the formal potential of the reference electrode ($E_{Ag/AgCl}$ = 0.210 V, I = 3 M KCl).

The number of electrons transferred in the electrode reaction (*n*) for a reversible couple can be determined from the separation between the peak potentials

$$\Delta E = E_{pa} - E_{pc} \cong \frac{0.059}{n} \tag{7}$$

Thus, a one-electron process such as the reduction of $[Fe^{III}(CN)_6]^{3-}$ to $[Fe^{II}(CN)_6]^{4-}$ exhibits a ΔE of 0.059 V. Slow electron transfer at the electrode surface, "irreversibility," causes the peak separation to increase.

The peak current for a reversible system is described by the Randles-Sevcik equation for the forward sweep of the first cycle

$$i_p = (2.69\times10^5)n^{3/2}AD^{1/2}Cv^{1/2} \tag{8}$$

where i_p is peak current (A), n is electron stoichiometry, A is electrode area (cm^2), D is diffusion coefficient (cm^2/s), C is concentration (mol/cm^3), and v is scan rate (V/s). Accordingly, i_p increases with $v^{1/2}$ and is directly proportional to concentration. The relationship to concentration is particularly important in analytical applications and in studies of electrode mechanisms. The values of i_{pa} and i_{pc} should be identical for a simple reversible (fast) couple. That is

$$\frac{i_{pa}}{i_{pc}} = 1 \tag{9}$$

However, the ratio of peak currents can be significantly influenced by chemical reactions coupled to the electrode process, as discussed below. Electrochemical irreversibility is caused by slow electron exchange of the redox species with the working electrode. In this case eqns. (5), (6), (7),(8) and (9) are not applicable. Electrochemical irreversibility is characterized by a separation of peak potentials greater than indicated by eqn. (7).

Instrumentation

Cyclic voltammetry requires a waveform generator to produce the excitation signal, a potentiostat to apply this signal to an electrochemical cell, a current-to-voltage converter to measure the resulting current, and an XY recorder or oscilloscope to display the voltammogram. The first three items are normally incorporated into a single electronic device although modular instruments are also used. The potentiostat insures that the working electrode potential will not be influenced by the reaction(s) which takes place. Data are typically obtained via XY recorder at slow scans, i.e., less than 500 mV/s, and storage oscilloscope at faster rates. Scan rates up to 20000 V/s have been used, however, rates faster than 100 V/s are rarely practical because of *iR* drop and charging current.

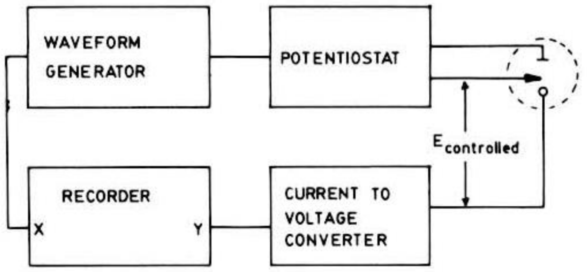


Figure 4. Instrumentation for cyclic voltammetry. Electrode designation: O— working, |— auxiliary, → reference.

Modern potentiostats utilize a three-electrode configuration as shown in Figure 4. The potentiostat applies the desired potential between a working electrode and a reference electrode. The working electrode is the electrode at which the electrolysis of interest takes place. The current required to sustain the electrolysis at the working electrode is provided by the auxiliary electrode. This arrangement prevents large currents from passing through the reference electrode that could change its potential. A three-electrode system also permits one to minimize voltage errors due to ohmic (or *iR*) loss through solution by placing the reference electrode close to the working electrode surface. The voltage represented by the product of the current and uncompensated resistance (mainly the solution resistance between the reference and working electrodes) is wasted and does not appear across the electrode/solution interface. Since the peak current increases with the square root of the scan rate, the voltage error increases at the same rate. In cases where the error is of the order of millivolts, the peaks from even a totally reversible redox couple will appear to separate as though the system were quasi-reversible. Therefore the experimenter should be cautious about drawing conclusions concerning electron transfer kinetics when either the current or uncompensated resistance is large. Some manufacturers incorporate a positive feedback circuit in their equipment to compensate for *iR* loss. Another source of error in the applied voltage arises from the variation in the rates at which ions diffuse across the ion bridge separating the reference electrode from the sample solution. The net difference in the movement of cations compared to anions results in a charge separation and, therefore an electrochemical potential difference. These junction potentials can be minimized by chwsing supporting electrolyte ions with similar diffusion coefficients (such as K^+ and $C1^-$).

A typical electrochemical cell is illustrated in Figure 5. Such a cell usually consists of a glass container with a cap having holes for introducing electrodes and nitrogen. Provision is made for oxygen removal from solution by bubbling with nitrogen gas. The cell is then maintained oxygen free by passing nitrogen over the solution. The reference electrode is typically a SCE or a Ag/AgCl electrode which often is isolated from the solution by a salt bridge to prevent contamination by leakage from the reference electrode. The auxiliary electrode is usually a platinum wire that is placed directly into the solution. Since the limiting (or peak) current in any type of voltammetry is temperature-dependent, the cell should he thermostated for the most exacting work. For most purposes, however, this is not necessary. Cells are commercially available which require as little as 1-2 ml of solution. Thin-layer cells enable voltammograms to be recorded on down to 60 µL.

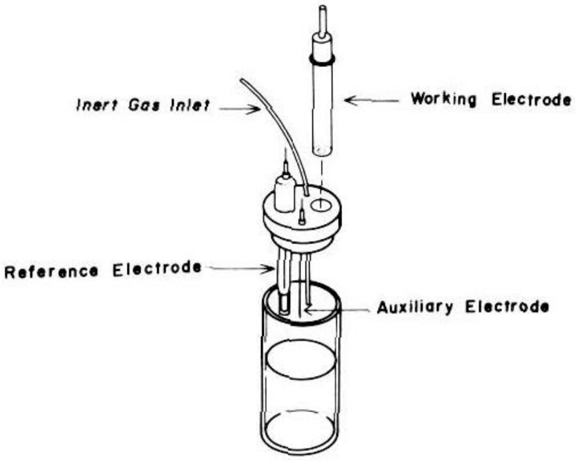
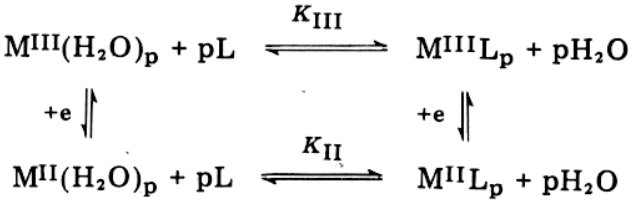


Figure 5. Electrochemical cell for voltammetry.

A large variety of working electrodes has been used with voltammetry. The voltammetric techniques termed polarography utilize the dropping mercury electrode (DME). This electrode consists of mercury drops continuously extruding from the end of a capillary. The hanging mercury drop electrode (HMDE) is commonly used for CV. Here a drop of mercury is suspended at the end of a capillary. A thin coat of mercury can he deposited on a substrate such as graphite to form a mercury film electrode (MFE). A significant advantage of mercury is its good negative potential range. Solid electrodes such as platinum, gold, glassy carbon, wax impregnated graphite, and carbon paste are also commonly used in CV. Such electrodes have a better positive potential range than mercury. Mercury working electrodes are limited to the negative potential range. Platinum and various carbon electrodes are popular for performing oxidations. However, solid electrodes are susceptible to adsorption, or surface fouling, and surface oxidation. For example, platinum forms an oxide film that shows a large reduction peak near +0.8 V in 0.5 M H_2SO_4 versus the normal hydrogen electrode. Fortunately, a surface current can be identified easily as such since the peak height is directly proportional to the scan rate. Often, judicious choice of solution conditions and electrode pretreatment can minimize this problem.

The calculation of formation constants

The formation constants for complexes in both the oxidized and reduced forms are useful in evaluating the σ-donor and π-acceptor properties of the ligands. The shift in the formal potential for the complex from the reduction potential for the aqua-complex is dependent on the ratio of the formation constants for the reduced and oxidized forms. For example, consider the reactions below.



$$E^0(M^{III}L_p)/M^{II}L_p) = E^0(M^{III}(H_2O)_p/\ M^{II}(H_2O)_p) + \frac{RT}{nF}\ln(K_{II}\ /\ K_{III})$$

Often the formal potential can be evaluated by cyclic voltanmetry when one of the complexes is too unstable to permit a direct determination of E^0 by potentiometric measurement of an equimolar solution of the two forms. If either K_{III} or K_{II} can be evaluated independently, then the other can be calculated from E^0 data.

In summary, cyclic voltammetry is a convenient tool for obtaining qualitative information about electron transfer processes. It is also a rapid method for obtaining good estimates of formal potentials, formation constants and, sometimes, the number of electrons transferred per reactant molecule and rate constants. if the user is aware of its limitations.

The tasks of the CV laboratory practice

1. *Determination of $K_3[Fe(CN)_6]$ solution concentration*

   To establish and use a calibration curve to determine the concentration of potassium hexacyanoferrate(III), $K_3[Fe(CN)_6]$ based on the absolute value of the cathodic current (i_{pc}) of cyclic voltammogram. Prepare 1-1 25 mL of 0.006 M, 0.01 M and 0.02 M $K_3[Fe(CN)_6]$ solution in distilled water solvent also containing 1M KNO_3. For each sample calculate the weight of the complex and the weight of the supporting electrolyte.

Record the cyclic voltammogram for all the prepared solutions in the 600-(–400) mV potential range, with 100 mV/s scan rate at 140 μA current range.

Draw the calibration graph showing the measured $|i_{pc}|$ as a function of the concentration of $K_3[Fe(CN)_6]$ based on the calibration series. Using the calibration graph, determine the concentration of $K_3[Fe(CN)_6]$ in the unknown concentration sample.

2. *Determination of the stability constant ($lg\beta_6$) of $K_4[Fe(CN)_6]$*

   Prepare a table (see below) about the measured and calculated parameters. Calculate the average of formal potential values and establish the $lg\beta_6$ of $K_4[Fe(CN)_6]$ by the Nernst equation.

File name	Complex concentration (M)	Scan rate (mV/s)	E_{pc} (V)	i_{pc} (μA)	E_{pa} (V)	i_{pa} (μA)	$E_{1/2}$ (V)	E^0 (V)

Cyclic voltammetry report grade sheet

1. Introduction (max 1 page)
2. Experimental

   The name of the equipment, used electrodes, potential range, current range, the table of the weight of the components.
3. Results and discussion

   The calibration curve, the calculated concentration, the table of the data, the calculated stability constant of $K_4[Fe(CN)_6]$ and evaluation of these parameters in some sentences.

References

Journal of Chemical Education, 702-706 (1983)

Journal of Chemical Education, 697-702 (1983)