Advanced Potentiometry
Erzsébet Néher-Neumann

Advanced Potentiometry

Potentiometric Titrations
and their Systematic Errors

Springer
To The Memory
of
My Mother

Erzsébet Rasztovich Mrs. Ferencné Néher

Born
on the 30th September, 1911
in Farád, Hungary
Died
on the 4th January, 1962
in Rábatamási

and
My Father
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List of Definitions and Symbols

a  a term in integrated form of potential functions $E_D$ and $E_{Df}$, defined by
\[ S_{TS1} = a = C(\lambda_A + \lambda_Y) \quad (1) \]

A($\gamma$)  theoretical Debye–Hückel coefficient: 0.5056 mol\(^{-1/2}\) kg\(^{1/2}\)
and 0.5115 mol\(^{-1/2}\) L\(^{1/2}\) for water at 25°C [1]

AY  ionic medium used, consisting of the ions $A^+$ and $Y^-$

B = $B^{2(B)+}$  potential-determining metal ion in the cell respective junction studied

C  concentration of a chosen ion of the medium respective the total ionic strength, I, kept constant during the potentiometric titration

J  particular ion type J considered

$c_J = c(J)$  molar concentration (mol L\(^{-1}\), denoted M) of ion J

D(I)  Debye–Hückel term \[ A(\gamma) I^{1/2} / (1 + 1.5 I^{1/2}) \quad (2) \]
the Debye–Hückel term [1], calculated with the ionic strength of the test solution (I), on the molar concentration scale

D(C)  Debye–Hückel term, calculated for the bridge solution of $CMAY$

D(C*)  Debye–Hückel term in the transition layer

E = total emf of the cell studied, in mV. It consists of the following terms [2,3]
\[ [E_{id,el} + E_{el,f}] + [E_D + E_{Df}] \quad (3) \]

$E_{el} = E_{id,el} + E_{el,f} = \text{the real cell emf defined as} \]
\[ E_{0J} + (g/z_J) \log_{10} (c_J f_J) \quad (4) \]
where $E_{0J}$ is a constant

$E_{id,el}$  ideal cell emf given by the Nernst equation in term of concentrations
\[ = E_J = E_{0J} + (g/z_J) \log_{10} c_J \quad (5) \]

$E_{el,f} = (g/z_J) \log_{10} f_J \quad (6)$

$E_D$  the ideal diffusion potential term, known as the Hendersson, Planck or Lewis and Sargent equation [4]
\[ = -g \int_{TS1}^{TS2} \Sigma_J (t_J^* / z_J) \, d \log_{10} c_J^* \quad (7) \]
E_D
the activity coefficient contribution to E_D
= \int_{TS1}^{TS2} \Sigma_J \left( \frac{t_j^*}{z_j} \right) d \log_{10} f_j^*
Eq. (1–15) in Ref. [5]

E_J
the so–called liquid junction potential corresponding to the
non–ideal diffusion potential term [2, 3]

= \int_{TS1}^{TS2} \Sigma_J \left( \frac{t_j^*}{z_j} \right) d \log_{10} (c_j^* f_j^*) = E_D + E_{Df}
(9)

\Delta E_J
total potential anomalies, appearing in an emf cell with liquid
junction, defined as

= (+or--) \left( \frac{g}{z_j} \right) \log_{10} f_j + E_j
= (+or--) \left( \frac{g}{z_j} \right) \log_{10} f_j + E_D + E_{Df}

The sign of the first term depends on the choice of the polarity for
the cell studied. Thus, the total cell emf can be given as

E_j = E_{0j} (+or--) \left( \frac{g}{z_j} \right) \log_{10} c_j + \Delta E_j
(11)

log_{10} f_j
log_{10} of the ionic activity coefficient of the ion J on the molar
scale, and can be expressed according to the specific interaction
theory (SIT) [6–13].

For cations (R)

log_{10} f_R = -z_R^2 D(I) + \Sigma_X \varepsilon''(R, X) c_X
(12)

where X denotes anions and the first term on the right hand side is
the Debye–Hückel term.

For anions (X)

log_{10} f_X = -z_X^2 D(I) + \Sigma_R \varepsilon''(R, X) c_R
(13)

Here, the terms of the summation count for the interaction effects
of short range forces between the ions. The standard state, here, is
chosen so that f_j \to 1 as I \to 0.

F_0
= \frac{1}{2.303 C(\lambda_A + \lambda_Y)}
appearing in functions E_D.

F_C
Faraday constant = 96484.56 (27) As (mol electrons)^{-1}. [14]

H = H^+
hydrogen ion

I
total ionic strength, in general and in the test solution, which gives
the charge density throughout the solution

= (1/2) \Sigma_J c_j z_j^2
(14)

I(C)
ionic strength in the bridge solution of C M A Y

(I*)
ionic strength in the transition layer of the junction, calculated
according to the principle of the continuous mixture junction

= x I + (1 - x) I(C)

L^y \equiv L^z(L)−
ligand in complex formation reaction
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>R</td>
<td>universal gas constant: 8.3145 J mol$^{-1}$K$^{-1}$ [14]</td>
</tr>
<tr>
<td>S</td>
<td>$(\Sigma J \lambda_J</td>
</tr>
<tr>
<td>t$_J^*$</td>
<td>electrical transport number [15] of the ion constituent J in the transition layer</td>
</tr>
<tr>
<td>t$_A$</td>
<td>$= \lambda_A / (\lambda_A + \lambda_Y)$, appearing in functions $E_{Df}$</td>
</tr>
<tr>
<td>t$_Y$</td>
<td>$= \lambda_Y / (\lambda_A + \lambda_Y)$, appearing in functions $E_{Df}$</td>
</tr>
<tr>
<td>T</td>
<td>absolute temperature in K</td>
</tr>
<tr>
<td>TS1</td>
<td>subscript and index indicating composition of the terminal solution 1 with the mixing fraction $x = 0$ at one end of the junction in the cell studied</td>
</tr>
<tr>
<td>TS2</td>
<td>subscript and index indicating composition of the terminal solution 2 with mixing fraction $x = 1$ at the other end of the junction in a given cell; i.e., the solution in contact with the positive pole of the cell</td>
</tr>
<tr>
<td>U</td>
<td>$(\Sigma J \lambda_J</td>
</tr>
<tr>
<td>$x$</td>
<td>mixing fraction at an intermediate plane in the transition layer of the junction: $0 \leq x \leq 1$</td>
</tr>
<tr>
<td>$y =</td>
<td>z_L</td>
</tr>
<tr>
<td>$z_J = z(J)$</td>
<td>algebraic charge number of ion J</td>
</tr>
<tr>
<td>$</td>
<td>z_J</td>
</tr>
<tr>
<td>Y</td>
<td>Y$^-$ common anion of the electrolyte mixture AY + HY + BY$_{z(B)}$</td>
</tr>
<tr>
<td>w</td>
<td>term in integrated form of potential functions $E_D$ and $E_{Df}$ defined by</td>
</tr>
<tr>
<td>$w = S_{TS2} - S_{TS1}$; $S_{TS2} = w + a$</td>
<td></td>
</tr>
<tr>
<td>$\varepsilon''(J, K)$</td>
<td>interaction coefficient (L solution, mol$^{-1}$) between ions J and K on the molarity scale</td>
</tr>
<tr>
<td>$\varepsilon(J, K)$</td>
<td>interaction coefficient (kg solvent, mol$^{-1}$) between ions J and K on the molality scale. The interaction coefficient $\beta$ used by Guggenheim is related to $\varepsilon$ by $\beta = (\varepsilon/2) \ln 10$.</td>
</tr>
<tr>
<td>$\log_{10} \gamma J$</td>
<td>logarithm of the ionic activity coefficient of the ion J on the molal scale. It can be calculated as given by Eqs. (12, 13), where the concentrations should be expressed in molal units (m$_K$: mol solute kg solvent$^{-1}$). Moreover, the molal interaction coefficients, $\varepsilon(J, K)$, should be used.</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>conductivity of the test solution (S cm$^{-1}$) = cell constant of the conductivity cell (cm$^{-1}$) / R (Ω); where R is the measured resistance of the solution in question.</td>
</tr>
</tbody>
</table>

\[ \kappa = \Sigma_{J} \lambda_{J} = 10^{-3} \Sigma_{J} \lambda_{J} |z_{J}| \lambda_{J} \] (17)  where  

\[ |z_{J}| \lambda_{J} \text{ is in (S cm}^{2} \text{ mol}^{-1}) \]

\[ 10^3 \kappa = \Sigma_{J} \lambda_{J} |z_{J}| c_{J} \] (18)
\[ \lambda_J \] ionic molar conductivity of ion J, concentration \( c_J \) in the test solution, 
\[
(\text{S cm}^2 \text{ mol ion}^{-1} |\text{charge}|^{-1}) \\
= 10^3 \kappa_J / (|c_J| |z_J|) \tag{19}
\]

\[ \lambda_{J^*} \] ionic molar conductivity of ion J, concentration \( c_{J^*} \) in the transition layer 
\[ \Lambda_{RX} \] molar conductivity (\text{S cm}^2 \text{ mol}^{-1}) of electrolyte RX of concentration \( c_M \)
\[ = \lambda_R + \lambda_X = 10^3 \kappa / c \tag{20} \]

\[ d \ D(I) = \left[ \frac{\partial D(I)}{\partial I} \right]_{c(B), c(H), \ldots} = 0.5115 \left[ 2^{1/2} (1 + 1.5 I^{1/2})^2 \right] \tag{21} \]

For simplicity, ionic charges are omitted in subscripts. Subscripts to subscripts are avoided, e.g. by writing \( \lambda_{Lk} \) and \( BY_{z(B)} \). Unless stated otherwise, concentrations are molarities (\text{mol L}^{-1}, denoted M).
Many phenomena in our environment, e.g. the acidity of natural waters (seas, lakes, rivers): pH = −log$_{10}$[H$^+$] are the results of many chemical reactions which are in *equilibrium*. The study of the chemical equilibrium is an important task. In the study of most equilibrium processes,

1. the equilibrium concentration of the participant molecules in M,
2. the composition of them and
3. the value of the equilibrium constants (e.g. p$K_a$ for the protolysis of a weak acid, where p$K_a$ = −log$_{10}$K$_a$) are the goals. The equilibrium constants characterize the different chemical equilibrium processes. In many of them the hydrogen ions participate. If we change and measure the equilibrium concentration of the H$^+$ ions, by addition of a strong acid (e.g. HClO$_4$) or a strong base (e.g. NaOH) or a buffer solution in a proper concentration to the system studied, we can answer for these questions. We measure the change of the concentration of the hydrogen ions by the use of an emf cell (emf stands for electromotive force). Such a study is called potentiometric titration.

Earlier, graphical methods (normalized curves) [16a] were used for the interpretation of emf data. These give the main species with good accuracy. Computer programs were used only for the refinement of the equilibrium constants found, in order to find the minor species.

Nowadays, the use of least-squares optimization programs [16b] is customary alone in the treatment of emf data. In this procedure, species are suggested until a theoretical and experimental function, e.g. $E_B$ or $E_H$, agree within 0.01 mV. Due to this assumption, *systematic errors* in the data may show up, for instance, as the formation of polynuclear species which are artefacts. The 0.01 mV uncertainty concerns the potential readings, but the *real experimental error is much higher*. Hence, the need arises to reduce the magnitude of the experimental uncertainties to the level of 0.01 mV. Therefore, it is very important to take into account the total potential anomalies (systematic errors), which depend on *all ion concentrations* to be present in the test solution and in the salt bridge used in emf cells. The author has made theoretical and experimental studies [5, 17–27] on the problems of potentiometric titrations connected to the appearance of the liquid junction potential and the total potential anomalies in the emf cells used at different experimental conditions.

The emf values, $E_B$ and $E_H$, supposed to be measured with a potentiometer (nowadays called digital voltmeter) with which the emf values can be measured with $\pm 0.02$ mV uncertainty. The use of a thermostat placed in a thermostated room is necessary. Solutions should be prepared and stored in such a room.

For the estimation of $\Delta E_B$ and $\Delta E_H$, the ionic molar conductivities in the transition layer of the junction are needed. They can be estimated as described in Ref. [17–19]. It will be shown that these are constant only under given experimental conditions.

All potentiometric titrations, this publication is based on, were carried out at 25 $^\circ$C and in acidic solutions ($pH < 7$) as forward and back titrations (except one), in order to show the reversibility of the equilibrium processes studied. This was valid for the conductivity measurements too, which were carried out at 25.000 $\pm 0.005$ $^\circ$C. The potentials and the resistance of the test solutions were read as a function of time, until constant values were obtained, namely, until equilibrium was reached. The uncertainty of the resistance measurements was, in general, ca. 0.02%.

The principal audiences for the book are high school teachers, researchers, doctorands and high school students in the field of Solution, Physical, Inorganic and Analytical Chemistry and Environmental research.

Stockholm, Sweden
16th April, 2008

Erzsébet Néher-Neumann
References

18. Néher-Neumann E (1998) The liquid junction potential in potentiometric titrations. 3. Determination of ionic molar conductivities in mixtures of \( \text{Cd(ClO}_4\text{)}_2 + \text{HClO}_4 + \text{NaClO}_4 \)
under the experimental condition that $[\text{ClO}_4^-] = 3 \text{ M}$ is kept constant. Acta Chem Scand 52: 1075–1080.


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Chapter 1
Introduction

In the studies of organic metal ion complexes, weak acids or their alkali metal salts are often used as ligands. In such studies, the protolysis of the weak acids should be investigated, first. This is done by potentiometric titrations with a strong base.

1.1 The Titration of Weak Acids (HL, H₃L) with a Strong Base

For the study of the protolysis of HL, the following equilibrium processes should be considered

\[
HL \rightleftharpoons H^+ + L^- \quad (1.1)
\]

with the protolysis constant

\[
K_{al} = \frac{[H^+][L^-]}{[HL]} \quad (1.2)
\]

according to the mass action law. Moreover, the hydrolysis of the formed salt anion (L⁻) occurs according to

\[
L^- + H_2O \rightleftharpoons HL + OH^- \quad (1.3)
\]

\[
K_h = \frac{[HL][OH^-]}{[L^-]} \quad (1.4)
\]

This process is important, if for the equilibrium concentration of the salt we have: \([L^-] \cong [H^+]\). This is the case in the nearity of the equivalence point. In alkaline solutions, the protolysis of water also has to be considered.

In these equations, the notation \([\ldots]\) denotes equilibrium concentration in M.

The mixture of a weak acid (HL) or weak base, denoted BOH, and its salt (e.g. NaL), which dissociates 100%, is a buffer system, if \(c_{salt} \gg [HL]\). Here, \(c\) stands for total, analytical concentration. The high concentration of the salt presses back the dissociation of the weak acid, and the following approximations are valid.
[HL] \cong c_{\text{acid}}, \text{ formal concentration, M}

[L^-] \cong c_{\text{salt}}, \text{ formal concentration, M}

Hence, the concentration of the H^+ ions will be from Eq. (1.2)

\[ [H^+] = K_{a1} \cdot \frac{c_{\text{acid}}}{c_{\text{salt}}} \]  (1.5)

Taking the minus logarithm of this equation, we obtain the so-called buffer formula.

\[ pH = pK_{a1} + \log_{10} \left( \frac{c_{\text{salt}}}{c_{\text{acid}}} \right) \]  (1.6)

In buffer solutions, the addition of a small quantity of a strong acid or base does not change the pH of the solution essentially, as only the ratio \( c_{\text{salt}}/c_{\text{acid}} \) changes a little. The buffer capacity is highest in the half-titration point, where 50% of HL is neutralised. As \([HL] = [L^-]\) in this point,

\[ pH = pK_a \]  (1.7)

If we titrate a weak acid of several base, e.g. H_2L or H_3L, the pH in the equivalence point is determined by the equilibrium with the smallest \( K_a \). For example, in the case of citric acid (H_3L) with \( pK_a \) values

\[ pK_{a1} = 3.09 \]
\[ pK_{a2} = 4.75 \]
\[ pK_{a3} = 5.45 \]

it can be titrated as an acid of one base, with \( pK_{a3} = 5.45 \).

### 1.2 The Measurement of the Concentration of the H⁺ or the Metal Ion B^{z(B)+} by Means of an Emf Cell

In accurate emf studies, where the concentration of the H⁺ ion (denoted \( c_H \) in mixtures of strong electrolytes and \( h \) in equilibrium systems) or that of the metal ion B^{z(B)+} (denoted \( c_B \) in mixtures of strong electrolytes and \( b \) in equilibrium systems) is measured by using a glass or amalgam/ion-selective indicator electrode, respectively, the following emf cells can be used.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Bridge solution</th>
<th>Test solution</th>
<th>Electrodes reversible to B^{z(B)+} and H⁺ ions.</th>
</tr>
</thead>
<tbody>
<tr>
<td>half-cell</td>
<td>E_{j(1,3)}</td>
<td>E_{j(1,2)}</td>
<td>Cell B and H</td>
</tr>
</tbody>
</table>

where the composition of the bridge solution is:
1.2 Concentration of the H\(^+\) or the Metal Ion B\(^{z(B)+}\) by Means of an Emf Cell

TS1, \(x = 0\),
CMAY
I(C) = CM
\(f_{j\text{tr}} = 1\) (here, \(\text{tr}\) denotes trace)

The composition of the test solution is:
TS2, \(x = 1\),
\([A^+] = \text{CM}\)

Here, the reference half-cell has the composition: Ag(s), AgCl(s) Pt/0.01 M AgY + 3 M NaY. The silver/silver chloride electrode was prepared according to Brawn [1].

Up to pH 9, we can use a glass electrode. In solutions, where pH > 9, only a H\(_2\) gas electrode can be used, because of the appearance of the sodium error.

The salt bridge was of Wilhelm type, shown in Ref. [2c].

In the constructions of emf cells, where solutions of different concentration meet, appears the liquid junction potential, which cannot be neglected. In these cells, there are two liquid junction potentials, \(E_j(1,3)\) and \(E_j(1,2)\). The term \(E_j(1,3)\) is constant and is included in the value of the experimental constants \(E_{0B}\) and \(E_{0H}\) in the expression of the total cell emf defined below.

### 1.2.1 The Total Emf of Cell B

The total cell emf is

\[
E_B = E_{0B} + (g/z_B) \log_{10} c_B + \Delta E_B, \text{ mV}
\]

where

\[
\Delta E_B = (g/z_B) \log f_{BTS2} + E_D + E_{Df} \equiv (g/z_B) \log_{10} f_{BTS2} + E_j
\]

is the total potential anomalies and

\[
E_j = E_D + E_{Df}
\]

is the liquid junction potential. The first term in the function \(\Delta E_B\) gives the contribution of the activity factor of the B\(^{z(B)+}\) ions to the ideal electrode potential defined by the Nernst equation. As is seen, the liquid junction potential is a part of the total potential anomalies.

*Theoretical equations* were derived by the author [3, 4] for the calculation of the total potential anomalies, \(\Delta E_B\) and \(\Delta E_H\), and the total cell emf \(E_B\) and \(E_H\) for different experimental conditions. For example, the function \(E_B\) could be described as

\[
E_B = E_{0B} + (g/z_B) \log_{10} c_B - g z_B [D(I) - D(C)] + g d_1 c_B + g d_2 c_H + \text{corr}
\]
where \(d_1\) and \(d_2\) denote functions of constant value in terms of some ionic molar conductivities \(\lambda_J\) and interaction coefficients. These functions are different for every experimental condition studied and will be given later on when Cell B will be treated at these conditions.

The function “corr” summarizes the Debye–Hückel terms in the potential function \(E_Df\).

The total potential anomalies can be given as

\[
\Delta E_B = -g z_B \left[D(I) - D(C)\right] + g d_1 c_B + g d_2 c_H + \text{corr} \quad (1.12)
\]

If we want to determine \(E_0B\) graphically, the function \(E_B\) should be redefined by introducing the total differential [5] for the total potential anomalies, \(\Delta E_B\). It means that this function should be separated in terms of the partial derivatives of the independent variables \((c_H, c_B \text{ and } C)\), if the function is total differential.

The mixtures \(HY + AY + BYz(B)\) are considered. We make an emf titration, carried out as forward and back titrations using an amalgam indicator electrode, where \(c_H\) is kept constant and \(c_B\) is varied. If the plots \(E_B - (g/z_B) \log_{10} c_B\) versus \(c_B\) coincide, then \(\Delta E_B\) is an unique function of \(c_B\). Similarly, in a titration where \(c_B\) is kept constant and \(c_H\) is varied, it can be shown by the coincidence of the plots \(E_B - (g/z_B) \log_{10} c_B\) versus \(c_H\) for a forward and back titration, that \(\Delta E_B\) is an unique function of \(c_H\) as well. Moreover, if \(c_H\) and \(c_B\) go independently to zero when \(\Delta E_B\) goes to zero, the function \(\Delta E_B\) is a total differential and can be defined as given below, when both \(c_B\) and \(c_H\) are changing.

\[
d\Delta E_B = \left[\partial \Delta E_B / \partial c_B\right]_{c(H)} dc_B + \left[\partial \Delta E_B / \partial c_H\right]_{c(B)} dc_H + \left[\partial \Delta E_B / \partial C\right]_{c(B), c(H)} dC
\]

As \(\partial \Delta E_B / \partial c_B\) \(= f_1(I f_2(C, c_B, c_H), c_B, c_H)\), we have

\[
\left[\partial \Delta E_B / \partial c_B\right]_{c(H)} = \left[\partial E_B^P / \partial c_B\right]_{c(H)} = \left[\partial E_B^P / \partial I\right] \cdot \partial I / \partial c_B \right]_{c(H)} + \left[\partial E_B^P / \partial c_B\right]_{c(H), 1}
\]

This function is identical with the slope of the plot \(E_B^P = E_B - (g/z_B) \log_{10} c_B\) versus \(c_B\) at constant \(c_H\). Moreover,

\[
\left[\partial \Delta E_B / \partial c_H\right]_{c(B)} = \left[\partial E_B^P / \partial c_H\right]_{c(B)} = \left[\partial E_B^P / \partial I\right] \cdot \partial I / \partial c_H \right]_{c(B)} + \left[\partial E_B^P / \partial c_H\right]_{c(B), 1}
\]

This equation is identical with the slope of the plot \(E_B^P = E_B - (g/z_B) \log_{10} c_B\) versus \(c_H\) at constant \(c_B\). By integration, we obtain
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\[
\Delta E_{BTS2} - \Delta E_{BTS1} = \int_{TS1}^{TS2} \int_0^{c(B)} \left[ \partial \Delta E_B / \partial c_B \right]_{c(H)=0} dc_B + \int_0^{c(H)} \left[ \partial \Delta E_B / \partial c_H \right]_{c(B)=0} dc_H
\]

(1.16)

Here, \(\Delta E_{BTS1} = 0\).

For the values of the integrals, we shall introduce the following notations

\[
F(B, c_B) = \int_0^{c(B)} \left[ \partial E'_B / \partial c_B \right]_{c(H)=0} dc_B
\]

(1.17)

\[
F(B, c_H) = \int_0^{c(H)} \left[ \partial E'_B / \partial c_H \right]_{c(B)=0} dc_H
\]

(1.18)

Hence, we can write

\[
\Delta E_{BTS2} = F(B, c_B) + F(B, c_H)
\]

(1.19)

The total emf of cell B can then be given, if both \(c_B\) and \(c_H\) are varied

\[
E_B = E_{0B}x + (g/z_B) \log_{10} c_B + F(B, c_B) + F(B, c_H)
\]

(1.20)

The function \(F(B, c_H)\) is given in Table 2 in Ref. [3].

The function \(E'_B\) can be given as

\[
E'_B = E_B - (g/z_B) \log_{10} c_B = E_{0B} - g z_B [D(I) - D(C)] + g d_1 c_B + g d_2 c_H + \text{corr},
\]

(1.21a)

The various \(F\) and slope functions have different values at the different experimental conditions used. These will be given for every experimental cell studied.

The estimation of the slope functions will be demonstrated on the example of the cell where \([A^+] = C\ M\), is kept constant.

For the common anion concentration and the ionic strength, we have

\[
c_Y = c_A + c_H + z_B c_B
\]

(1.21b)

\[
I = c_A + c_H + (1/2) (z_B^2 + z_B) c_B
\]

(1.21c)

The value of the partial derivative in the function \(F(B, c_B)\) is

\[
SL(B, c_B) = [\partial E'_B / \partial c_B]_{c(H)} = -g z_B dD(I) (1/2) (z_B^2 + z_B) + g d_1 + [\partial \text{corr} / \partial c_B]_{c(H)}
\]

(1.21d)

according to Eqs. (1.14) and (1.21 a,c).

The term “corr” is defined by Eq. (19) in Part 2 in Ref. [4]. This was estimated and was found to be negligible in 3 M Na(ClO\(_4\)).
Moreover, the value of the partial derivative in the function $F(B, c_H)$ is

$$SL(B, c_H) = \left[ \frac{\partial E'_B}{\partial c_H} \right]_{c(B)} = -g z_B dD(I) + g d_2 + \left[ \frac{\partial corr}{\partial c_H} \right]_{c(B)}$$  \hspace{1cm} (1.22)$$

We give the term “corr” again, because it can have importance at lower C values.

$$corr = -g \int_{x=0}^{x=1} [dD(I^+)/dx] \Phi_1(x) dx / (wx + a)$$  \hspace{1cm} (1.23)$$

where

$$(I^*) = xI(TS2) + (1 - x) I(TS1) = xI + (1 - x) I(C),$$  \hspace{1cm} (1.24)$$

$\Phi_1(x)$ is a function in the integral $E_\text{Df}$ and will be given in forthcoming chapters, together with w and a.

The partial derivatives of “corr” are also given in Part 3A [4].

For the derivative in the integral, we have

$$\frac{dD(I^*)}{dx} = \left[ \frac{dD(I^*)}{dx} \right] D(I^*)/dx = \left[ 0.5115/2I^{*1/2} \left( 1 + 1.5I^{*1/2} \right)^2 \right] \times [I(TS2) - I(TS1)]$$

$$\times [I(TS2) - I(TS1)]$$  \hspace{1cm} (1.25)$$

Hence, “corr” can be obtained by graphical integration. As $dD(I^*)/dI^*$ is very small and $[I(TS2) - I(TS1)] \cong 0$, this term is probably negligible.

**The experimental constant $E_{0B}$** can be obtained by two plots.

**Plot 1**

The plot $E_B' = E_B - (g/z_B) \log_{10} c_B + g z_B [D(I) - D(C)] - corr$ versus $c_B$, at constant $c_H$, gives the *conditional constant* as intercept

$$E_{0B1} = E_{0B} + gd_2 c_H \text{ mV}$$  \hspace{1cm} (1.26)$$

and the slope

$$SL(B, c_B)_1 = gd_1 \text{ mV.M}^{-1}$$  \hspace{1cm} (1.27)$$

on the basis of Eq. (1.11). From the intercept, the constant $E_{0B}$ can be calculated by subtracting the term $g d_2 c_H$ using the ionic molar conductivities measured in the present mixture and the necessary interaction coefficients involved. This plot is the most convenient way for the determination of the constant $E_{0B}$ and is introduced for the first time, here. The slope is valid only in this mixture and can be used to check the theory.
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**Plot 2**

In the present practice, the plot \(E'_B = E_B - (g/z_B) \log_{10} c_B\) versus \(c_B\), at constant \(c_H\), is used for the graphical determination of the constant \(E_{0B}\) and the slope function \(S_L(B, c_B)\), on the basis of the equation

\[
e_B = E_{0B}^x + (g/z_B) \log_{10} c_B + F(B, c_H) + F(B, c_B) \tag{1.28}
\]

For this plot, we have the conditional constant for the intercept

\[
E_{0B2} = E_{0B}^x + F(B, c_H) \tag{1.29}
\]

where

\[
E_{0B}^x = E_{0B} + f_1(C) \tag{1.30}
\]

Here, the term \(f_1(C)\) is the partial derivative of \(\Delta E_B\) with respect to \(c_A = C M\). This is given in Table 2 in Ref. [3]. The function \(F(B, c_H)\) is also given there. These functions are rather complicated for practical use. This plot is not recommended for the determination of \(E_{0B}\).

For the slope, we have

\[
\text{the slope}_2 = S_L(B, c_B) \tag{1.31}
\]

as given by Eqs. (1.14) and (1.21d). This slope is valid only in this mixture, and can be used for checking the theory.

It is important to mention that the conditional constants, \(E_{0B1}\) and \(E_{0B2}\), can not be used in cells with complex formation, only \(E_{0B}\).

### 1.2.2 The Total Emf of Cell \(H\)

The total cell emf is according to definition

\[
E_H = E_{0H} + g \log_{10} c_H + \Delta E_H, \text{ mV} \tag{1.32a}
\]

where \(\Delta E_H\) is the total potential anomalies, in mV, defined as

\[
\Delta E_H = g \log_{10} f_{HTS2} + E_D + E_{Dr} \equiv g \log_{10} f_{HTS2} + E_j \tag{1.32b}
\]

The theoretical equation for \(E_H\), derived by the author [3, 4], can be described as

\[
E_H = E_{0H} + g \log_{10} c_H - g[D(I) - D(C)] + g d_3 c_B + g d_4 c_H + \text{corr} \tag{1.33}
\]

where \(d_3\) and \(d_4\) define functions of constant value, in terms of some ionic molar conductivities and interaction coefficients. They have different values at different
experimental conditions and will be given when the experimental Cell H will be treated at these conditions.

Now, the total potential anomalies can be given as

$$\Delta E_H = -g[D(I) - D(C)] + gd_3 c_B + gd_4 c_H + \text{corr} \quad (1.34)$$

If we want to determine the experimental constant $E_{0H}$ graphically, the total cell emf $E_H$ should be redefined by introducing the total differential for the total potential anomalies $\Delta E_H$. We use the same treatment as in the previous chapter. We obtain

$$d\Delta E_H = [\partial \Delta E_H/\partial c_B]_{c(H)} dc_B + [\partial \Delta E_H/\partial c_H]_{c(B)} dc_H + [\partial \Delta E_H/\partial C]_{c(B),c(H)} dC \quad (1.35)$$

where

$$[\partial \Delta E_H/\partial c_B]_{c(H)} = [\partial E'_H/\partial c_B]_{c(H)} = [(\partial E'_H/\partial I) \cdot \partial I/\partial c_B]_{c(H)} + [\partial E'_H/\partial c_B]_{c(H),I}$$

$$= SL(H, c_B) \quad (1.36)$$

This function is identical with the slope of the plot $E'_H = E_H - g \log_{10} c_H$ versus $c_B$, at constant $c_H$. Moreover,

$$[\partial \Delta E_H/\partial c_H]_{c(B)} = [\partial E'_H/\partial c_H]_{c(B)} = [(\partial E'_H/\partial I) \cdot \partial I/\partial c_H]_{c(B)} + [\partial E'_H/\partial c_H]_{c(B),I}$$

$$= SL(H, c_H) \quad (1.37)$$

This function is identical with the slope of the plot $E'_H - g \log_{10} c_H$ versus $c_H$, at constant $c_B$.

By integration, we obtain

$$\Delta E_{HTS2} - \Delta E_{HTS1} = \int_{TS1}^{TS2} d\Delta E_H = \int_0^{c(H)} [\partial E'_H/\partial c_H]_{c(B)} dc_H + \int_0^{c(B)} [\partial E'_H/\partial c_B]_{c(H) = 0} dc_B \quad (1.38)$$

Here, $\Delta E_{HTS1} = 0$

For the values of the integrals, we shall introduce the following notations

$$F(H, c_H) = \int_0^{c(H)} [\partial E'_H/\partial c_H]_{c(B)} dc_H \quad (1.39)$$

$$F(H, c_B) = \int_0^{c(B)} [\partial E'_H/\partial c_B]_{c(H) = 0} dc_B \quad (1.40)$$

For the total potential anomalies, we can write
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$$\Delta E_{HTS2} = F(H, c_H) + F(H, c_B)$$  \hspace{1cm} (1.41)

The total emf of Cell H can then be given, if both $c_B$ and $c_H$ are varied

$$E_H = E_{0H}^x + g \log_{10} c_H + F(H, c_B) + F(H, c_H)$$  \hspace{1cm} (1.42)

The estimation of the slope functions given below, e.g. for the cell where $[A^+] = CM$, is kept constant.

The function $E'_H$ is defined as

$$E'_H = E_H - g \log_{10} c_H = E_{0H} - g[D(I) - D(C)] + gd_3c_B + gd_4c_H + corr$$  \hspace{1cm} (1.43)

From Eqs. (1.36), (1.43) and (1.21 b,c), we obtain the slope function

$$SL(H, c_B) = \left[ \frac{\partial E'_H}{\partial c_B} \right]_{c(H)} = -(1/2)(z_B^2 + z_B)gdD(I) + gd_3 + \left[ \frac{\partial corr}{\partial c_B} \right]_{c(H)}$$  \hspace{1cm} (1.44)

From Eqs. (1.37), (1.43) and (1.21 b,c), we obtain the slope function

$$SL(H, c_H) = \left[ \frac{\partial E'_H}{\partial c_H} \right]_{c(B)} = -gdD(I) + gd_4 + \left[ \frac{\partial corr}{\partial c_H} \right]_{c(B)}.$$

The constant $E_{0H}$ can be determined in three ways.

**Plot 1**

In a potentiometric titration, where $c_B$ is kept constant and $c_H$ is varied, we plot the data as $E'_H = E_H - g \log_{10} c_H + g[D(I) - D(C)] - corr$ versus $c_H$, at constant $c_B$, and we obtain a conditional constant as the intercept

$$E_{0H1} = E_{0H} + gd_3c_B \text{ mV}$$  \hspace{1cm} (1.46)

and the slope will be

$$SL(H, c_H) = gd_4 \text{ mV.M}^{-1}$$  \hspace{1cm} (1.47)

on the basis of Eq. (1.33). $E_{0H}$ can be obtained from the intercept by subtracting the term $gd_3c_B$, using ionic molar conductivities determined in the same mixture and the interaction coefficients involved. The slope is valid only in this mixture and can be used for checking the theory. This plot is the simplest way to get $E_{0H}$.

If we do not have conductivity data, $E_{0H}$ should be determined in the absence of the metal ions $Bz(B)^+$. 