

Verification of the Nernst Equation and Determination of a Standard Electrode Potential

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The "oxidation potential" concept and the "standard electrode potentials" tables are introduced in our general chemistry courses because of their basic importance in understanding reactions and "redox" equilibria and to establish quantitative relationships about the oxidation or reduction power of each chemical system.

The notion of "oxidation potential" is bound with that of "galvanic cell" as an experimental technique. Its electromotive force (emf) allows a relative value to be assigned from a standard electrode (normal hydrogen electrode, NHE) to the system potential. It is common practice to formulate the Nernst equation in order to discover the influence on the potential value of concentration of the system's components.

It is usually in the physical chemistry curriculum that the thermodynamic meaning of an electrode potential is developed and the Nernst equation (in reversible equilibrium without net current flow) is reformulated in terms of the component "activities." A step to obtain the electrode potential of a system under study is the determination of the "cell standard emf," which implies the description of reference electrodes and also the introduction of equations from the Debye-Hückel theory to calculate the "ionic activity coefficients," which emphasize the influence of the "ionic strength."

In view of the above, we think experiments should be programmed to offer students the chance to become familiar with electrodes and galvanic cell techniques. The experimental study proposed in this article is easy to develop and does not require expensive equipment. Moreover, it offers the student many challenge and rewards, such as

- 1) preparation of a calomel electrode and an easily handled redox system at different ionic strengths,
- 2) assembling of a galvanic cell with a "salt bridge,"
- 3) electrometric determination of the emf with a potentiometer or a high-impedance multimeter,
- 4) analysis of data by both plots and linear regression methods, and
- 5) verification of the Nernst equation, standard potential of a redox system and ion-ion interaction theory.

The redox system chosen is



which will be further referred to as Fe(III)/Fe(II). This system, when connected to a saturated calomel electrode SCE, forms the cell



the emf of which is given by

$$E_{\text{cell}} = E_{\text{Fe}(\text{III})/\text{Fe}(\text{II})} - E_{\text{SCE}} + E_j \quad (2)$$

$$E_{\text{cell}} \approx E_{\text{Fe}(\text{III})/\text{Fe}(\text{II})} - \text{constant} \quad (3)$$

As shown, E_{cell} depends on the potential of the redox system in eqn. (1), because the salt bridge with KCl_{sat} greatly reduces the liquid junction potential E_j and E_{SCE} remains constant.

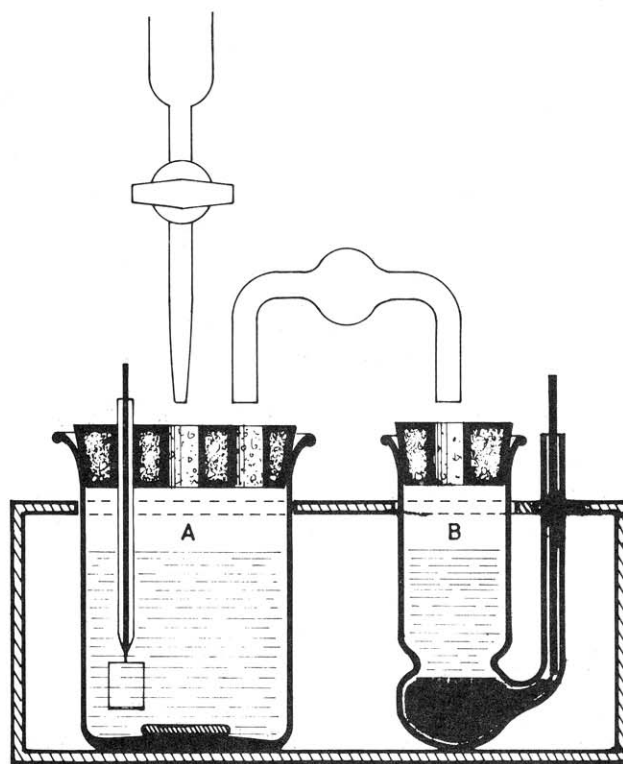


Figure 1. Section of the cell used in the experiment on the Nernst equation

Nernst Equation

The potential of redox system (1) is a function of the ratio between the activities of both species in the solution according to

$$E_{\text{Fe}(\text{III})/\text{Fe}(\text{II})} = E_{\text{Fe}(\text{III})/\text{Fe}(\text{II})}^{\circ} - \beta \log(a_{\text{II}}/a_{\text{III}}) \quad (4)$$

This expression, developed by Nernst in terms of concentrations, can be further verified by measuring E_{cell} with solutions of the same concentration in different ratios. The value of the coefficient $\beta = 2.303RT/nF$, is $0.059/n$ V at 25°C (in system (1), $n = 1$)

Experimental

The cell, Figure 1, is made from (1) a 50-ml beaker (A) containing the solutions and a small magnetic bar; (2) a 2-cm i.d. tube (B) for the SCE that has a round bottom and a lateral arm providing the connection to mercury (a nickel wire extended with a copper wire to the outside), and (3) a salt bridge filled with KCl saturated in agar. Both beaker and SCE are provided with corks having holes to fix the salt bridge and the platinum electrode (a thin 10×10 -mm sheet) and also to introduce the sample of solution inside the beaker. These elements are held together by a wooden or plastic support that gives stability to the cell and simplifies handling operations.

In the cleaned and dried tube (B) (which can also be made hydrophobic with silicone preparations to prevent the "wedge effect" (1)), distilled mercury is placed first, and over this a thin layer of "calomel paste" is carefully poured. Crystals of pure KCl are added, and the tube is then filled with the saturated solution of KCl. The paste is prepared by shaking pure calomel, to which a few drops of mercury have been added, with successive portions of KCl_{sat} solution, to remove traces of mercuric compounds; this is followed by decantation. (We have observed that the calomel-mercury "skin" in the dry state, recommended to obtain an electrode of satisfactory reversibility (1), shows a short life in the presence of a KCl_{sat} solution.)

Solutions (16 mM) of Fe(III) and Fe(II) are separately prepared by weighing both salts, $K_4(Fe(CN)_6)3H_2O$ and $K_3(Fe(CN)_6)$ (analytical grade), and dissolving them in freshly distilled water. The prepared solutions are placed in 25-ml burets; 16 ml Fe(II) solution, for example, and 1 ml Fe(III) solution are transferred to the beaker of the cell. After this the salt bridge is set up and the first measurement of E_{cell} is taken. (For these measurements a Keithley digital Multimeter, 179DMM, has been used successfully in our experiments.) A value of practically stable emf is achieved after 4–7 min.

The experiment is continued by adding 1-ml volumes of Fe(III) solution, shaking well after each addition and measuring E_{cell} each time. When the added total volume of Fe(III) solution reaches 5 ml, the following additions might be used to provide a new sequence: 3, 4, 4, and 4 ml, to complete a total volume of 20 ml.

Treatment of the Results

The analysis of the experimental data must consider not only the concentration ratio of both species (corrected by the dilution effect when each mixture is formed) but also the ionic activity coefficients, very important with highly charged ions such as Fe(III) and Fe(II).

If c_{II}^0 and c_{III}^0 are the initial concentration of Fe(II) and Fe(III) solutions, respectively, ($c_{II}^0 = c_{III}^0$ in our experiment); v_{II}^0 , the initial volume of Fe(II) solution, and v_{III} , the total volume added of Fe(III) solution, then

$$\begin{aligned} \log(a_{II}/a_{III}) &= \log[(v_{II}^0 c_{II}^0 \gamma_{II}) / (v_{III} c_{III}^0 \gamma_{III})] \\ &= \log(v_{II}^0 / v_{III}) + \log(\gamma_{II} / \gamma_{III}) \end{aligned} \quad (5)$$

In order to introduce the ionic activity coefficients γ_j , we can make use of

$$\log \gamma_j = -Az_j^2 \sqrt{I} / (1 + \sqrt{I})$$

where z_j is the ion charge and $I = \frac{1}{2} \sum c_i z_i^2$ the ionic strength. This expression (2) is a simple approximation of the extended equation of Debye-Hückel: for aqueous solutions in the concentration range of the experiments, it is more accurate than the well-known "Debye-Hückel limiting law," $\log \gamma_j = -Az_j^2 \sqrt{I}$. With it we can obtain

$$\log(\gamma_{II} / \gamma_{III}) = -A\sqrt{I} (z_{II}^2 - z_{III}^2) / (1 + \sqrt{I}) = -7A\sqrt{I} / (1 + \sqrt{I}) \quad (6)$$

After the substitution of eqn. (6) in eqn. (5), and finally in eqns. (4) and (3), we obtain

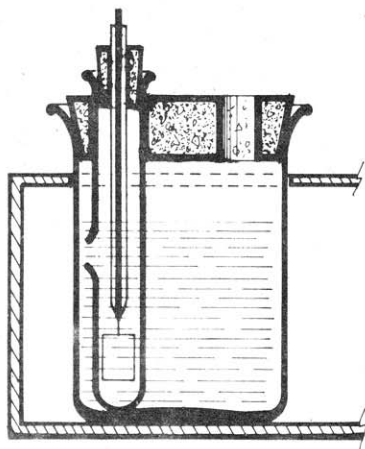


Figure 2. Modification of the cell for ϵ° determination.

$$E_{cell} \approx \epsilon_{Fe(III)/Fe(II)}^0 - \beta[\log(v_{II}^0 / v_{III}) - 7A \sqrt{I} / (1 + \sqrt{I})] + \text{constant} \quad (7)$$

This equation shows a linear correlation between E_{cell} and $\log(v_{II}^0 / v_{III}) - 7A \sqrt{I} / (1 + \sqrt{I})$. The slope β is the Nernst equation coefficient.

In aqueous medium, at 25°C, $A = 0.507 \approx 0.5$. The ionic strength might be expressed as a function of the concentration of both solutions and of the ratio of the volumes v_{III} / v_{II}^0 , according to

$$I = 2c^0[3 + 2/(1 + v_{III}/v_{II}^0)]$$

The results might be presented in a table with headings v_{II}^0 , v_{III} , I , $7A \sqrt{I} / (1 + \sqrt{I})$, $\log(v_{II}^0 / v_{III}) - 7A \sqrt{I} / (1 + \sqrt{I})$, and E_{cell} .

A plot of the data from the last two columns would allow us to verify their linear dependence and also to determine the slope of the straight line. This slope can be compared with that of the Nernst equation. In addition, the line can be fitted by the least-squares method.

Determination of the Standard Potential ϵ° of the Hexacyanoferrate(III)-(II) System

The above treatment can be used to obtain a rough value for the standard potential through the intercept $\epsilon^\circ + \text{constant}$ of eqn. (7). However, the extrapolation method of E_{cell} to zero ionic strength (3) is more rigorous.

Equation (2) can be developed according to

$$E_{cell} = \epsilon_{Fe(III)/Fe(II)}^0 + \beta \log(a_{III}/a_{II}) - E_{SCE} + E_j$$

and after substituting $a_j = c_j \gamma_j$ and $\log \gamma_j = -Az_j^2 \sqrt{I} / (1 + \sqrt{I})$

$$E_{cell} = \epsilon_{Fe(III)/Fe(II)}^0 - E_{SCE} + E_j + \beta \log(c_{III}/c_{II}) + 7\beta A \sqrt{I} / (1 + \sqrt{I})$$

Grouping terms we obtain

$$E' = E^0 + 7\beta A \sqrt{I} / (1 + \sqrt{I}) \quad (9)$$

where

$$E' = E_{cell} - \beta \log(c_{III}/c_{II})$$

and

$$E^0 = \epsilon_{Fe(III)/Fe(II)}^0 - E_{SCE} + E_j$$

As shown, eqn (9) defines a linear dependence between E' and $\sqrt{I} / (1 + \sqrt{I})$. This allows the E^0 value to be determined by graphic extrapolation (plotting the data) or by computation (applying linear regression methods) and after that the $\epsilon_{Fe(III)/Fe(II)}^0$ value. In addition we can also verify the expression for $\log \gamma_j$ through the slope value $7\beta A$.

Experimental

With the previously described Fe(III) and Fe(II) solutions and distilled water, the following mixtures can be prepared from burets:

Fe(II)/ml	Fe(III)/ml	H ₂ O/ml	($c_{III} = c_{II}$)/mM
2.5	2.5	35	1
5.0	5.0	30	2
10	10	20	4
15	15	10	6
20	20	...	8

(in order to simplify, the equimolecular ratio $c_{III} = c_{II}$ is maintained, but the ionic strength, as is indicated, is gradually modified).

The solutions are preserved in 50-ml amber bottles and transferred to the cell beaker in which a tube with a lateral window is placed (Fig. 2). The platinum electrode is introduced inside this tube. This procedure is used to protect the solution under study from KCl diffusion from the salt bridge end, otherwise the ionic strength might be increased.

Once a stable E_{cell} measurement is achieved, the solution is discarded and both beaker and tube are rinsed with small amounts of the next solution to be studied. The beaker is then filled with this solution and another measurement is taken. Error will be minimized if solutions are utilized in the order indicated.

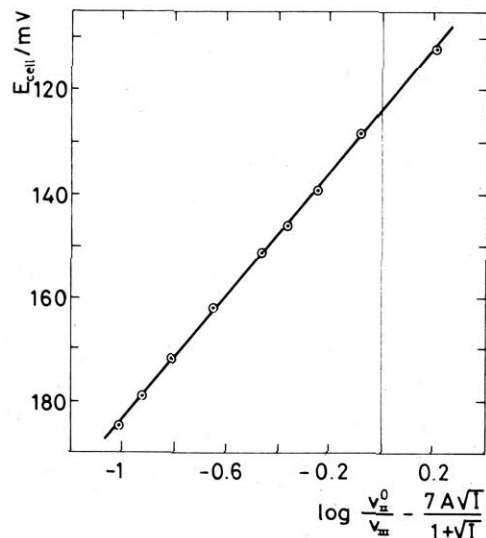


Figure 3. Nernst equation experiment. Plot E_{cell} versus $[\log(v_{\text{III}}^0/v_{\text{II}}) - 7AV\sqrt{I}/(1 + \sqrt{I})]$.

Treatment of the Results

Taking the relation between ionic strength and concentration $I = 16c$, a table can be prepared with headings c , $\sqrt{I}/(1 + \sqrt{I})$, and $E' = E_{\text{cell}} - \beta \log(c_{\text{III}}/c_{\text{II}})$. With the data from the last two columns we could plot a graph to extrapolate the E° value at $I \rightarrow 0$ and also obtain the slope of the straight line.

Finally $\epsilon_{\text{Fe(III)/Fe(II)}^\circ$ is determined by considering $E_{\text{SCE}} = 0.244$ V versus NHE and $E_j \approx 0$

Discussion

Figures 3 and 4 will illustrate representative results.

The expected linearity in the Nernst equation is correctly proved in all the runs and the slope coincides with the theoretical value $\beta = 0.0591$ V (Fig. 3).

As can be seen in Figure 4, the straight line of extrapolation proves to be, in general, well defined and the intercept leads to values of ϵ° within the limits 368 ± 3 mV. These values can be compared with the literature values given below.

$\epsilon_{\text{Fe(III)/Fe(II)}^\circ$ (25°C)	Ref.
356.0	(4)
364.4	(5)
370.4 ± 0.5	(6)
355 ± 1	(7)
361.0 ± 0.5	(8)

In order to verify the Debye-Hückel theory, the agreement of the slope is less satisfactory and there is greater dispersion among the different runs. The plot in Figure 4 shows a value

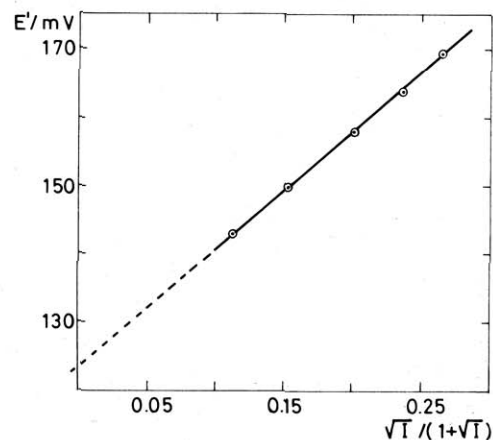


Figure 4. Determination of ϵ° . Plot E' versus $\sqrt{I}/(1 + \sqrt{I})$.

of 0.174. However, results have also been obtained which coincide with that of the theoretical slope 0.204.

When analyzing possible causes of error, it is obvious to refer first to the quality of the salts used in the experiments, and also defective preparation of the mixtures. Another source of error such as the instability of the temperature during each run and the presence of dissolved oxygen, which can alter the Fe(III)/Fe(II) ratio, might be minimized by operating under thermostated conditions and maintaining an inert atmosphere (nitrogen or argon). This would, however, introduce tedious operations that might distract from the main objective of the study. It is also possible to determine the initial and final temperatures and estimate the average value, in order to use the correct value of β and A . The use of freshly distilled water minimizes the presence of dissolved air.

The protonation of $\text{Fe}(\text{CN})_6^{4-}$ ions, studied by Kolthoff (9) and the ion-association equilibria involving K^+ and the anions $\text{Fe}(\text{CN})_6^{4-}$ and $\text{Fe}(\text{CN})_6^{3-}$, studied by Eaton et al. (10), are important since both facts modify the hypothesis of strong electrolytes hitherto accepted for both salts.

These limitations suggest other points to discuss with the students, according to the experimental results obtained.

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