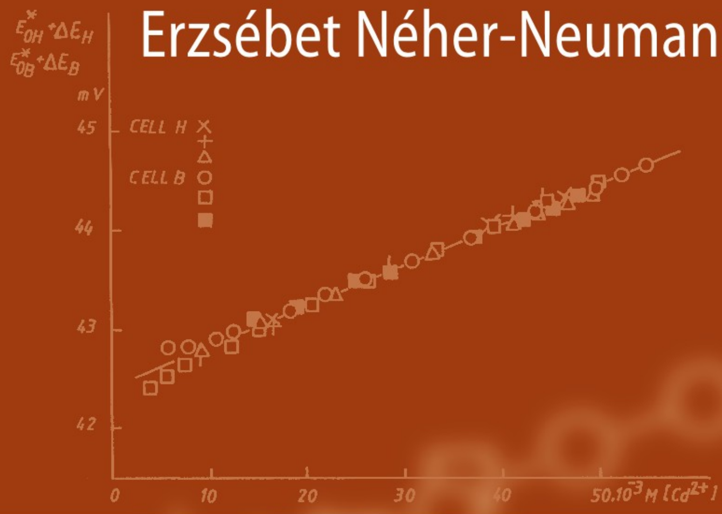
Erzsébet Néher-Neumann



Advanced Potentiometry

Potentiometric Titrations and their Systematic Errors

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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
Ferenc Néher

Born
on the 19th August, 1903
in Rábatamási, Hungary
Died
on the 31st March, 1972
in Rábatamási

Contents

List of Definitions and Symbols

a	a term in integrated form of potential functions E_D and E_{Df}, defined by $S_{TS1} = a = C(\lambda_A + \lambda_Y)$ (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^-
$B = B^{z(B)+}$	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)	$A(\gamma)\ I^{1/2} / (1 + 1.5\ I^{1/2})$ (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 C M A Y
$D(C^*)$	Debye–Hückel term in the transition layer
E =	total emf of the cell studied, in mV. It consists of the following terms [2,3] $[E_{id.el} + E_{el.f}] + [E_D + E_{Df}]$ (3)
E_{el} =	$E_{id.el} + E_{el.f}$ = the real cell emf defined as $E_{0J} + (g/z_J) \log_{10} (c_J f_J)$ (4) where E_{0J} is a constant
$E_{id.el}$	ideal cell emf given by the Nernst equation in term of concentrations $= E_J = E_{0J} + (g/z_J) \log_{10} c_J$ (5)
$E_{el.f}$	$= (g/z_J) \log_{10} f_J$ (6)
E_D	the ideal diffusion potential term, known as the Hendersson, Planck or Lewis and Sargent equation [4] $= -g \int_{TS1}^{TS2} \Sigma_J (t_J^* / z_J)\ d \log_{10} c_J^*$ (7)

	$= -(g/2.303)\left[(U_{TS2} - U_{TS1}) / (S_{TS2} - S_{TS1})\right] \ln (S_{TS2}/S_{TS1})$, Eq. (1–15) in Ref. [5]
E_{Df}	the activity coefficient contribution to E_D $= -g \int_{TS1}^{TS2} \Sigma_J (t_J^* / z_J) \, d \log_{10} f_J^*$ (8) Eq. (1.7) in Ref. [5]
E_J	the so–called liquid junction potential corresponding to the non-ideal diffusion potential term [2, 3] $= -g \int_{TS1}^{TS2} \Sigma_J (t_J^* / z_J) \, d \log_{10} (c_J^* f_J^*) = E_D + E_{Df}$ (9) The summation is over all cations and anions present in the transition layer.
ΔE_J	total potential anomalies, appearing in an emf cell with liquid junction, defined as $= (+\text{or}-)\ (g/z_J) \log_{10} f_J + E_j$ $= (+\text{or}-)\ (g/z_J) \log_{10} f_J + E_D + E_{Df}$ (10) 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 $E_J = E_{0J}\ (+\text{or}-)\ (g/z_J) \log_{10} c_J + \Delta E_J$ (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	$= 1 / [2.303\ C(\lambda_A + \lambda_Y)]$, appearing in functions E_D.
F_C	Faraday constant = 96484.56 (27) As (mol electrons)$^{-1}$. [14]
g	$(RT \ln_{10} / F_C).10^3 = 59.159$ mV at 25°C.
$H = H^+$	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

R	universal gas constant: 8.3145 J mol $^{-1}$K^{-1} [14]	
S	$(\Sigma_J\ \lambda_J\lvert z_J\rvert c_J)_{cations} + (\Sigma_J\ \lambda_J\lvert z_J\rvert c_J)_{anions}$	
t_{J*}	electrical transport number [15] of the ion constituent J in the transition layer	
	$= \lambda_J^*\ c_J^*\lvert z_J\rvert / (\Sigma_J\ \lambda_J^*\ c_j^*\lvert z_J\rvert)$	(15)
	It must always be positive and $\Sigma_J\ t_J^* = 1$.	
t_A	$= \lambda_A / (\lambda_A + \lambda_Y)$, appearing in functions E_{Df}	
t_Y	$= \lambda_Y / (\lambda_A + \lambda_Y)$, appearing in functions E_{Df}	
T	absolute temperature in K	
T	subscript denoting total analytical concentration	
TS1	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	
TS2	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	
U	$(\Sigma_J\lambda_J\ c_J)_{cations} - (\Sigma_J\lambda_J\ c_J)_{anions}$	
x	mixing fraction at an intermediate plane in the transition layer of the junction: $0 \leq x \leq 1$	
$y \equiv \lvert z_L\rvert$	absolute value of the charge number for the ligand ion	
$z_J \equiv z(J)$	algebraic charge number of ion J	
$\lvert z_J\rvert$	absolute value of the charge number of ion J	
$Y = Y^-$	common anion of the electrolyte mixture AY + HY + $BY_{z(B)}$	
w	term in integrated form of potential functions E_D and E_{Df} defined by	
	$w \equiv S_{TS2} - S_{TS1}$; $S_{TS2} = w + a$	(16)
*	superscript denoting a property of the transition layer	
ε'' (J, K)	interaction coefficient (L solution. mol $^{-1}$) between ions J and K on the molarity scale	
ε(J, K)	interaction coefficient (kg solvent. mol $^{-1}$) between ions J and K on the molality scale. The interaction coefficient β used by Guggenheim is related to ε by $\beta = (\varepsilon/2)$ ln 10.	
$\log_{10} \gamma_J$	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, ε (J, K), should be used.	
κ	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.	
	$= \Sigma_J\kappa_J = 10^{-3}\Sigma_J c_J\lvert z_J\rvert\lambda_J$	(17)
	where	
	$\lvert z_J\rvert\lambda_J$ is in (S cm^2 mol^{-1})	
$10^3\kappa$	$= \Sigma_J\lambda_J\lvert z_J\rvert c_J$,	(18)

λ_J	ionic molar conductivity of ion J, concentration c_J in the test solution, (S cm ^{2} mol ion $^{-1}$|charge|$^{-1}$) $= 10^3 \kappa_J / (c_J \lvert z_J \rvert)$	(19)
λ_{J*}	ionic molar conductivity of ion J, concentration c_{J*} in the transition layer	
$\wedge_{RX}$	molar conductivity (S cm^2 mol^{-1}) of electrolyte RX of concentration c M $= \lambda_R + \lambda_X = 10^3 \kappa / c$	(20)
d D(I)	$= [\partial D(I) / \partial I]_{c(B),c(H)\ldots} = 0.5115 / [2\, I^{1/2}\, (1 + 1.5\, I^{1/2})^2]$	(21)

For simplicity, ionic charges are omitted in subscripts. Subscripts to subscripts are avoided, e.g. by writing λ_{Lk} and $BY_{z(B)}$. Unless stated otherwise, concentrations are molarities (mol L^{-1}, denoted M).

Preface

Many phenomena in our environment, e.g. the acidity of natural waters (seas, lakes, rivers): $\mathrm{pH} = -\log_{10} [\mathrm{H}^+]$ 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. $\mathrm{p}K_\mathrm{a}$ for the protolysis of a weak acid, where $\mathrm{p}K_\mathrm{a} = -\log_{10} \mathrm{K_a}$) 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 present book is a summary of the series of the author entitled “The Liquid Junction Potential in Potentiometric Titrations”, consisting of 10 Part [5,17–26] and the thesis “The Liquid Junction EMF” [27].

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 ± 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 ΔE_B and ΔE_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 °C and in acidic solutions ($\mathrm{pH} < 7$) 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 $25.000 \pm 0.005°\mathrm{C}$. The potentials and the resistance of the test solutions were red 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

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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, H_3L) with a Strong Base

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

$$\mathrm{HL} \rightleftharpoons \mathrm{H^+ + L^-} \tag{1.1}$$

with the protolysis constant

$$\mathrm{K_{al} = [H^+][L^-]/[HL]} \tag{1.2}$$

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

$$\mathrm{L^- + H_2O \rightleftharpoons HL + OH^-} \tag{1.3}$$

$$\mathrm{K_h = [HL][OH^-]/[L^-]} \tag{1.4}$$

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 [. . .] 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 $c_{salt} >> [HL]$. 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

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$$[HL] \cong c_{acid}, \text{formal concentration, M}$$

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

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

$$[H^+] = K_{a1}.\ c_{acid}/c_{salt} \tag{1.5}$$

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

$$pH = pK_{a1} + \log_{10}\ (c_{salt}/c_{acid}) \tag{1.6}$$

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_{salt}/c_{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,

$$pH = pK_a \tag{1.7}$$

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.

– Reference || Bridge solution || Test solution | Electrodes reversible to +
half-cell $B^{z(B)+}$ and H^+ ions.
$E_{j\,(1,3)}$ $E_{j\,(1,2)}$ Cell B and H

where the composition of the bridge solution is:

TS1, $x = 0$,
C M AY
$I(C) = C$ M
$f_J^{tr} = 1$ (here, tr denotes trace)

The composition of the test solution is:

TS2, $x = 1$,
$[A^+] = C$ M

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

$$E_B = E_{0B} + (g/z_B)\log_{10} c_B + \Delta E_B, \text{ mV} \tag{1.8}$$

where

$$\Delta E_B = (g/z_B)\log f_{BTS2} + E_D + E_{Df} \equiv (g/z_B)\log_{10} f_{BTS2} + E_j \tag{1.9}$$

is the total potential anomalies and

$$E_j = E_D + E_{Df} \tag{1.10}$$

is the *liquid junction potential.* The first term in the function ΔE_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, ΔE_B and ΔE_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

$$E_B = E_{0B} + (g/z_B)\log_{10} c_B - gz_B[D(I) - D(C)] + gd_1 c_B + gd_2 c_H + \text{corr} \tag{1.11}$$

where d_1 and d_2 denote functions of constant value in terms of some ionic molar conductivities (λ_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

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

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, ΔE_B. It means that this function should be separated in terms of the partial derivatives of the independent variables (c_H, c_B and C), if the function is total differential.

The mixtures HY + AY + $BY_{z(B)}$ 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 ΔE_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 ΔE_B is an unique function of c_H as well. Moreover, if c_H and c_B go independently to zero when ΔE_B goes to zero, the function ΔE_B is a total differential and can be defined as given below, when both c_B and c_H are changing.

$$d\Delta E_B = [\partial \Delta E_B/\partial c_B]_{c(H)} dc_B + [\partial \Delta E_B/\partial c_H]_{c(B)} dc_H + [\partial \Delta E_B/\partial C]_{c(B),c(H)}\, dC \tag{1.13}$$

As$[\partial \Delta E_B/\partial c_B]_{c(H)} = [\partial E'_B/\partial c_B]_{c(H)} = f_1(I\ f_2(C, c_B, c_H), c_B, c_H)$, we have

$$\begin{aligned}[\partial \Delta E_B/\partial c_B]_{c(H)} &= [\partial E'_B/\partial c_B]_{c(H)} = [(\partial E'_B/\partial I).\partial I/\partial c_B]_{c(H)} + [\partial E'_B/\partial c_B]_{c(H),I} \\ &= SL(B, c_B)\end{aligned} \tag{1.14}$$

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

$$\begin{aligned}[\partial \Delta E_B/\partial c_H]_{c(B)} &= [\partial E'_B/\partial c_H]_{c(B)} = [(\partial E'_B/\partial I)\cdot \partial I/\partial c_H]_{c(B)} + [\partial E'_B/\partial c_H]_{c(B),I} \\ &= SL(B, c_H)\end{aligned} \tag{1.15}$$

This equation is identical with the slope of the plot $E'_B = E_B - (g/z_B)\log_{10} c_B$ versus c_H, at constant c_B. By integration, we obtain

$$\Delta E_{BTS2} - \Delta E_{BTS1} = \int_{TS1}^{TS2} dE_B \int_0^{c(H)} [\partial \Delta E_B/\partial c_H]_{c(B)=0}\, dc_H + \int_0^{c(B)} [\partial \Delta E_B/\partial c_B]_{c(H)}\, dc_B \tag{1.16}$$

Here, $\Delta E_{BTS1} = 0$.

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

$$F(B, c_B) = \int_0^{c(B)} [\partial E'_B/\partial c_B]_{c(H)}\, dc_B \tag{1.17}$$

$$F(B, c_H) = \int_0^{c(H)} [\partial E'_B/\partial c_H]_{c(B)=0}\, dc_H \tag{1.18}$$

Hence, we can write

$$\Delta E_{BTS2} = F(B, c_B) + F(B, c_H) \tag{1.19}$$

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

$$E_B = E_{0B}{}^{x} + (g/z_B)\log_{10} c_B + F(B, c_B) + F(B, c_H) \tag{1.20}$$

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

The function E'_B can be given as

$$E'_B = E_B - (g/z_B)\log_{10} c_B = E_{0B} - g z_B[D(I) - D(C)] + g d_1 c_B + g d_2 c_H + \text{corr}, \tag{1.21a}$$

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

$$c_Y = c_A + c_H + z_B c_B \tag{1.21b}$$

$$I = c_A + c_H + (1/2)\left(z_B^2 + z_B\right) c_B \tag{1.21c}$$

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

$$SL(B, c_B) = [\partial E'_B/\partial c_B]_{c(H)} = -g z_B dD(I)(1/2)(z_B^2 + z_B) + g d_1 + [\partial \text{corr}/\partial c_B]_{c(H)} \tag{1.21d}$$

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

$$SL(B, c_H) = [\partial E'_B/\partial c_H]_{c(B)} = -gz_B dD(I) + gd_2 + [\partial corr/\partial c_H]_{c(B)} \tag{1.22}$$

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

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

where

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

$\Phi_1(x)$ is a function in the integral E_{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

$$\begin{aligned} dD(I^*)/dx = [dD(I^*)/dx].\ D(I^*)/dx = \left[0.5115/2I^{*1/2}\left(1 + 1.5I^{*1/2}\right)^2\right] \\ \times [I(TS2) - I(TS1)] \end{aligned} \tag{1.25}$$

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

$$E_{0B1} = E_{0B} + gd_2c_H \text{ mV} \tag{1.26}$$

and the slope

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

on the basis of Eq. (1.11). From the intercept, the constant E_{0B} can be calculated by subtracting the term g d_2c_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.

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 $SL(B, c_B)_2$, 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 ΔE_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

$$\text{the slope}_2 = SL(B, c_B)_2 \tag{1.31}$$

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 ΔE_H is the total potential anomalies, in mV, defined as

$$\Delta E_H = g\log_{10} f_{HTS2} + E_D + E_{Df} \equiv g\log_{10} f_{HTS2} + E_j \tag{1.32b}$$

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

$$E_H = E_{0H} + g\log_{10} c_H - g[D(I) - D(C)] + gd_3 c_B + gd_4 c_H + \text{corr} \tag{1.33}$$

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

$$\Delta \mathrm{E_H} = -\mathrm{g}[D(I) - D(C)] + \mathrm{gd_3c_B} + \mathrm{gd_4c_H} + \mathrm{corr} \tag{1.34}$$

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

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

where

$$\begin{aligned}[\partial \Delta \mathrm{E_H}/\partial \mathrm{c_B}]_{\mathrm{c(H)}} &= [\partial \mathrm{E'_H}/\partial \mathrm{c_B}]_{\mathrm{c(H)}} = [(\partial \mathrm{E'_H}/\partial \mathrm{I}).\partial \mathrm{I}/\partial \mathrm{c_B}]_{\mathrm{c(H)}} + [\partial \mathrm{E'_H}/\partial \mathrm{c_B}]_{\mathrm{c(H),I}} \\ &= \mathrm{SL(H, c_B)}\end{aligned} \tag{1.36}$$

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

$$\begin{aligned}[\partial \Delta \mathrm{E_H}/\partial \mathrm{c_H}]_{\mathrm{c(B)}} &= [\partial \mathrm{E'_H}/\partial \mathrm{c_H}]_{\mathrm{c(B)}} = [(\partial \mathrm{E'_H}/\partial \mathrm{I}).\partial \mathrm{I}/\partial \mathrm{c_H}]_{\mathrm{c(B)}} + [\partial \mathrm{E'_H}/\partial \mathrm{c_H}]_{\mathrm{c(B),I}} \\ &= \mathrm{SL(H, c_H)}\end{aligned} \tag{1.37}$$

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

By integration, we obtain

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

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

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

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

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

For the total potential anomalies, we can write

$$\Delta E_{HTS2} = F(H, c_H) + F(H, c_B) \tag{1.41}$$

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

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

The estimation of the slope functions given below, e.g. for the cell where

$$[A^+] = CM, \text{iskeptconstant}$$

The function E'_H is defined as

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

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

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

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

$$SL(H, c_H) = [\partial E'_H/\partial c_H]_{c(B)} = -gdD(I) + gd_4 + [\partial \text{corr}/\partial c_H]_{c(B)}, \tag{1.45}$$

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

$$E_{0H1} = E_{0H} + gd_3c_B \text{ mV} \tag{1.46}$$

and the slope will be

$$SL(H, c_H)_1 = gd_4 \text{ mV.M}^{-1} \tag{1.47}$$

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 $B^{z(B)+}$.

Plot 2

In the present practice, the plot $E'_H = E_H - g\log_{10} c_H$ versus c_H, at constant c_B, is used for the determination of E_{0H}, but not in the correct way. For the total cell emf, the following equation is valid.

$$E_H = E_{0H}{}^{x} + g\log_{10} c_H + F(H, c_B) + F(H, c_H) \tag{1.48}$$

The intercept of this plot is a *conditional constant* which depends on $c_{B,}$ consequently, on B_T (total concentration) too.

$$E_{0H2} = E_{0H}{}^{x} + F(H, c_B) \tag{1.49}$$

where

$$E_{0H}{}^{x} = E_{0H} + f_3(C) \tag{1.50}$$

The term $f_3(C)$ is the partial derivative of the function ΔE_H with respect to $c_A = C$. This is given in Table 2 in Ref. [3] for $[A^+] = C$ M, constant. This is a complicated function and is not suitable for practical use. This plot is not recommended for the determination of E_{0H}.

The slope of this plot is $SL(H, c_H)_2$, defined by Eqs. (1.37) and (1.45). The function $F(H, c_B)$ is given in Table 2 in Ref. [3] for $c_A = C$ M, constant. In the present practice, the conditional constant E_{0H2} is taken for the constant we are looking for. This is wrong.

Neglect ΔE_B and ΔE_H could result in erroneous interpretation of emf data, especially in the suggestion of minor species, often polynuclear, and in the formation of weak complexes.

The Third Method

If we do not have conductivity data, we can determine E_{0H} in the absence of the metal ions $B^{z(B)+}$. In this case, we should adjust B_T to the correct start values at the end of the determination of E_{0H}.

1.2.3 The Constant Ionic Medium Method

In equilibrium studies, all solutions should contain a neutral salt of high concentration, in order to stabilize the concentration, the conductivity and other physical properties of the ions. Up to now, it was believed that the ionic medium ensures the constancy of the activity factors of the ions. In the studies of the author, it was found [3] that this not the case.

This method is called **constant ionic medium type**. The most frequently used salts are: $NaClO_4$, $LiClO_4$ and NaCl. The emf studies can be carried out in three ways.

(a) The concentration of the cation of the ionic medium, $[A^+]$, can be kept constant. This method is used, if anionic complexes are formed.
(b) The concentration of the anion of the ionic medium, $[Y^-]$, is kept constant. This version is chosen, if cationic complexes are formed.
(c) The ionic strength (I) of the mixed solutions is constant and high.

The most frequently used concentrations of the ionic medium salt (C) are: $C = 0.5$, 1 and 3 M. These are suitable, because the change of the activity coefficients of the ions are smaller than e.g. at $C = 0.1$ M. In the concentration range 0.5–3 M, the interaction coefficients (ε'') in the expression for the ionic activity factors, $\log_{10} f_J$ [cf. Eqs. (1.12), (1.13), are constant [6]. In this range, more accurate $\log_{10}$ K values can be obtained.

If $C < 0.5$ M, the ε'' values are changing with the ionic strength. Moreover, the Debye–Hückel term [cf. Eq. (2)], in the expressions for $\log_{10} f_J$, is very high.

It is important to mention that the trace activity coefficient of ion J (denoted $f_J{}^{\mathrm{trace}}$) is chosen to be 1, when $c_J \rightarrow 0$ in C M ionic medium as solvent. This is the *reference state* of the ionic activity coefficients.

The different $\log_{10}$ K values, determined at the experimental conditions (a-c), will be different, if the change of the composition of the ionic medium was neglected at the calculation of $\log_{10}$ K. This is the result of the newest research in this field [3, 6–15].

Moreover, the determined $\log_{10}$ K values are the function of the ionic medium too. This is the result of the contribution of the total potential anomalies, ΔE_B or ΔE_H, to E_B and E_H.

Because of these facts, many values of $\log_{10}$ K, characterizing different equilibrium processes and determined earlier, *can be erroneous*, especially in the assumption of minor species, *often polynuclear*, and in the formation of *weak complexes.*

Different formation constants, also called stability constants, determined up to now, are summarized in several monographs, e.g. in Refs. [16–18].

1.3 On the Curve-Fitting Computer Treatment [2d]

Nowadays, computer programs, e.g. LETAGROP ETITR [19] and LAKE [20], minimizing least-square sums are used for the treatment of emf data. The determination of the composition and the stability constants of the species formed are the goals.

The complex formation reaction to be studied can be defined as

$$pB^{z(B)+} + qH^+ + rL^{y-} \rightleftharpoons B_pH_qL_r^{pz(B)+q-ry}\ (cpx) \qquad (1.51)$$

with the equilibrium constant, so-called concentration constant,

$$\beta_{pqr} = [cpx]/(b^p h^q l^r) \qquad (1.52)$$

where b, h, and l are the free, equilibrium concentrations for the $B^{z(B)+}$, H^+ and L^{y-} ions, respectively. The measured data are: E_H or E_B in mV.

During the curve-fitting computer treatment, a residual-squares sum is minimized.

Residual-squares sum [2b]
Both variables of the experimental data, e.g. $E_H = f(v_T)$, $E_B = f(v_T)$ and $\eta = \log_{10} (B_T/b) = f(v_T)$, are subject to experimental error. Here, v_T denotes ml added titrant. In most programs, the independent variables, v_T, pH, b, etc. are considered to be correct, and all experimental uncertainty is assigned to the dependent variables, E_H, $E_{B,}B_T$, etc.

The residual-squares sum U can be expressed by

$$U = \Sigma_i w_i (y_{exp} - y_{calc})_i^2 = \Sigma_i w_i r^2 \tag{1.53}$$

where exp denotes experimental and calc stands for calculated.
w_i is the statistical weight, and *y is the dependent variable*, being a function of some parameters:

(a) common parameters (β_{pqr} and p, q, r)
(b) group parameters ($E_{0\,J}$, E_j, j_a, j_b, B_T, L_T, etc.)

where j_a and j_b denote liquid junction terms in acid (a) or base (b) solutions.

The total cell emf is defined up to now as

$$E_J = E_{0\,J} + (g/z_J)\log_{10} c_J + E_j \tag{1.54}$$

The liquid junction term is generally assumed to be

$$E_j = j_a h + j_b K_w/h \tag{1.55}$$

Here a denotes acid, b base and K_w is the ion product of water.

Anyhow, in the new version of LETAGROP, called LETAGROP ETITR NYTIT [2d], the functions

$$E_j = j_a h + j_b K_w/h + j_l l + j_m m \tag{1.56}$$

$$E_j = j_a h + j_b K_w/h + j_l L + j_M M \tag{1.57}$$

where m and M denote free and total metal ion concentrations, respectively, and these terms can be selected from the subroutine EJBER.

As we can see, the potential contribution of the activity factors to the ideal electrode potential, $(g/z_J) \log_{10} f_{JTS2}$, and the composition change of the ionic medium were not taken into account. These are dominating terms [3, 6–15]. Moreover, these authors did not recognize that the correction coefficients determined in mixtures of strong electrolytes are not valid in equilibrium systems.

In minimizing U, the "best" values for the common parameters and various group parameters (B_T, L_T, $E_{0\,J}$, j_a, j_b, j_l) are sought to give the best fit. Here, B_T, L_T, H_T are total concentrations.

The quantity used in evaluation of the residual r can be: E_B, E_H, pH, v_T, L_T, $Z = (H_T - h)/B_T$ or $Z = (L_T - l)/B_T$ and η. It should be mentioned that in minimizing secondary (transformed) variables, Z, η, pH, random distribution of errors cannot be expected. So, if possible, only primary variables, the quantities measured (E_B, E_H, v_T), should be considered in the statistical treatment.

Theoretically, there are some restrictions on the data if a correct minimum is to be obtained.

(1) The model chosen must be correct, i.e. the species assumed to be present are the correct ones.
(2) There are no systematic errors.
(3) The random errors in y have a normal (Gaussian) distribution.
(4) The weight w_i assigned to each measurements y_i is an exact measure of its accuracy.

None of these conditions is usually strictly fulfilled.

In the present work, it will be investigated how large the total potential anomalies (systematic errors) are in potentiometric titrations, and what effects they have on the equilibrium constants to be determined. The correction coefficients are estimated on exact theoretical basis, independently of some computer treatments. It should be pointed out that the total potential anomalies, called systematic errors in the present study, appear due to theoretical errors in E_B and E_H, which cause systematic errors in the functions $\log_{10} [B^{z(B)+}]$, $\log_{10} [H^+]$ and are not caused by instrumental errors.

Anyhow, the authors of Ref. [2] conclude that if a systematic error is overlooked, a least-squares adjustment becomes meaningless, as the residual function becomes distorted.

1.4 On the Deduction of Theoretical Equations

Theoretical equations were deduced by E. Néher-Neumann for the calculation of the total cell emf E_H and E_B including the total potential anomalies, ΔE_B and ΔE_H, in Cells B and H, at different experimental conditions: $[A^+] = C$ M, $[Y^-] = C$ M and $I = C$ M, constant, respectively. These studies were published in a thesis and in a series of articles [3, 4, 6–15]. Calculated and measured values of ΔE_B and ΔE_H were compared for the different systems: mixtures of strong electrolytes and equilibrium systems where complex formation takes place.

The original deductions of the equations concerning mixtures of strong electrolytes and equilibrium systems were presented in the thesis of the doctor degree of the author [4] and in Refs. [10, 11].

In these deductions, the *general assumptions* given below were made.

(a) The liquid junctions are of the continuous mixture and constant ionic medium type. This means that the concentration of the ion J at some intermediate plane in the transition layer of the junction, $c_J{}^*$, can be calculated as

$$c_J^* = xc_{JTS2} + (1 - x)c_{JTS1} \tag{1.58}$$

(b) The ionic molar conductivities in the transition layer ($\lambda_J{}^*$) are assumed to be constant. These are not known, and in the calculations, approximate values measured experimentally in the test solution (λ_J) have been used. The trace ionic molar conductivities are used for the ions being present in minor concentrations, $c_J < 0.1$ M, in the ionic medium used. Such measurements were done by the author in mixtures of

$$Cd(ClO_4)_2 + HClO_4 + NaClO_4\ [7 - 9].$$

(c) The ionic activity coefficients can be calculated by the specific interaction theory, SIT [21–28], as defined by Eqs. (12, 13) which proved to be useful even in case of complex formation. The interaction coefficients are considered to be constant throughout the junction.
(d) The equations are valid for the experimental conditions $C = 0.5 - 3$ M, at $[A^+] = C$ M, $[Y^-] = C$ M and $I = C$ M, constant, respectively.

In the studies of the author, the following questions were considered.

(1) Are the activity factors constant in the solutions studied? [3, 6–15]
(2) Which factors depend the liquid junction potential on? In the studies of the formation of metal ion complexes, many researchers believe that by the use of constant total concentrations for the metal ions (B_T), the liquid junction potential can be avoided. This reasoning is completely wrong.
(3) Which experimental condition results in the best emf cell, where the total potential anomalies are on a minimum level? [3, 14, 15]
(4) Is the suggestion of the formation of polynuclear complexes in the study of metal ion complex equilibria and the assumption of dimer, trimer, etc. species at the protolysis of the weak acids used as ligands, *always* motivated? [3, 11, 14, 15]
(5) Why do change the equilibrium constants with the ionic medium? [14, 15]
(6) Can we use the criterion $E_{measured} - E_{calculated} = 0.01$ mV, in curve-fitting computer programs? [3, 11, 14]
(7) Are the ionic molar conductivities constant in liquid junctions of constant ionic medium type? [7–9]

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Chapter 2

Emf Cells with Mixtures of Strong Electrolytes and Liquid Junctions of the Type $AY \mid AY + HY + BY_{z(B)}$

In *all emf studies* of this kind *and* in the determination of the concerning *ionic molar conductivities*, the mixtures of $HClO_4 + Cd(ClO_4)_2 + NaClO_4$ were used in solutions of the following compositions.

Mixture 1
$c_H = 0.025$ M $HClO_4$, is kept constant,
c_B was varied,
$NaClO_4$ in such concentrations that
(a) $[A^+] = 3$ M, is kept constant,
(b) $[Y^-] = 3$ M, is kept constant,
(c) $I = 3$ M, is kept constant, respectively.

Mixture 2
$c_B = 0.050$ M $Cd(ClO_4)_2$, is kept constant,
c_H was varied,
X M $NaClO_4$ in such experimental conditions as above.

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2.1 Studies on Emf Cells Where $[A^+] = C$ M, Constant [1]

The derived equations of this chapter can be used if the approximation $\ln[(w/a)+1] \cong w/a$ is valid, for small values of w/a [1]. Here,

$$w \equiv S_{TS2} - S_{TS1} = z_B\, c_B(\lambda_B + \lambda_Y) + c_H(\lambda_H + \lambda_Y) \tag{2.1}$$

$$a = C(\lambda_A + \lambda_Y) \tag{2.2}$$

according to Eqs. (3), (5) in Part 3A in Ref. [2].

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The validity of this approximation *should be checked* by using the ionic molar conductivities determined in the mixtures studied. This is generally the case, if the ion concentrations are: c_H and $c_B \leq 0.1$ M, and using the ionic medium AY in the mixtures studied, in the concentration range $0.5 \leq C \leq 3$ M, according to the calculations of the author.

2.1.1 Cell B Using an Amalgam/Ion-Selective Indicator Electrode

2.1.1.1 The Determination of E_{0B} and Some Slope Functions

In this case, c_H should be kept constant and c_B varied. This can be done if we use Mixture 1 where c_B is varied within the range 5–50 milli molar (mM). For example, 50 ml solution Mixture 1 containing 5 mM Cd^{2+} was titrated with solution S_1 of the composition: 0.025 M $HClO_4$, 0.1 M $Cd(ClO_4)_2$, 3 M $NaClO_4$. Both an amalgam and a glass electrode were present in the test solution.

The total cell emf, E_B, is given by Eq. (1.11). The functions d_1 and d_2 have the values given below.

$$d_1 = \varepsilon''(B,Y) - F_0(\lambda_B - z_B\lambda_Y) - z_B t_A \varepsilon''(A,Y) + t_Y \varepsilon''(B,Y) \tag{2.3}$$

$$d_2 = \varepsilon''(B,Y)/z_B - F_0(\lambda_H - \lambda_Y) - t_A \varepsilon''(A,Y) + t_Y \varepsilon''(H,Y) \tag{2.4}$$

where

$$F_0 = 1/[2.303\, C(\lambda_A + \lambda_Y)] \tag{2.5}$$

$$t_A = \lambda_A/(\lambda_A + \lambda_Y) \text{ and } t_Y = \lambda_Y/(\lambda_A + \lambda_Y) \tag{2.6}$$

Moreover, in corr we have the function

$$\Phi_1(x) = x[c_B z_B(\lambda_Y - z_B\lambda_B) + c_H(\lambda_Y - \lambda_H)] + C(\lambda_Y - \lambda_A) \tag{2.7}$$

First, the systematic error in the conditional constant E_{0B1} was estimated: gd_2c_H, on the basis of Plot 1 (cf. Eq. (1.26)). The plot of the function $E_B' = E_B - (g/z_B) \log_{10} c_B + gz_B\,[D(I) - D(C)]$ versus c_B, at constant c_H, gives the conditional constant E_{0B1}. The error is presented in Table 2.1. The ionic molar conductivities determined in Mixture 1 and summarized in Table 2.2 [3]; moreover, the necessary interaction coefficients, given in Table 2.3, were used in the calculations. As is seen, the systematic error is relatively low (–0.38 mV), but it is not 0.01 mV. The slope of this plot is $SL(B,c_B)_1 = gd_1$.

Table 2.1 Survey of the total potential anomalies, in mV, appearing in Cells B and H, defined as $\Delta E_B{}^x$ and $\Delta E_H{}^x$ due to the use of conditional constants, at the end of the determination of E_{0B} and E_{0H}, at 25°C

Experimental condition	$[Na^+] = 3$ M constant,	$[ClO_4{}^-] =$ 3 M, constant	I = 3 M, constant
For Cell B:			
gd_2c_H	−0.38	−0.61	−0.71
$SL(B,c_B)_1c_B$	2.21	0.94	0
$\Delta E_B{}^x$	1.83	0.33	−0.71
For Cell H:			
gd_3c_B	2.01	0.56	−0.86
$SL(H,c_H)_1\ c_H$	0	−0.02	−0.02
$\Delta E_H{}^x$	2.01	0.54	−0.88

For Cell B: $\Delta E_B{}^x = gd_2c_H + SL(B,c_B)_1c_B$
The calculations were made for: $c_H = 0.025$ M, $c_B = 0.050$ M.
For Cell H: $\Delta E_H{}^x = gd_3c_B + SL(H,c_H)_1c_H$
The calculations were made for: $c_B = 0.050$ M, $c_H = 1 \times 10^{-3}$ M.

Table 2.2 Survey of the values of the ionic molar conductivities in S cm^2 mol ion^{-1}|charge|$^{-1}$ for mixtures of 3.00 M $NaClO_4$, 0.025 M $HClO_4$, $0 \le [Cd(ClO_4)_2] \le 0.187$ M at 25.000 ± 0.005°C. Presentation of some quantities ($\lambda_{Yadd(3)}$, t_Y, t_A, etc.) which appear in the potential functions. Here, Y denotes $ClO_4{}^-$, $[Na^+] = 3.00$ M, is kept constant

	$0.014127 \le [Cd(ClO_4)_2] \le 0.080$ / M
Graphical analysis	
$\lambda_{Na} = 23.48$	
$\lambda_H{}^{tr} = 170.20 \pm 4.20$	$30.98 \le \lambda_{Yadd(3)} \le 30.08$
In the ranges	$0.57 \le t_Y = \dfrac{\lambda_{Yadd(3)}}{\lambda_{Na} + \lambda_{Yadd(3)}} \le 0.56$
$0 \le [Cd(ClO_4)_2] \le 0.086$ M:	
$\lambda_{Cd}{}^{tr} = 7.54 - 0.90 = 6.64$	
$0.086 \le [Cd(ClO_4)_2] \le 0.187$ M:	$0.43 \le t_{Na} = \dfrac{\lambda_{Na}}{\lambda_{Na} + \lambda_{Yadd(3)}} \le 0.44$
$\lambda_{Cd}{}^{tr} = 7.54 - 5.25 = 2.29$	
Computer Analysis	$-0.15 \le \dfrac{\lambda_{Cd} - z_{Cd}\lambda_{Yadd(3)}}{2.303C(\lambda_{Na} + \lambda_{Yadd(3)})} \le -0.14$
In the range $0 \le [Cd(ClO_4)_2] \le 0.086$ M;	
$\lambda_{Cd}^{tr} = 6.85$, $\lambda_H^{tr} = 167.85$, $\lambda_{Na} = 23.52$	
In the range $0.086 \le [Cd(ClO_4)_2] \le 0.187$ M;	
$\lambda_{Cd}^{tr} = 2.23$, $\lambda_H^{tr} = 196.73$, $\lambda_{Na} = 23.55$	

Here, the values of $\lambda_{Yadd(3)}$ change according to $\lambda_{Yadd(3)} = 31.19 - [Cd^{2+}] \times 13.87$.
Source: Reproduced by permission of the Royal Society of Chemistry from Néher-Neumann E (1998) Acta Chem Scand 52: 873–882 (Table 5).

Moreover, the total potential anomalies (excluded the Debye–Hückel term) were estimated, at the end of the determination of E_{0B}, according to the definition

$$\Delta E_B^x = gd_2c_H + SL(B,c_B)_1c_B \tag{2.8}$$

Table 2.3 Survey of some interaction coefficients on the molar ($\widetilde{\varepsilon}$, ε'') and the molal (ε) scale

	$\widetilde{\varepsilon}$ $\frac{\text{dm}^3\text{solution}}{\text{mole solute}}$	ε $\frac{\text{kg solvent}}{\text{mole solute}}$
$NaClO_4$	0.03; 0.045 [4]	0.03 [5]
$LiClO_4$		0.34 [6]
$Ca(ClO_4)_2$		0.27 [7]
$Mg(ClO_4)_2$		0.33 [7]
$NaHCO_3$	0.01 [5]	
$HClO_4$	0.18*	0.14 [7]
$Cd(ClO_4)_2$	0.40 [4]	0.32 [4]
$Zn(ClO_4)_2$	0.38*	0.30 [9]
$Pb(ClO_4)_2$	0.24*	0.15 [8]
$Cu(ClO_4)_2$	0.39*	0.32 [7]
$Fe(ClO_4)_3$		0.56 [7]

*Recalculated by the author from the corresponding ε value. Source: Reproduced by permission of the Royal Society of Chemistry from Néher-Neumann E (1997) Acta Chem Scand 51: 1141–1154 (Table 6).

It was found that from the slope of this plot, $SL(B,c_B)_1c_B = 2.21$ mV, and $\Delta E_B^x = 1.83$ mV (cf. Table 2.1). This potential contribution is not negligible.

As a second step, we evaluated the data according to Plot 2. We plotted the function $E_B' = E_B - (g/z_B)\log_{10} c_B$ versus c_B, at constant c_H.

The slope function $SL(B,c_B)_2$ was determined as given by Eqs. (1.14) and (1.21d). This gives the potential contribution of the $B^{z(B)+}$ ions to the total potential anomalies ΔE_B. In this function, the term dD(I) appears. This can be given as

$$dD(I) = [\partial D(I)/\partial(I)]_{c(H),c(B)} = 0.5115/[2I^{1/2}(1 + 1.5I^{1/2})^2] \tag{2.9}$$

and can be estimated by graphical integration. For Mixture 1, we obtained

$$\int_0^{c(B)} [gdD(I)]_{c(H)}\,.dc_B = 0.63\,c_B\ \text{mV} \tag{2.10}$$

The derivative of Eq. (2.10), with respect to c_B, gives g dD(I) = 0.63 mV M^{-1}.

The slope of the plot $E_B' = E_B - (g/z_B)\log_{10} c_B$ versus c_B, at constant c_H, gives the slope $SL(B,c_B)_2$. This plot is shown in Fig 2.1. The comparison with the calculated slope is given in Table 2.4. This slope was found to be 40.5 ± 0.5 mV M^{-1} Cd^{2+}. As we can see from Table 2.4, *the agreement is very good.* This means that the theory is correct, which is the fundament for this determination. A more detailed analysis of the results will come at the end of the chapter.

If we make a potentiometric titration in Mixture 2, using an amalgam electrode again, we can determine the slope function $SL(B,c_H)_2$. This gives the potential

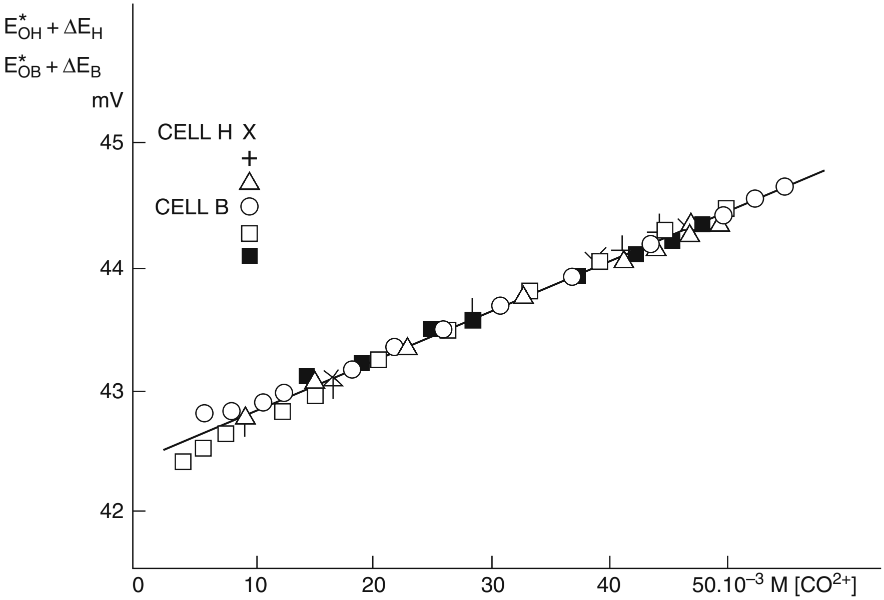

Fig. 2.1 Determination of the experimental slope function SL(B,c_B) and the conditional constant $E_{0B2} = E_{0B}{}^x + F(B,c_H)$. Moreover, the slope function SL(H,c_B) is determined and the conditional constant $E_{0H2} = E_{0H}{}^x + F(H,c_H)$, for Mixture 1, where $[Na^+] = 3$ M, is kept constant. Points with symbols Δ were shifted along the ordinate by 14.30, open circles ○ by 977.34 and the symbols □ ■ by 987.76. Filled symbols correspond to points from a reverse titration. Reproduced by permission of the Royal Society of Chemistry from Néher-Neumann E (1997) Acta Chem Scand 51: 1141–1154 (Fig. 1)

Table 2.4 Survey of the calculated and measured slopes in mV M^{-1}, for cell B and H, with the experimental condition $[Na^+] = 3$ M, constant, in Mixture 1. The graphical results for the ionic molar conductivities of Table 2.2 was used. The term "corr" was neglected

	Slope SL(B,c_B) cf. Eq. (1.21d)	Slope SL(H,c_B) cf. Eq. (1.44)
$\left[\frac{(g/z_J)\partial \log f_J}{\partial c_B}\right]_{c_H}$	−3.77 + 23.66 = 19.89	−1.88 + 21.29 = 19.41
$\left[\frac{\partial E_D}{\partial c_B}\right]_{c_H}$	8.57	8.57
$\left[\frac{\partial (E_{Df} - \text{corr})}{\partial c_B}\right]_{c_H}$	−1.55 + 13.25 = 11.70	−1.55 + 13.25 = 11.70
Calculated slope (at $[Cd^{2+}] = 71$ mM)	40.16	39.68
Experimental slope	40.5 ± 0.5	40.5 ± 0.5

Source: Reproduced by permission of the Royal Society of Chemistry from Néher-Neumann E (1997) Acta Chem Scand 51: 1141–1154 (Table 1).

Table 2.5 Survey of the calculated and measured slopes in mV M^{-1}, for cell H and B, with the experimental condition $[Na^+] = 3$ M, constant, in Mixture 2. The ionic molar conductivities given in Table 2.6 have been used in the calculations, assuming $\lambda_{ClO_4}^{MED}$ to be valid. The term "corr" was neglected

	Slope SL(H,c_H) cf. Eq. (1.45)	Slope SL(B,c_H) cf. Eq. (1.22)
$\left[\frac{(g/z_J)\partial \log f_J}{\partial c_H}\right]_{c_B}$	$-0.62 + 10.65 = 10.03$	$-1.24 + 11.83 = 10.59$
$\left[\frac{\partial E_D}{\partial c_H}\right]_{c_B}$	-18.46	-18.46
$\left[\frac{\partial (E_{Df} - \text{corr})}{\partial c_H}\right]_{c_B}$	$-0.76 + 5.96 = 5.20$	5.20
Calculated slope	-3.23	-2.67
Experimental slope	-4.8 ± 1	

Source: Reproduced by permission of the Royal Society of Chemistry from Néher-Neumann E (1997) Acta Chem Scand 51: 1141–1154 (Table 3).

contribution of the H^+ ions to the total potential anomalies of the amalgam electrode. This slope function is defined by Eqs. (1.15) and (1.22). The calculated value of it is presented in Table 2.5. The ionic molar conductivities measured in Mixture 2 are presented in Table 2.6 [3].

2.1.1.2 The Estimation of the Systematic Errors in the Equilibrium Constants, $\Delta \log_{10} \beta_{pqr}$, Caused by the Use of the Conditional Experimental Constant E_{0B1}

This experimental conditional constant for E_{0B1} has been determined in Mixture 1. We study the equilibrium process described by Eqs. (1.51) and (1.52). Then we have

$$\log_{10} \beta_{pqr} = \log_{10}[\text{complex}] - p \log_{10} b - q \log_{10} h - r \log_{10} l \tag{2.11}$$

Inserting the expression for E_{0B1} (cf. Eq. (1.26)) into E_B, valid for cells with complex formation (cf. Ref. [4]), and expressing $\log_{10}$ b from it, we obtain

$$\begin{aligned}\log_{10} b = (E_B - E_{0B} - g\, d_2 c_H)(z_B/g) + z_B^2[D(I) - D(C)] - (z_B/g) \\ \Sigma_V\, Q(B,V)V - (z_B/g)\,\text{corr}\end{aligned} \tag{2.12}$$

The systematic error in $\log_{10}\beta_{pqr}$ will be (cf. Eqs. (2.11) and (2.12))

$$\Delta \log_{10} \beta_{pqr} = -p\Delta \log_{10} b = p(g\, d_2 c_H)\, z_B/g \tag{2.13}$$

Equation (2.12) is valid in the *preliminary data treatment,* when only the presence of the ions H^+, $B^{z(B)+}$, L^{y-}, A^+ and Y^- is considered. Here, Q(B,V) denotes func-

Table 2.6 Survey of the values for the ionic molar conductivities in S cm^2 mol ion^{-1} $|charge|^{-1}$, valid in the mixtures of 3.00 M $NaClO_4$, 0.050 M $Cd(ClO_4)_2$, $0.046 \leq [HClO_4] \leq 0.100$ M at 25.000 ± 0.005°C. The validity of $\lambda_{Yadd(3)}$ was assumed, describing the three-component system studied. Presentation of some quantities like $\lambda_{Yadd(3)}$, t_A, t_Y and so on which appear in the potential functions. Here, Y denotes ClO_4^-. $[Na^+] = 3.00$ M, is kept constant

	$0.046 \leq [HClO_4]/M \leq 0.102$
Graphical analysis	
$\lambda^{tr}_H = 137.78$	$30.42 \leq \lambda_{Yadd(3)} \leq 30.69$
$\lambda^{tr}_{cd} = 18.68 \pm 1.12$	
$\lambda_{Na} = 23.48$	$0.56 \leq t_Y = \dfrac{\lambda_{Yadd(3)}}{\lambda_{Na} + \lambda_{Yadd(3)}} \leq 0.56$
	$0.43 \leq t_{Na} = \dfrac{\lambda_{Na}}{\lambda_{Na} + \lambda_{Yadd(3)}} \leq 0.43$
	$0.29 \leq \dfrac{\lambda_H - \lambda_{Yadd(3)}}{2.303\,C(\lambda_{Na} + \lambda_{Yadd(3)})} \leq 0.29$
Computer Analysis	
$\lambda^{tr}_H = 136.35$	
$\lambda^{tr}_{Cd} = 16.48$	
$\lambda_{Na} = 23.52$	

Here, the values of $\lambda_{Yadd(3)}$ change according to $\lambda_{Yadd(3)} = 30.41 + 2.80 \times [H^+]$.

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tions of constant value, in terms of some interaction coefficients and ionic molar conductivities measured in the equilibrium solution studied. V denotes the equilibrium concentrations b, h, and l and the composition change of the ionic medium, $\Delta c_Y = c_Y - C$.

Assuming values for the term g d_2 c_H mV, the hypothetical systematic errors can be estimated. These are presented in Table 2.7. As is seen from this table, the systematic errors are not negligible and are a function of c_H.

With the E_{0B1}value determined in Mixture 1, the systematic error, $\Delta\log_{10}\beta_{pqr}$, was calculated for different p values. These are presented in Table 2.8. This is the *minimum error* which can appear.

2.1.2 Cell H Using a Glass Indicator Electrode

2.1.2.1 The Determination of E_{0H} and Some Slope Functions

If we study Cell H, using only a glass electrode, c_B should be kept constant and c_H varied. This determination can be used in experiments where the formation of metal ion complexes is studied (so-called main titration) and B_T is kept constant. This can

Table 2.7 The estimation of the systematic error in the formation constants $\log_{10}\beta_{pqr}$, caused by the neglected potential contribution of the H^+ ions to E_{0B}

Cell B	$-p\ \Delta \log b = p\ gd_2\ c_H\ z(B)/g$		
For $z(B) = 2$ $E_{0B} + gd_2c_H$ /mV	$p = 1$	$p = 2$	$p = 3$
E_{0B} + 0.50	0.017	0.034	0.050
E_{0B} + 1.00	0.034	0.067	0.101
E_{0B} + 2.00	0.067	0.135	0.203
E_{0B} + 5.00	0.169	0.338	0.507
E_{0B} + 7.00	0.236	0.473	0.710
For $z(B) = 3$			
$E_{0B} + gd_2\ c_H$ /mV	$p = 1$	$p = 2$	$p = 3$
E_{0B} + 0.20	0.010	0.020	0.030
E_{0B} + 0.50	0.025	0.050	0.075
E_{0B} + 1.00	0.051	0.101	0.153
E_{0B} + 2.00	0.101	0.203	0.303
E_{0B} + 5.00	0.253	0.507	0.759
E_{0B} + 7.00	0.355	0.710	1.065

Source: Reproduced by permission of the Royal Society of Chemistry from Néher-Neumann E (1998) Acta Chem Scand 52: 873–882 (Table 1).

be done as follows. We can use Mixture 2, where c_H is varied within the range, e.g. 2−30 mM. This can be done through an acid–base titration.

In this case, e.g. $v_0 = 50$ ml solution Mixture 2, containing $[H^+]_0 \cong 30$ mM $HClO_4$, should be titrated with $v_1 = v_2$ ml solutions T_1 and T_2 using two burettes. The composition of the titrating solutions should be:

Table 2.8 Estimation of the systematic errors in the equilibrium constants, $\Delta\log_{10}\beta_{pqr}$, appearing due to the use of the conditional experimental constants E_{0B1} (cell B) and E_{0H1} (cell H), in $\log_{10}\beta_{pqr}$ units at 25°C

Experimental conditions $[Na^+] = 3.00$ M, is kept constant, For $z_B = 2$		
	Cell B Mixture 1: $c_H = 0.025$ M, constant $E_{0B1} = E_{0B} + gd_2\ c_H$ mV	Cell H Mixture 2: $c_B = 0.050$ M, constant $E_{0H1} = E_{0H} + gd_3c_B$ mV
Systematic error/mV	in E_{0B1}: $gd_2c_H = -0.38$	in E_{0H1}: $gd_3c_B = 2.01$
E_{0B} or E_{0H}/mV	$E_{0B1} + 0.38$	$E_{0H1} - 2.01$
	Systematic errors in $\log_{10}\beta_{pqr}$	
$\log_{10}\beta_{pqr}$	$-\ p\Delta\log_{10} b = p(gd_2\ c_H)z_B/g$	$-q\Delta\log_{10} h = q(gd_3\ c_B)/g$
	$p = 1$ $p = 2$ $p = 3$	$q = 1$ $q = 2$ $q = 3$
	−0.013 −0.026 −0.038	0.034 0.068 0.102

$$T_1 : 2B_T \text{ M } B(ClO_4)_2,\ [H^+]_1\text{M } HClO_4,\ 3\text{M } NaClO_4,$$
$$T_2 : 0.1 \text{ M NaOH},\ (C - c_{NaOH}) \text{ M } NaClO_4.$$

$v_1 = v_2 \sim 15$ ml NaOH is necessary to reach the equivalence point. We should finish the E_0 titration at around $[H^+] \sim 1 \times 10^{-3}$ M, in order to avoid alkaline solutions, which are not good for the glass electrode (sodium error).

The total cell emf for this cell is given by Eq. (1.43), the total potential anomalies, ΔE_H by

$$\Delta E_H = g\ d_3 c_B + g\ d_4 c_H - g\ [D(I) - D(C)] \tag{2.14}$$

These equations include the functions d_3 and d_4. These are defined as

$$d_3 = z_B \varepsilon''(H, Y) - F_0(\lambda_B - z_B\lambda_Y) - z_B t_A \varepsilon''(A, Y) + t_Y \varepsilon''(B, Y) \tag{2.14a}$$

$$d_4 = \varepsilon''(H, Y) - F_0(\lambda_H - \lambda_Y) - t_A \varepsilon''(A, Y) + t_Y \varepsilon''(H, Y) \tag{2.14b}$$

The interpretation of the data can start with a Gran plot [5] in order to check the acidity level of the start solution. This calculation method will be demonstrated at the protolysis of a weak acid in Section 4.2.1.2.

The experimental constant E_{0H} can be obtained by Plot 1. We plot the data as $E_H' = E_H - g \log_{10} c_H + g[D(I) - DC]$ versus c_H, at constant c_B. The intercept will be a conditional constant, E_{0H1}, which depends on c_B.

$$E_{0H1} = E_{0H} + g\ d_3 c_B \tag{2.15}$$

The term $g\ d_3\ c_B$ was estimated for Mixture 2, and it was found to be 2.01 mV (cf. Table 2.1) and not 0.01 mV, what is assumed to be the level of the uncertainty of the data, using a curve-fitting computer program. The slope of this plot is $SL(H,c_H)_1 = gd_4$.

The total potential anomalies (excluded the Debye–Hückel term) were also estimated, at the end of the determination of E_{0H}, according to the definition

$$\Delta E_H^x = g\ d_3 c_B + SL(H, c_H)_1 c_H \tag{2.16}$$

The term $SL(H,c_H)_1 c_H$ was found to be zero, therefore, $\Delta E_H{}^x = 2.01$ mV (cf. Table 2.1).

The slope function $SL(H,c_B)_1$ can also be determined in Mixture 1.

We interpreted the data according to Plot 2 also, plotted the data as $E_H' \equiv E_H - g \log_{10} c_H$ versus c_H, at constant c_B. The intercept is the conditional constant E_{0H2}

$$E_{0H2} = E_{0H}^x + F(H, c_B) \tag{2.17}$$

The function $F(H,c_B)$ is given in Table 2 in Ref. [1].

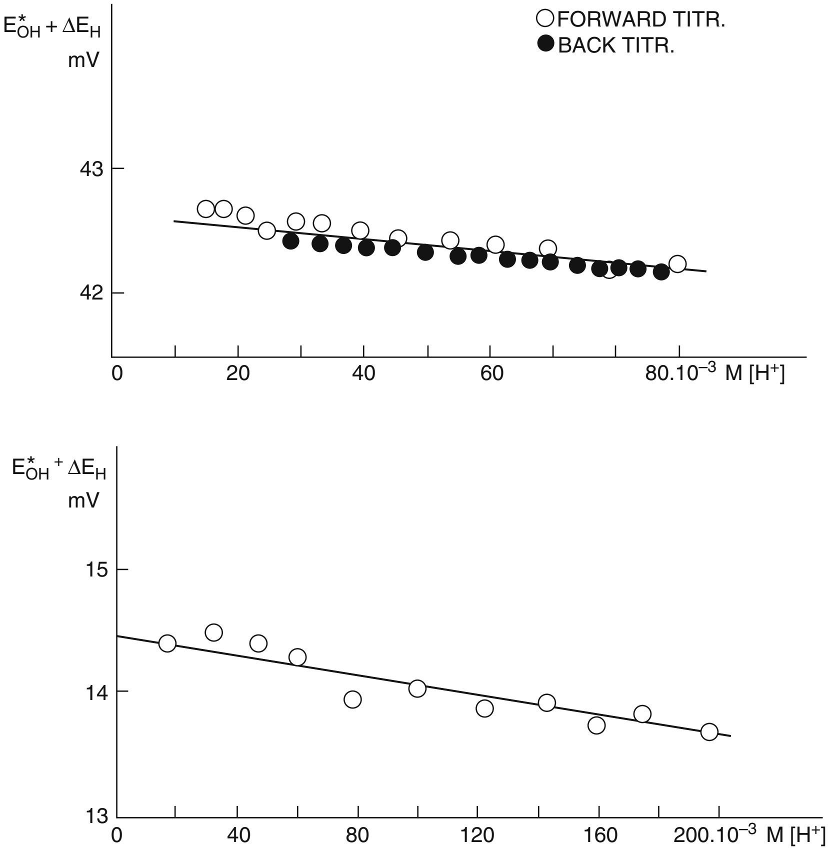

Fig. 2.2 Determination of the experimental slope function SL(H,c_H) and the conditional constant $E_{0H2} = E_{0H}{}^{x} + F(H,c_B)$, for Mixture 2, where $[Na^+] = 3$ M is kept constant. Reproduced by permission of the Royal Society of Chemistry from Néher-Neumann E (1997) Acta Chem Scand 51: 1141–1154 (Fig. 2)

The slope of this plot is SL(H,c_H)$_2$ and is defined by Eqs. (1.37) and (1.45). This plot is shown in Fig. 2.2. The slope was found to be -4.8 ± 1 mV M^{-1} H^+. The calculated and measured slopes were compared in Table 2.5. We can see from this table, that *the agreement is rather good.* The necessary ionic molar conductivities are given in Table 2.6. The term $[g\ d\ D(I)]_{c(B)}$ was estimated as before (cf. Eq. (2.10)).

$$\int_0^{c(H)} [g\ d\ D(I)]_{c(B)}\ dc_H = 0.62\ c_H \tag{2.18}$$

It was found to be 0.62 mV.

The slope SL(H,c_B)$_2$ was also estimated in Mixture 1. It was obtained through the plot $E_H' \equiv E_H - g \log_{10} c_H$ versus c_B, at constant c_H. This slope is defined by Eqs. (1.36), (1.44), and the intercept is

$$E_{0H2} = E^{x}_{0H} + F(H, c_H) \tag{2.19}$$

where

$$E^{x}_{0H} = E_{0H} + f_3(C) \tag{2.20}$$

The functions $F(H,c_H)$ and $f_3(C)$ are given in Table 2 in Ref. [1].

The experimental and theoretical slopes were found to be 40.5 ± 0.5 and 39.7 mV M^{-1} H^+, respectively. The plot is shown in Fig. 2.1. The comparison between measured and calculated slopes is given in Table 2.4. These results show that *all ions present in the test solution* contribute to the potential of the indicator electrode.

2.1.2.2 The Estimation of the Systematic Errors in the Equilibrium Constant, $\Delta\log_{10}\beta_{pqr}$, Caused by the Use of the Conditional Experimental Constant E_{0H1}

We shall follow the same treatment as in Cell B (cf. Section 2.1.1.2). We obtain

$$\log_{10} h = (E_H - E_{0H} - g\, d_3\, c_B)/g + [D(I) - D(C)] - (1/g)\Sigma_V\, Q(H, V)V - (1/g)\,\text{corr}, \tag{2.21}$$

where Q(H,V) denotes constant functions, again.

The systematic error in question will be, according to Eqs. (1.46), (2.11) and (2.21)

$$\Delta \log_{10} \beta_{pqr} = -q\Delta \log_{10} h = q\,(g\, d_3 c_B)/g \tag{2.22}$$

Assuming values for the term $g\ d_3\ c_B$ mV, a hypothetical error can be estimated, as given in Table 2.9. This systematic error causes the dependence of the β value with c_B, consequently with B_T too. This will be interpreted as the formation of polynuclear complexes which are *artefacts.*

Table 2.9 The estimation of the systematic error in the formation constants $\log_{10}\beta_{pqr}$, caused by the neglected potential contribution of the $B^{z(B)+}$ ions to E_{0H}

Cell H	$-q\ \Delta \log h = q\ gd_3\ c_B\ /\ g$		
$E_{0H} + gd_3\ c_B$ /mV	q = 1	q = 2	q = 3
E_{0H} + 0.5	0.008	0.016	0.024
E_{0H} + 1.00	0.017	0.034	0.051
E_{0H} + 2.00	0.034	0.067	0.102
E_{0H} + 5.00	0.084	0.169	0.252
E_{0H} + 7.00	0.118	0.236	0.354
E_{0H} + 10.00	0.169	0.338	0.507

Source: Reproduced by permission of the Royal Society of Chemistry from Néher-Neumann E (1998) Acta Chem Scand 52: 873–882 (Table 2).

Table 2.10 Survey of the anionic transport numbers [6] for some electrolytes often used in emf measurements

Electrolyte	Concentration range/m	t_{Y}^{-} (anionic)
$HClO_4$	$0.100-3.47_5$	0.17 (3.5−2.5 m) 0.16 (2.5−1.5 m) 0.15 (1.5−0.1 m)
$NaClO_4$	$0.690-3.49_5$	0.57
$LiClO_4$	$0.360-3.46_7$	0.65
NaCl	$0.641-3.19_6$	0.64
	$1.598-3.19_6$	0.63

Source: Reproduced by permission of the author Douhéret G (1980) from Biedermann G (deceased), Douhéret G Chemica Scripta 16: 138–140 (Table I).

Table 2.11 The molar conductivities of some pure electrolytes [7] often used as ionic medium in emf measurements, in S cm^2.g mol^{-1}

3 M $LiClO_4$ 52.53	3 M $NaClO_4$ 54.60	1 M $NaClO_4$ 77.10	0.5 M $NaClO_4$ 85.12
3 M NaCl 65.60	3 M $HClO_4$ 233.1	1 M $HClO_4$ 329.3	3 M HCl 237.7

Source: Reproduced by permission of the author Douhéret G (1980) from Biederman G (deceased), Douhéret G Chemica Scripta 16: 141–143 (Table I).

The systematic error in E_{0H1}, for the glass electrode in Mixture 2, was estimated (cf. Table 2.1). It was found to be g c_B d_3 = 2.01 mV. This means that the smallest systematic error in the measurement of E_H is 2.01 and not 0.01 mV.

Using this value, the experimental systematic error, $\Delta \log_{10} \beta_{pqr}$, was calculated for different q values. These are given in Table 2.8. As is seen, the systematic error in the equilibrium constant changes with q, and it is not negligible.

The anionic transport numbers (t_Y) for some electrolytes, often used in emf measurements, are given in Table 2.10 taken from Ref. [6]. *The molar conductivities* (Λ) of some pure electrolytes, often used as ionic medium in emf measurements, are presented in Table 2.11 [7].

2.2 Studies on Emf Cells Where $[Y^-]$ = C M, Constant [1]

The derived equations of this chapter can be used if the approximation ln[(w/a) + 1] ≅ w/a is valid, for small values of w/a [1]. Here,

$$w = S_{TS2} - S_{TS1} = z_B\ c_B(\lambda_B - \lambda_A) + c_H(\lambda_H - \lambda_A) \tag{2.23}$$

$$a = S_{TS1} = C(\lambda_A + \lambda_Y) \tag{2.24}$$

according to Eqs. (4), (6) in Part 4 in Ref. [2].

The validity of this approximation should be checked by using the ionic molar conductivities determined in the mixtures studied. This was found to be the case, when the ion concentrations were: $c_H \leq 0.1$ M and $c_{Cd} \leq 0.1$ M in the ionic medium $NaClO_4$ and for the concentration range $0.5 \leq C \leq 3$ M.

In these systems, we have

$$c_A = C - z_B\, c_B - c_H \text{ M} \tag{2.25}$$

$$I = C + c_B\, (z_B^2 - z_B)/2 \tag{2.26}$$

In the potential function E_{Df} and in the term "corr", the function $\Phi_1(x)$ is included. This summarizes the Debye–Hückel terms of the activity coefficients. In the present experimental condition, it has the following value.

$$\Phi_1(x) = x\,[z_B\, c_B(\lambda_A - z_B\lambda_B) + c_H(\lambda_A - \lambda_H)] + C(\lambda_Y - \lambda_A) \tag{2.27}$$

2.2.1 Cell B Using an Amalgam/Ion-Selective Indicator Electrode

2.2.1.1 The Determination of E_{0B} and Some Slope Functions

The determination of E_{0B} can be done in a similar way as it was discussed earlier in Section 2.1.1.1. This cell is also suitable for the determination of different slope functions in order to investigate, e.g. the two contributions of the activity factors to the total potential anomalies.

For this cell, the potential functions given below are valid. The total cell emf, E_B mV, is defined by Eq. (1.11), where

$$d_1 = -F_0(\lambda_B - \lambda_A\, z_B) + t_Y[\varepsilon''(B, Y) - \varepsilon''(A, Y) z_B] \tag{2.28}$$

$$d_2 = -F_0(\lambda_H - \lambda_A) + t_Y[\varepsilon''(H, Y) - \varepsilon''(A, Y)] \tag{2.29}$$

According to Plot 1, for Mixture 1, the conditional constant

$$E_{0B1} = E_{0B} + g\, d_2\, c_H \text{ mV}$$

can be determined as the intercept of the plot $E_B{}' = E_B - (g/z_B) \log_{10} c_B + g\, z_B\, [D(I) - DC]$ versus c_B, at constant c_H. We estimated the systematic error gd_2c_H. This is given in Table 2.1. Then the total potential anomalies $\Delta E_B{}^x$ was calculated according to Eq. (2.8). The result is given in Table 2.1. The necessary ionic molar

Table 2.12 Survey of the values for the ionic molar conductivities (λ_J) in S cm^2 (mol ion)$^{-1}$ |charge|$^{-1}$ at 25.000 ± 0.005°C for

(1) Mixture 1: 0.025 M $HClO_4$, constant, X M $NaClO_4$, $0 \leq [Cd(ClO_4)_2] \leq 0.100$ M
and $[ClO_4^-] = 3$ M, constant
(2) Mixture 2: 0.050 M $Cd(ClO_4)_2$, constant, X M $NaClO_4$, 2.10^{-3} M $\leq [HClO_4] \leq 0.1$ M
and $[ClO_4^-] = 3$ M, constant

	Mixture 1	Mixture 2
λNa	23.48	23.48
$\lambda ClO_{4(3)}$	32.37^a	30.38^b
f_1		5.89^b
$\lambda_{Cd}{}^{tr}$	0	48.0 ± 2.7
$\lambda_H{}^{tr}$	215.9 ± 10.9	189.73

a: $\lambda_{Y(3)} = 31.19 + f_1 z_B[B^{z(B)+}]$
f_1 was calculated from the slope of the plot
$10^3\kappa$ versus $[Cd^{2+}]$, at $[H^+] = 0.025$ M, constant: $z_B(\lambda_B{}^{tr} - \lambda_A + Cf_1) = -11.60$.
b: at $c_{Cd} = 0.1$ M, otherwise $\lambda_{Y(3)} = 30.38 + 2.76\,[H^+]$
Source: Reproduced by permission of the Royal Society of Chemistry from Néher-Neumann E (1998) Acta Chem Scand 52: 1075–1080.

conductivities were determined by the author [8]. The values presented in Table 2.12 were obtained.

The knowledge of the systematic error in question can be used for the calculation of E_{0B} and the minimum error in $\log_{10} \beta_{pqr}$.

The slope of this plot, determined in Mixture 1, is

$$SL(B, c_B)_1 = g\ d_1 mV\ M^{-1}(Cd^{2+}) \tag{2.30}$$

According to Plot 2, for Mixture 1, we plotted the data as $E'_B = E_B - (g/z_B) \log_{10} c_B$ versus c_B, at constant c_H. We obtain a conditional constant for the intercept

$$E_{0B2} = E^x_{0B} + F(B, c_H) \tag{2.31}$$

where the involved functions are given in Table 9 in Ref. [1]. The slope of this plot is $SL(B,c_B)_2$. This function can be given, due to Eqs. (1.14), (1.11) and (80) in Ref. [1] as

$$\begin{aligned} SL(B, c_B)_2 \equiv [\partial E'_B/\partial c_B]_{c(H)} = -g z_B\ d\ D(I)(z_B^2 - z_B)/2 + g d_1 \\ + [\partial corr/\partial c_B]_{c(H)} \end{aligned} \tag{2.32}$$

The calculated value of it is given in Table 2.13.

The slope function $SL(B,c_H)_2$ can be determined in Mixture 2 with Cell B through the plot $E_B' = E_B - (g/z_B) \log_{10} c_B$ versus c_H, at constant c_B. The intercept of this plot is

$$E_{0B2} = E^x_{0B} + F(B, c_B) \tag{2.33}$$

Table 2.13 Survey of the calculated and measured slopes in mV M^{-1}, for cell B and H, at the experimental condition $[ClO_4^-] = 3$ M, constant, in Mixture 1. The term "corr" is neglected

Slope $SL(H, c_B)$ cf. Eq. (2.37)		Slope $SL(B, c_B)$ cf. Eq. (2.32)	
$\left(\frac{\partial(g \log f_H)}{\partial c_B}\right)_{c_H}$	−0.66	$\left(\frac{(g/z_B) \log f_B)}{\partial c_B}\right)_{c_H}$	−1.32
$\left(\frac{\partial E_D}{\partial c_B}\right)_{c_H}$	7.20	$\left(\frac{\partial E_D}{\partial c_B}\right)_{c_H}$	7.20
$\left(\frac{\partial(E_{Df} - \mathrm{corr})}{\partial c_B}\right)_{c_H}$	11.64	$\left(\frac{\partial(E_{Df} - \mathrm{corr})}{\partial c_B}\right)_{c_H}$	11.64
Calculated total slope	18.18	Calculated total slope	17.52
Experimental slope	18.4	Experimental slope	

Source: Reproduced by permission of the Royal Society of Chemistry from Néher-Neumann E (1997) Acta Chem Scand 51: 1141–1154 (Table 7).

Table 2.14 Survey of the calculated and measured slopes in mV M^{-1}, for cell B and H, at the experimental condition $[ClO_4^-] = 3$ M, constant, in Mixture 2. The term "corr" is neglected

Slope $SL(H, c_H)$cf. Eq. (2.35)		Slope $SL(B, c_H)$ cf. Eq. (2.34)	
$\left(\frac{\partial(g \log f_H)}{\partial c_H}\right)_{c_B}$	0	$\left(\frac{(g/z_B) \log f_B)}{\partial c_H}\right)_{c_B}$	0
$\left(\frac{\partial E_D}{\partial c_H}\right)_{c_B}$	−26.43	$\left(\frac{\partial E_D}{\partial c_H}\right)_{c_B}$	−26.43
$\left(\frac{\partial(E_{Df} - \mathrm{corr})}{\partial c_H}\right)_{c_B}$	5.00	$\left(\frac{\partial(E_{Df} - \mathrm{corr})}{\partial c_H}\right)_{c_B}$	5.00
Calculated total slope	−21.43	Calculated total slope	−21.43
Experimental slope	−21.8	Experimental slope	

Souce: Reproduced by permission of the Royal Society of Chemistry from Néher-Neumann E (1997) Acta Chem Scand 51: 1141–1154 (Table 8).

The involved functions are given in Table 9 in Ref. [1].

The slope of this plot will be, due to Eqs. (1.15), (1.11) and (86) in Ref. [1] as

$$SL(B, c_H)_2 \equiv [\partial E'_B/\partial c_H]_{c(B)} = g\, d_2 + [\partial \mathrm{corr}/\partial c_H]_{c(B)} \qquad (2.34)$$

The calculated value of it is given in Table 2.14.

2.2.1.2 The Estimation of the Systematic Errors in the Equilibrium Constant, $\Delta \log_{10} \beta_{pqr}$, Caused by the Use of the Conditional Experimental Constant E_{0B1}

This was done as in Section 2.1.1.2. The results are presented in Table 2.15.

Table 2.15 The estimation of the systematic errors in the formation constants $\log_{10}\beta_{pqr}$, caused by the systematic errors in E_{0B} (cell B) and E_{0H} (cell H) under different experimental conditions

	Cell B Mixture 1: $c_H = 0.025$ M constant			Cell H Mixture 2: $c_B = 0.050$ M constant		
Conditional constants/mV	$E_{0B1} = E_{0B} + gc_H\ d_2$			$E_{0H1} = E_{0H} + gc_B\ d_3$		
Experimental conditions	Systematic errors in $\log_{10}\beta_{pqr}$					
	p = 1	p = 2	p = 3	q = 1	q = 2	q = 3
$[Na^+] = 3$ M is kept constant:						
systematic error/mV	in E_{0B1} : $gd_2c_H = -0.17$			in E_{0H1}: $gd_3c_B = 1.99$		
E_{0B} resp. E_{0H}/mV	$E_{0B1} + 0.17$			$E_{0H1} - 1.99$		
$\Delta\log\beta_{p,q,r}$	negligible for z(B) = 2			0.034	0.067	0.102
$[ClO_4^-] = 3$ M is kept constant:						
systematic error/mV	in E_{0B1} : $gd_2c_H = -0.63$			in E_{0H1} : $gd_3c_B = 0.56$		
E_{0B} resp. E_{0H}/mV	$E_{0B1} + 0.63$			$E_{0H1} - 0.56$		
$\Delta\log\beta_{p,q,r}$	− 0.017	−0.034	−0.050	0.008	0.016	0.024
	for z(B) = 2					
I = 3 M is kept constant:						
systematic error/mV	in E_{0B1} : $gd_2c_H = -0.71$			in E_{0H1} : $gd_3c_B = -0.86$		
E_{0B} resp. E_{0H}/mV	$E_{0B1} + 0.71$			$E_{0H1} + 0.86$		
$\Delta\log\beta_{p,q,r}$	−0.024	−0.048	−0.071	−0.014	−0.029	−0.043
	for z(B)=2					

Source: Reproduced by permission of the Royal Society of Chemistry from Néher-Neumann E (1999) Acta Chem Scand 53: 1–6 (Table 2).

2.2.2 *Emf Studies in Cell H Using a Glass Indicator Electrode*

2.2.2.1 The Determination of the Constant E_{0H} and Some Slope Functions

In this cell, the following potential functions are valid.

The total cell emf, E_H mV, is defined by Eq. (1.33), where

$d_3 = d_1$, is given by Eq. (2.28)
$d_4 = d_2$, is given by Eq. (2.29)

The constant E_{0H} can be determined in Mixture 2 as before, in Section 2.1.2.1, through Plot 1, as $E_H' = E_H - g \log_{10} c_H + g[D(I) - DC]$ versus c_H, at constant c_B. The intercept is the conditional constant

$$E_{0H1} = E_{0H} + g\ d_3c_B$$

and the slope is

$$SL(H, c_H)_1 = g\ d_4$$

The term gd_3c_B was estimated and is given in Table 2.1. The necessary ionic molar conductivities are presented in Table 2.12. The total potential anomalies, $\Delta E_H{}^x$, were also calculated (cf. Eq. (2.16)) and are given in Table 2.1.

The data were evaluated according to Plot 2 also. The slope of the plot $E_H{}' = E_H - g \log_{10} c_H$ versus c_H, at constant c_B gave

$$SL(H, c_H)_2 \equiv [\partial E'_H/\partial c_H]_{c(B)} = g\, d_4 = g\, d_2 = [\partial E'_B/\partial c_H]_{c(B)} = SL(B, c_H)_2 \tag{2.35}$$

cf. Eq. (83) in Ref. [1].

The intercept of this plot is

$$E_{0H2} = E^x_{0H} + F(H, c_B) \tag{2.36}$$

where the function $F(H,c_B)$ and $E_{0H}{}^x$ is given in Table 9 in Ref. [1].

The slope function $SL(H,c_H)_2$ was determined by the author and is given by Fig. 2.3. The calculated slope and the comparison between calculated and measured values are presented in Table 2.14.

The slope function $SL(H,c_B)_2$ was determined in Mixture 1 also, through the plot $E_H{}' = E_H - g \log_{10} c_H$ versus c_B, at constant c_H, using a glass electrode. We obtained

$$SL(H, c_B)_2 \equiv [\partial E'_H/\partial c_B]_{c(H)} = -g\, d\, D(I)(z^2_B - z_B)/2 + g\, d_3 + [\partial corr/\partial c_B]_{c(H)}, \tag{2.37}$$

according to Eqs. (1.36), (1.33) and (77) in Ref. [1]. The intercept of this plot is

$$E_{0H2} = E^x_{0H} + F(H, c_H) \tag{2.38}$$

where the function $F(H,c_H)$ and $E_{0H}{}^x$ are given in Table 9 in Ref. [1].

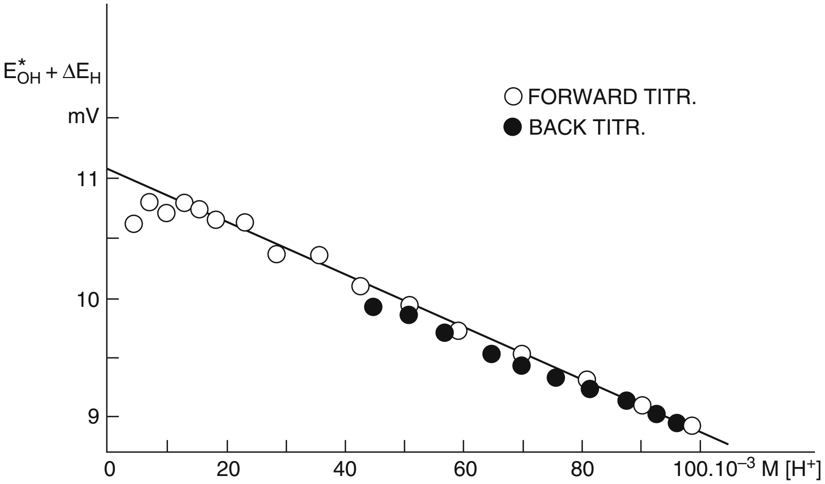

Fig. 2.3 Determination of the experimental slope function $SL(H,c_H)$ and the conditional constant $E_{0H2} = E_{0H}{}^x + F(H,c_B)$, for Mixture 2, where $[ClO_4{}^-] = 3$ M is kept constant. Reproduced by permission of the Royal Society of Chemistry from Néher-Neumann E (1997) Acta Chem Scand 51: 1141–1154 (Fig. 4)

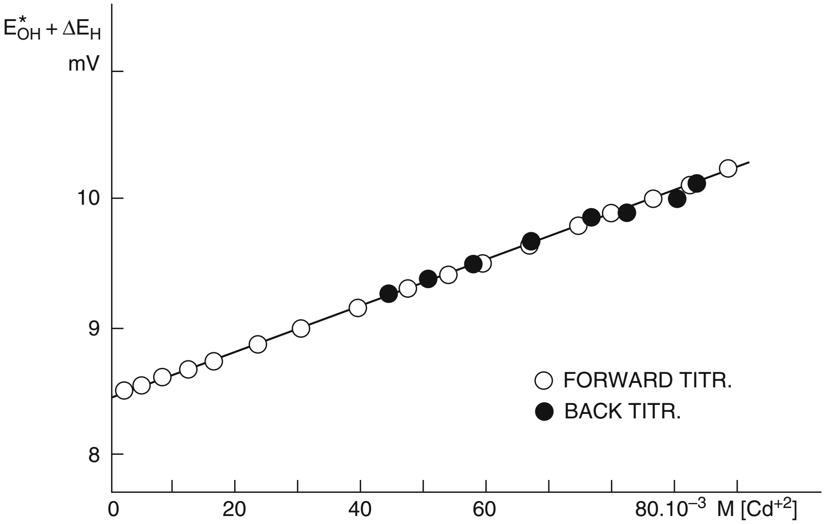

Fig. 2.4 Determination of the experimental slope function $SL(H,c_B)_2$ and the conditional constant $E_{0H2} = E_{0H}{}^{x} + F(H,c_H)$, for Mixture 1, where $[ClO_4{}^-] = 3$ M is kept constant. Reproduced by permission of the Royal Society of Chemistry from Néher-Neumann E (1997) Acta Chem Scand 51: 1141–1154 (Fig. 3)

The slope function $SL(H,c_B)_2$ was determined by the author. This plot is presented in Fig. 2.4. The comparison between measured and calculated slopes is given in Table 2.13.

As we can see from Table 2.1, the total potential anomalies for Cells B and H are much smaller then those of the experimental condition $[Na^+] = 3$ M, constant, and the experimental uncertainties are not 0.01 mV.

2.2.2.2 The Estimation of the Systematic Errors in the Equilibrium Constants, $\Delta \log_{10} \beta_{pqr}$, Caused by the Use of the Conditional Constant E_{0H1}

This can be done as in Section 2.1.2.2. These are presented in Table 2.15 (cf. Table 2.1 also). These systematic errors are half as high for the glass electrode than that of the amalgam electrode.

2.3 Studies on Emf Cells Where the Ionic Strength (I) = C M, Constant [1]

The derived equations of this chapter can be used if the approximation ln [(w/a) + 1] $\cong$ w/a is valid, for small values of w/a [1]. Here,

$$\mathrm{w} \equiv \mathrm{S_{TS2}} - \mathrm{S_{TS1}} = \mathrm{c_B\, z_B}(\lambda_\mathrm{B} + \lambda_\mathrm{Y}) + \mathrm{c_H}(\lambda_\mathrm{H} - \lambda_\mathrm{Y}) - \mathrm{c_B}(\lambda_\mathrm{A} + \lambda_\mathrm{Y})\,(\mathrm{z_B^2} + \mathrm{z_B})/2, \quad (2.39)$$

$$\mathrm{a} \equiv \mathrm{S_{TS1}} = \mathrm{C}(\lambda_\mathrm{A} + \lambda_\mathrm{Y}) \quad (2.40)$$

The validity of this approximation should be checked by using the ionic molar conductivities determined in the mixtures studied. This was found to be the case, if the ion concentrations are: $c_H \leq 0.1$ M and $c_B \leq 0.1$ M in the ionic medium $NaClO_4$ and for $0.5 \leq C \leq 3$ M.

The composition of the test solution (TS2) is:

$$\mathrm{c_B} = [\mathrm{B}^{z(B)+}] = [\mathrm{BY}_{z(B)}]\ \mathrm{M}$$

$$\mathrm{c_H} = [\mathrm{H}^+] = [\mathrm{HY}]\ \mathrm{M}$$

$$\mathrm{c_A} = \mathrm{C} - \mathrm{c_H} - \mathrm{c_B}(\mathrm{z_B^2} + \mathrm{z_B})/2\,\mathrm{M} \quad (2.41)$$

$$\mathrm{c_Y} = \mathrm{C} + \mathrm{z_B\, c_B} - \mathbf{c_B}(\mathrm{z_B^2} + \mathrm{z_B})/2\,\mathrm{M} \quad (2.42)$$

The composition of e.g. Mixture 1 can be established as follows.

I = 3 M, constant, should be insured. The ionic strength for Mixture 1/Mixture 2 can be given as

$$\mathrm{I} = (1/2)(\mathrm{c_A} + \mathrm{c_H} + \mathrm{c_Y} + \mathrm{c_B\, z_B^2}) = \mathrm{C\ M,\ constant} \quad (2.43)$$

where

$$\mathrm{c_Y} = \mathrm{AY_T} + \mathrm{c_H} + \mathrm{z_B\, c_B} \quad (2.44)$$

Here, T denotes total, analytical concentration in M.

Inserting c_Y into Eq. (2.43) and expressing AY_T from it, we obtain the concentration of the ionic medium to be used.

$$\mathrm{AY_T} = \mathrm{C} - \mathrm{c_H} - [(\mathrm{z_B^2} + \mathrm{z_B})/2]\ \mathrm{c_B\ M} \quad (2.45)$$

If NaOH (AOH) is added to the mixture also, e.g. at the determination of E_{0H} through an acid–base titration, we have

$$\mathrm{c_A} = \mathrm{AY_T} + \mathrm{AOH_T} \quad (2.46)$$

and for the test solution

$$\mathrm{AY_T} = \mathrm{C} - \mathrm{c_H} - [(\mathrm{z_B^2} + \mathrm{z_B})/2]\ \mathrm{c_B} - (1/2)\,\mathrm{AOH_T} \quad (2.47)$$

2.3.1 Emf Studies in Cell B Using an Amalgam Indicator Electrode

2.3.1.1 The Determination of E_{0B} and Some Slope Functions

The determination of E_{0B} can be done in a similar way as it was discussed in Section 2.1.1.1. For this cell, the potential functions given below are valid. The total cell emf, E_B mV, is defined by the equation

$$E_B = E_{0B} + (g/z_B)\log_{10} c_B + g\, d_1 c_B + g\, d_2 c_H \tag{2.48}$$

as D(I) – D(C) = 0. The functions d_1 and d_2 were found to be

$$d_1 = \varepsilon''(B,Y)(1 - z_B)\,(1/2) - [\lambda_B - z_B\lambda_Y + (\lambda_Y - \lambda_A)\,(z_B^2 + z_B)/2]\,F_0 - t_A\varepsilon''(A,Y)\,(z_B - z_B^2)\,(1/2) + t_Y[\varepsilon''(B,Y) - \varepsilon''(A,Y)\,(z_B^2 + z_B)/2] \tag{2.49}$$

$$d_2 = -(\lambda_H - \lambda_A)F_0 + t_Y[\varepsilon''(H,Y) - \varepsilon''(A,Y)] \tag{2.50}$$

The conditional constant, E_{0B1}, can be obtained as the intercept of the plot $E'_B = E_B - (g/z_B)\log_{10} c_B$ versus c_B, at constant c_H:

$$E_{0B1} = E_{0B} + g\, d_2 c_H \text{ mV}$$

We estimated the systematic error $g\, d_2\, c_H$. This is given in Table 2.1. The necessary ionic molar conductivities were determined by the author [9] for Mixture 1 and Mixture 2. The values presented in Table 2.16 were obtained. The total potential anomalies, $\Delta E_B{}^x$, were also calculated (cf. Eq. (2.8)) and are given in Table 2.1. With the systematic error in question, the value of E_{0B} and the minimum error in $\log_{10}\beta_{pqr}$ can be calculated. The slope of this plot is

Table 2.16 Survey of the values for the ionic molar conductivities (λ_J) in S.cm^2. (mol ion)$^{-1}$ |charge|$^{-1}$ at 25.000 ± 0.005°C for

(1) Mixture 1: 0.025 M $HClO_4$, constant, X M $NaClO_4$, $0 \leq [Cd(ClO_4)_2] \leq 0.1$ M, I = 3 M, constant.
(2) Mixture 2: 0.050 M Cd $(ClO_4)_2$, constant, X M $NaClO_4$, 2.10^{-3} M $\leq [HClO_4] \leq 0.1$ M and I = 3 M, constant

	Mixture 1	Mixture 2
λ_{Na}	23.48	23.48
$\lambda[ClO_{4(3)}]$	$31.19 - 15.03\,[Cd^{2+}]$	$30.37 + 2.83\,[H^+]$
$\lambda_{Cd}{}^{tr}$	52.77	66.31 ± 0.38
$\lambda_H{}^{tr}$	235.08 ± 1.60	179.91

Source: Reproduced by permission of the Royal Society of Chemistry from Néher-Neumann E (1999) Acta Chem Scand 53: 1–6.

Table 2.17 Survey of the calculated and measured slopes in mV M^{-1}, for cell H and B, at the experimental condition $I = 3$ M, constant, in Mixture 1: $[HClO_4] = 0.025$ M, constant, $0 \leq [Cd(ClO_4)_2] \leq 0.1$ M, and X M $NaClO_4$

Slope SL (H,c_B) cf. Eq. (2.58)		Slope SL (B,c_B) cf. Eq. (2.51)	
$\left(\frac{g\partial \log f_H}{\partial c_B}\right)_{c_H}$	−10.65	$\left(\frac{(g/z_B)\partial \log f_B}{\partial c_B}\right)_{c_H}$	−11.83
$\left(\frac{\partial E_D}{\partial c_B}\right)_{c_H}$	−2.03	$\left(\frac{\partial E_D}{\partial c_B}\right)_{c_H}$	−2.03
$\left(\frac{\partial E_{Df}}{\partial c_B}\right)_{c_H}$	11.11	$\left(\frac{\partial E_{Df}}{\partial c_B}\right)_{c_H}$	11.11
Calculated total slope	−1.57 ± 0.06	Calculated total slope	−2.75 ± 0.06
Experimental slope	1.6	Experimental slope	0 ± 0.5

Source: Reproduced by permission of the Royal Society of Chemistry from Néher-Neumann E (1997) Acta Chem Scand 51: 1141–1154 (Table 10).

$$SL(B, c_B)_1 \equiv [\partial E'_B/\partial c_B]_{c(H)} = g\, d_1 \tag{2.51}$$

The calculated and measured values for it can be found in Table 2.17. The value $SL(B,c_B) = 0 \pm 0.5$ mV M^{-1} Cd^{2+} was measured by Leden [10].

The slope of the plot $E'_B = E_B - (g/z_B) \log_{10} c_B$ versus c_H, at constant c_B, determined in Mixture 2, gives

$$SL(B,c_H) \equiv [\partial E'_B/\partial c_H]_{c(B)} = g\, d_2 \tag{2.52}$$

and for the intercept

$$E_{0B1} = E_{0B} + g\, d_1 c_B \text{mV} \tag{2.53}$$

The calculated value for $SL(B,c_H)$ is shown in Table 2.18.

2.3.1.2 The Estimation of the Systematic Errors in the Equilibrium Constants, $\Delta \log_{10} \beta_{pqr}$, Caused by the Use of the Conditional Constant E_{0B1}

This was done as discussed in Section 2.1.1.2. The results are presented in Table 2.15.

2.3.2 Emf Studies in Cell H Using a Glass Indicator Electrode

For this system, the potential functions given below are valid. The total cell emf is

$$E_H = E_{0H} + g \log_{10} c_H + g\, c_B\, d_3 + g\, c_H d_4 \text{ mV} \tag{2.54}$$

Table 2.18 Survey of the calculated and measured slopes in mV M^{-1}, for cell B and H, at the experimental condition I = 3 M, constant, in Mixture 2: 0.05 M $Cd(ClO_4)_2$ is kept constant, $0.003 \leq [HClO_4] \leq 0.1$ M and X M $NaClO_4$

Slope SL(H,c_H) cf. Eq. (2.57)		Slope SL(B,c_H) cf. Eq. (2.52)	
$\left(\frac{g\partial \log f_H}{\partial c_H}\right)_{c_B}$	0	$\left(\frac{(g/z_B)\partial \log f_B}{\partial c_H}\right)_{c_B}$	0
$\left(\frac{\partial E_D}{\partial c_H}\right)_{c_B}$	−24.81	$\left(\frac{\partial E_D}{\partial c_H}\right)_{c_B}$	−24.81
$\left(\frac{\partial E_{Df}}{\partial c_H}\right)_{c_B}$	5.01	$\left(\frac{\partial E_{Df}}{\partial c_H}\right)_{c_B}$	5.01
Calculated total slope: −19.80 ± 0.08		Calculated total slope: −19.80 ± 0.08	
Experimental slope: −17.70			

Source: Reproduced by permission of the Royal Society of Chemistry from Néher-Neumann E (1997) Acta Chem Scand 51: 1141–1154 (Table 11).

where

$$d_3 = \varepsilon''(H,Y)\,(z_B - z_B^2)\,(1/2) - [\lambda_B - z_B\lambda_Y + (\lambda_Y - \lambda_A)\,(z_B^2 + z_B)/2]\,F_0 - t_A\varepsilon''(A,Y)\,(z_B - z_B^2)\,(1/2) + t_Y[\varepsilon''(B,Y) - \varepsilon''(A,Y)\,(z_B^2 + z_B)/2] \tag{2.55}$$

$$d_4 = d_2 \tag{2.56}$$

2.3.2.1 The Determination of E_{0H} and Some Slope Functions

The conditional constant E_{0H1} can be obtained as the intercept of the plot $E'_H = E_H - g \log_{10} c_H$ versus c_H, at constant c_B, determined in Mixture 2 as

$$E_{0H1} = E_{0H} + g\,c_B\,d_3\ \text{mV}$$

The term gc_Bd_3 was estimated and is given in Table 2.1. The necessary ionic molar conductivities were measured by the author [9]. These are presented in Table 2.16. The slope of this plot is

$$SL(H,c_H) \equiv [\partial E_H'/\partial c_H]_{c(B)} = g\,d_4 = g\,d_2 = [\partial E_B'/\partial c_H]_{c(B)} = SL(B,c_H) \tag{2.57}$$

The total potential anomalies, $\Delta E_H{}^x$, were calculated (cf. Eq. (2.16)) and are given in Table 2.1. The slope function SL(H,c_H) was determined by the author. The plot is shown in Fig. 2.5. The experimental and calculated values for it are presented in Table 2.18.

The plot $E_H' = E_H - g \log_{10} c_H$ versus c_B, at constant c_H, determined in Mixture 1, gives the slope function

$$SL(H, c_B) = g\,d_3 \tag{2.58}$$

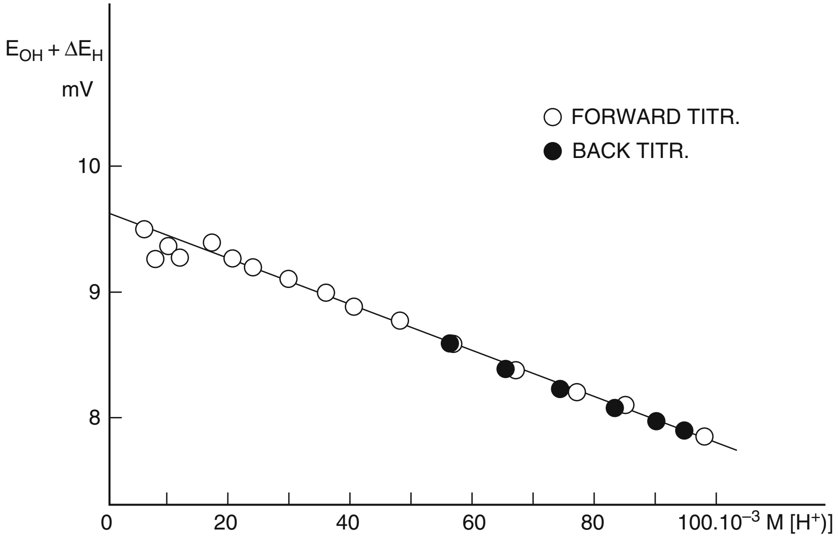

Fig. 2.5 Determination of the experimental slope function SL(H, c_H) and the conditional constant $E_{0H1} = E_{0H} + g\ d_3\ c_B$, for Mixture 2, where I = 3 M is kept constant. Reproduced by permission of the Royal Society of Chemistry from Néher-Neumann E (1997) Acta Chem Scand 51: 1141–1154 (Fig. 6)

The intercept is

$$E_{0H1} = E_{0H} + g\ d_4 c_H \tag{2.59}$$

This slope function was determined by the author. The plot is presented in Fig. 2.6. The measured and calculated values for it can be found in Table 2.17. The concerning ionic molar conductivities are given in Table 2.16.

2.3.2.2 The Estimation of the Systematic Errors in the Equilibrium Constants, $\Delta\ \log_{10}\beta_{pqr}$, Caused by the Use of the Conditional Constant E_{0H1}

This estimation was done for Mixture 2, as discussed earlier in Section 2.1.2.2. The results are presented in Table 2.15. In Cell H, this systematic error is half as high as in Cell B.

2.4 Conclusion on Emf Studies of Mixtures of Strong Electrolytes

The conclusions which can be drawn from the emf studies on mixtures of strong electrolytes in chapter 2 are summarized below.

(1) The individual slope functions determined at a given experimental condition, show the potential contribution of the ideal diffusion potential (E_D) and the different activity factor terms ((g/z_J) $\log_{10} f_{JTS2}$ + E_{Df}) to ΔE_J. Such slope

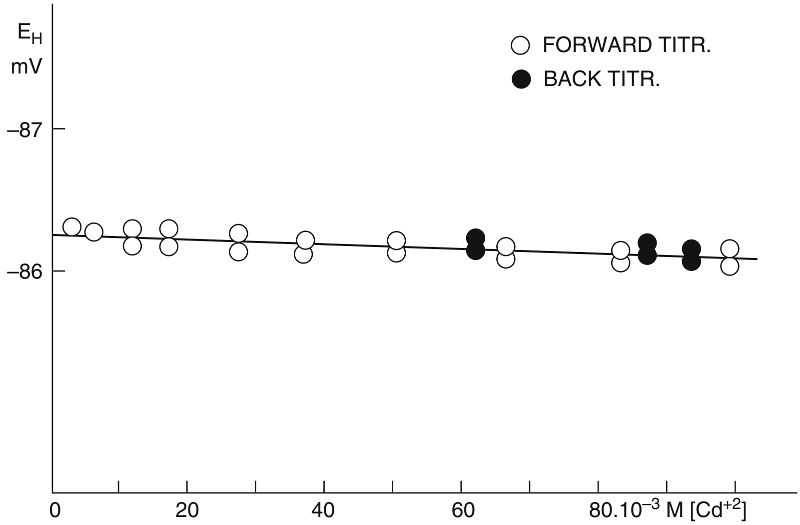

Fig. 2.6 Determination of the experimental slope function SL(H,c_B) and the conditional constant $E_{0H1} = E_{0H} + gd_4\ c_H$, for Mixture 1, where I = 3 M is kept constant. Reproduced by permission of the Royal Society of Chemistry from Néher-Neumann E (1997) Acta Chem Scand 51: 1141–1154 (Fig. 5)

functions are e.g. SL(B,c_B), as given in Table 2.19A, and SL(H,c_H), as given in Table 2.19B.

(1.1) From the study of SL(B,c_B), using an amalgam indicator electrode and determined at different experimental conditions, the following conclusions can be obtained (cf. Table 2.19A).

Table 2.19A Survey of the participate potential terms to the slope function SL(B,c_B), determined in mixtures of $HClO_4 + Cd(ClO_4)_2 + NaClO_4$ (in Mixture 1) at different experimental conditions, using cell B, in mV M^{-1} Cd^{2+} at 25° C

Experimental conditions	$[A^+]$ = C M, constant	$[Y^-]$ = C M, constant	I = C M, constant
$\left(\frac{(g/z_B)\partial \log_{10} f_{BTS2}}{\partial c_B}\right)_{c_H}$	19.89	−1.32	−11.83
$\left(\frac{\partial E_D}{\partial c_B}\right)_{c_H}$	8.57	7.20	−2.03
$\left(\frac{\partial E_{Df}}{\partial c_B}\right)_{c_H}$	11.70	11.64	11.11
Calculated slope	40.16	17.52	−2.75
Experimental slope	40.5 ± 0.5		0 ± 0.5

Source: Reproduced by permission of the Royal Society of Chemistry from Néher-Neumann E (1997) Acta Chem Scand 51: 1141–1154 (Tables 1, 7, 10).

(a) The contribution of the term $(g/z_B)\ \log_{10} f_{BTS2}$ to the slope is *highest* at $[A^+] = C$ M, constant, and is *around zero* at $[Y^-] = C$ M, constant.
(b) The contribution of the term E_D to this slope is *highest and equal* at $[A^+] = C$ M, constant, and $[Y^-] = C$ M, constant, is *smallest, around zero,* at $I = C$ M, constant.
(c) The contribution of the term E_{Df} is approximately *equal at all experimental conditions* studied.
(d) The total change of the activity factors, $(g/z_B)\ \log_{10} f_{BTS2} + E_{Df}$, is *highest* at $[A^+] = C$ M, constant, is a third of it at $[Y^-] = C$ M, constant, and is *around zero* at $I = C$ M, constant.
(e) The total value of the slope function $SL(B,c_B)$ is *highest* at $[A^+] = C$ M, constant, is half as much at $[Y^-] = C$ M, constant, and is *around zero* at $I = C$ M, constant.
(f) For the amalgam electrode, the total potential anomalies, $\Delta E_B{}^x$, is *smallest* at $[Y^-] = C$ M, constant (cf. Table 2.1).

(1.2) From the study of $SL(H,c_H)$, using a glass indicator electrode and determined at different experimental conditions, the following conclusion can be obtained (cf. Table 2.19B).

(a) The potential contribution of the term $g\ \log_{10} f_{HTS2}$ to the slope is *highest* at $[A^+] = C$ M constant, and is *around zero* at $[Y^-] = C$ M constant, and at $I = C$ M constant. This is a contribution of the activity coefficient, f_{HTS2}, to the ideal electrode potential, defined by the Nernst equation.
(b) The potential contribution of the term E_D to the slope is approximately equal at all experimental conditions studied, except $[Y^-] = C$ M, constant.

Table 2.19B Survey of the participate potential terms to the slope function $SL(H,c_H)$, determined in mixtures of $HClO_4 + Cd(ClO_4)_2 + NaClO_4$ (in Mixture 2), at different experimental conditions, using cell H, in mV M^{-1} H^+, at 25° C

Experimental conditions	$[A^+] = C$ M, constant	$[Y^-] = C$ M, constant	$I = C$ M, constant
$\left(\frac{g\partial \log_{10} f_{HTS2}}{\partial c_H}\right)_{c_B}$	10.03	0	0
$\left(\frac{\partial E_D}{\partial c_H}\right)_{c_B}$	−18.46	−26.43	−21.48
$\left(\frac{\partial E_{Df}}{\partial c_H}\right)_{c_B}$	5.20	5.00	5.01
Calculated slope	−3.23	−21.43	−19.80
Experimental slope	−4.8 ± 1	−21.8	−17.7

Source: Reproduced by permission of the Royal Society of Chemistry from Néher-Neumann E (1997) Acta Chem Scand 51: 1141–1154 (Tables 3, 8, 11).

(c) The contribution of the term E_{Df} to the slope is approximately equal at all experimental conditions studied.
(d) The total change of the activity factors, g $\log_{10} f_{HTS2} + E_{Df}$, is *highest* at $[A^+] = C$ M, constant, and is *smallest and equal* at $[Y^-] = C$ M, constant, and $I = C$ M, constant.
(e) The total value of the slope function $SL(H,c_H)$ is highest and equal at $[Y^-] = C$ M, constant, and at $I = C$ M, constant, and is very near to zero at $[A^+] = C$ M, constant.
(f) The systematic error in the conditional constant E_{0H1} is very high at the experimental condition $[A^+] = C$ M, constant (2.01 mV), is a fourth of it at $[Y^-] = C$ M, constant, and is a little higher at $I = C$ M, constant (cf. Table 2.1).
(g) For a glass electrode, the total potential anomalies are zero at every experimental condition, if we avoid using the conditional constant E_{0H1} (cf. Table 2.1).

E_{0H} should be determined in the absence of the metal ions $B^{z(B)+}$ and in the presence of the ligand, e.g. HL, when we study the formation of metal ion complexes.

(2) *All ions which are present in the test solution contribute as an extra term to the ideal electrode potential of every measuring electrode.* For the mixtures studied, it was found that the total potential anomalies in Cells B and H can be given as follows.

For Cell B:

$$\Delta E_B = -g\, z_B\, [D(I) - D(C)] + g\, d_2 c_H + SL(B,c_B)_1 c_B \tag{2.60}$$

For Cell H:

$$\Delta E_H = -g\, [D(I) - D(C)] + g\, d_3 c_B + SL(H,c_H)_1 c_H \tag{2.61}$$

For the estimation of E_{0B} and E_{0H}, moreover, the *calculated slope functions*, we need accurate conductivity data, which were determined in *exactly the same* mixtures what were used in the emf studies, for the determination of E_{0B} and E_{0H}.

(3) *The good agreement between calculated and measured slopes* (cf. Tables 2.20A and 2.20B) shows that

(a) the theory, for the establishment of the theoretical equations for emf studies for the estimation of the total potential anomalies, ΔE_J, is correct, developed by the author [2,11].
(b) The calculation methods used for the determination of the ionic molar conductivities are *correct* as well, developed by the author [2].
(c) By having these slope functions, we can calculate the *real, minimum uncertainty level of the emf data*, to be used in curve-fitting computer treatment of the data.

Table 2.20A Survey of the total values of the slope functions which participate in $\Delta E_B{}^x$, determined in mixtures of $HClO_4$ + $Cd(ClO_4)_2$ + $NaClO_4$ solutions, at different experimental conditions, in mV M^{-1} ion J, using cell B, at 25° C. The total potential anomalies for cell B are (reduced by the Debye-Hückel terms) $\Delta E_B{}^x = SL(B,c_B)_1\ c_B + SL(B,c_H)_1\ c_H$ mV

Experimental conditions	$[A^+] = 3$ M, constant	$[Y^-] = 3$ M, constant	$I = 3$ M, constant
Slopes			
$SL(B, c_B)_1$			
Mixture 1			
Calculated	43.93	18.84	− 2.75
Experimental	44.3 ± 0.5		0 ± 0.5
$SL_{calc} - SL_{exp}$	− 0.34		−2.75
$SL(B, c_H)_1$			
Mixture 2			
Calculated	− 1.43	− 21.43	− 19.80

Source: Reproduced by permission of the Royal Society of Chemistry from Néher-Neumann E (1997) Acta Chem Scand 51: 1141–1154.

(4) Knowing the experimental slope functions and $g\ d_2\ c_H$ /resp. $g\ d_3\ c_B$, we can determine the accurate values for E_{0B} and E_{0H}, and we can calculate the systematic errors in equilibrium constants caused by the use of the conditional constants given below.

$$E_{0B1} = E_{0B} + g\ d_2 c_H \qquad (2.62)$$

$$E_{0H1} = E_{0H} + g\ d_3\ c_B \qquad (2.63)$$

Table 2.20B Survey of the total values of the slope functions which participate in $\Delta E_H{}^x$, determined in mixtures of $HClO_4$ + $Cd(ClO_4)_2$ + $NaClO_4$ solutions, at different experimental conditions, in mV M^{-1} ion J, using cell B, at 25.00° C. The total potential anomalies for cell H are (reduced by the Debye – Hückel terms) $\Delta E_H{}^x = SL(H,c_H)_1 c_H + SL(H,c_B)_1\ c_B$, mV

Experimental conditions	$[A^+] = 3$ M, constant	$[Y^-] = 3$ M, constant	$I = 3$ M, constant
Slopes			
$SL(H,c_H)_1$			
Mixture 2			
Calculated	−2.61	−21.43	−19.80
Experimental	−4.18 ± 1	−21.8	−17.7
$SL_{calc} - SL_{exp}$	1.57	0.37	−2.10
$SL(H,c_B)_1$			
Mixture 1			
Calculated	41.5	18.84	−1.57
Experimental	42.4 ± 0.5	19.06	1.6
$SL_{calc} - SL_{exp}$	−0.88	−0.22	−3.17

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In this case, we can avoid the first suggestion of polynuclear complexes, when glass indicator electrode is used.
During the studies of the formation of metal ion complexes, *other systematic errors will also appear* due to the neglection of the total potential anomalies valid in cells with complex formation. These new systematic errors can also result in the suggestion of polynuclear complexes, or dimer, trimer, etc. species during the study of the protolysis of weak acids also. These new errors will be discussed in Chapter 4.

(5) On the experimental uncertainties of the total slope functions which participate in the total potential anomalies (cf. Tables 2.20A and 2.20B).
For Cell B: the experimental uncertainty, $SL_{calc} – SL_{exp}$, in the slope $SL(B,c_B)_1$, is smallest (– 0.34 mV M^{-1} Cd^{2+}) at $[A^+]$ = C M, constant, and is highest at I = 3 M, constant. It is difficult to determine a slope ~ 0 with higher accuracy. Here, calc denotes calculated, exp experimental. The slope $SL(B,c_H)_1$ is smallest at $[Na^+]$ = 3 M, constant (cf. Table 2.20A).
For Cell H: the experimental uncertainty in the slope $SL(H,c_H)_1$, $SL_{calc} – SL_{exp}$ is smallest (0.37 mV M^{-1} H^+) at $[Y^-]$ = C M, constant. The slope $SL(H,c_B)_1$ is highest at $[A^+]$ = C M, constant, and is smallest (around zero) at I = C M, constant. The experimental uncertainty in it is smallest (– 0.22 mV M^{-1} Cd^{2+}) at $[Y^-]$ = C M, constant (cf. Table 2.2B).
Concerning *all slope functions* determined in these studies, the experimental uncertainties are, *in general*, ≤ 1 mV M^{-1} ion J. Taking into account the experimental fact that $c_J \leq 0.1$ M in potentiometric titrations, the slope functions studied could be determined with ≤ 0.1 mV uncertainties. Slope functions which have a value *around zero* could be determined with ≤ 0.3 mV uncertainties.

(6) *The total potential anomalies* (reduced by the Debye–Hückel term of the indicator electrode), $\Delta E_B{}^x$ and $\Delta E_H{}^x$, appearing at the end of the determination of the experimental constants E_{0B} and E_{0H}, are presented in Table 2.1. As is seen from this table, $\Delta E_H{}^x$ is smallest (0.54 mV) at $[ClO_4{}^-]$ = 3 M, constant, and $\Delta E_B{}^x$ is smallest (0.33 mV) at the same experimental condition. This means that *Cell H is best (0 mV uncertainty) at all experimental conditions, in the estimation of the E_{0H} values, if we determine them in the absence of the metal ions.* This term is highest (2.01 mV) at $[Na^+]$ = 3 M, constant, and at I = 3 M, constant is −0.88 mV, if E_{0H} was determined in the presence of the $B^{z(B)+}$ ions. Moreover, $\Delta E_B{}^x$ is highest at the experimental condition $[Na^+]$ = 3 M, constant.

These are *the smallest possible systematic errors which appear in the total cell emf during the determination of E_{0B} and E_{0H}, and not 0.01 mV.* These should be considered as the levels of uncertainties in the curve-fitting treatment of emf data by a computer program, if we did not correct for them before.

(7) *The estimation of the of the systematic errors in the formation constants*, $\Delta \log_{10} \beta_{pqr}$, *caused by the use of the conditional constants E_{0B1} and E_{0H1}*, under different experimental conditions, is presented in Tables 2.8 and 2.15.

For Cell B, we obtained:

$$\begin{aligned}\Delta \log_{10} \beta_{\mathrm{pqr}} &= \text{negligible for z(B)} = 2 \text{ at } [\mathrm{Na}^+] = 3\,\mathrm{M}, \text{ constant}, \\ &< [\mathrm{ClO}_4^-] = 3\,\mathrm{M}, \text{ constant}, < \mathrm{I} = 3\mathrm{M}, \text{ constant}.\end{aligned}$$

For Cell H, we obtained:

$$\begin{aligned}\Delta \log_{10} \beta_{\mathrm{pqr}} &= \text{smallest at } [\mathrm{ClO}_4^-] = 3\,\mathrm{M}, \text{ constant}, \\ &< \mathrm{I} = 3\,\mathrm{M}, \text{ constant}, < [\mathrm{Na}^+] = 3\,\mathrm{M}, \text{ constant}.\end{aligned}$$

These systematic errors depend on $c_B = B_T$ (the total concentration of the metal ions used at the determination of E_{0H} and during the study of the formation of the metal ion complexes). Consequently, *it will look as the formation of polynuclear complexes, which are artefacts.*

(8) *The total potential contribution of the activity coefficients is not constant*, in spite of that the constant ionic medium method was used in the studies (cf. Tables 2.4, 2.5, 2.13, 2.14, 2.17, 2.18). Their contribution to the ideal diffusion potential (E_{Df}) in the slopes is rather constant in one mixture, but is quite different in the other. The term (g/z_J) $\log_{10}$ f_{JTS2} in the slopes is rather high, in general, rather constant in a given mixture and at a given experimental condition, and is quite different in another mixture. This contribution is ~ 0 mV M^{-1} at $[ClO_4^-] = 3$ M, constant, in Mixtures 1 and 2, and at I = 3 M, constant, in Mixture 2.

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Chapter 3
Determination of the Ionic Molar Conductivities in Mixtures of the Strong Electrolytes $HClO_4 + NaClO_4 + Cd(ClO_4)_2$

In order to calculate accurate values for E_{0B} and E_{0H} in emf studies, without systematic errors, as $E_{0B} = E_{0B1} - gd_2c_H$ and $E_{0H} = E_{0H1} - gd_3c_B$, moreover, for the estimation of the systematic errors in the equilibrium constants, $\Delta \log_{10} \beta_{pqr}$, we need to know the values of the ionic molar conductivities. The systematic errors in the equilibrium constants are, if the species $B_pH_qL_r$ are formed:

For Cell B:

$$\Delta \log_{10} \beta_{pqr} = -p\Delta \log_{10} b = p(g\ d_2\ c_H)z_B/g \quad \text{and}$$

for Cell H:

$$\Delta \log_{10} \beta_{pqr} = -q\Delta \log_{10} h = q(g\ d_3\ c_B)/g$$

As is seen, in both cases, the knowledge of the systematic error terms, gd_2c_H and gd_3c_B, is necessary. For the calculation of these functions, we need to know the ionic molar conductivities.

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3.1 Introduction

In these studies, Mixture 1 and Mixture 2 were used as in the emf measurements. The specific conductance of the test solutions, κ, was measured in cm^{-1} ohm^{-1} units = cell constant of the conductivity cell (cm^{-1})/ R (ohm), where R is the measured resistance of the solution in question.

Moreover,

$$10^3\kappa = \Sigma_J \lambda_J / z_J / c_J \tag{3.1}$$

where λ_J denotes the ionic molar conductivity of the ion J is expressed in (S cm^2 mol ion^{-1} $|charge|^{-1}$) . The molar conductivity of electrolyte RX, Λ_{RX}, is expressed

E. Néher-Neumann, *Advanced Potentiometry*,
DOI 10.1007/978-1-4020-9525-2_3,

in (S cm^2 mol^{-1}). These units are generally omitted in the text for simplicity. c_J denotes the concentration of ion J in M. We introduce the following notations:

$$c_A = [Na^+], c_H = [H^+], c_B = [Cd^{2+}], c_Y = [ClO_4^-]$$

The conductivity of the mixtures studied can be given as

$$10^3\kappa = z_B c_B \lambda_B{}^{tr} + c_H \lambda_H{}^{tr} + c_Y \lambda_{Yadd(3)} + c_A \lambda_A \tag{3.2}$$

where tr is trace, the index add(3) denotes λ_Y in the three-component mixture, calculated according to additivity, in terms of the ionic strength fractions, as

$$\begin{aligned}\lambda_{Yadd(3)} = {} & c_A \lambda_Y(C\,M\,AY)/I + c_H \lambda_Y(C\,M\,HY)/I \\ & + [(z_B{}^2 + z_B)/2] c_B \lambda_Y(C/z_B M\,BY_{z(B)})/I\end{aligned} \tag{3.3}$$

where

$$I = C + c_H + (z_B{}^2 + z_B)\ c_B/2, \text{ for } \ c_A = C\text{ M}, \ \text{ constant, using the condition} \tag{3.4}$$

$$c_Y = C + c_H + z_B c_B \tag{3.5}$$

$$\lambda_H(C\,M\,HY) = t_H(C\,M\,HY)\Lambda(C\,M\,HY) \tag{3.6a}$$

$$\lambda_B(C/z_B M\,BY_{z(B)}) = t_B(C/z_B M\,BY_{z(B)})\Lambda(C/z_B M\,BY_{z(B)}) \tag{3.6b}$$

$$\lambda_A(C\,M\,AY) = t_A(C\,M\,AY)\Lambda(C\,M\,AY) \tag{3.6c}$$

In the equations above, t_J stands for the transport number of the ion J and Λ is the molar conductivity of the electrolyte noted in (S cm^2 mol^{-1}).

$10^3\ \kappa$, calculated according to additivity, is

$$10^3\kappa_{add} = c_H \lambda_H(C\,M\,HY) + c_A \lambda_A(C\,M\,AY) + c_Y \lambda_{Yadd(3)} + z_B c_B \lambda_B(C/z_B M\,BY_{z(B)}) \tag{3.7}$$

The ionic molar conductivities were determined from the measured $10^3\ \kappa$ mostly by graphical methods.

3.2 Conductivity Measurements

3.2.1 Conductivity Measurements in Mixtures Where [Na$^+$] = 3 M, Constant [1]

3.2.1.1 Conductivity Measurements in Mixture 1 Where c_B is Varied While c_H is Kept Constant

The Percentage Deviations of Conductivity from Additivity

These deviations have been investigated through the plot of $10^2\ (10^3\kappa - 10^3\kappa_{add})/10^3\kappa$ versus c_B. In these calculations, the approximation t_{Cd} [1.5 M Cd(ClO$_4$)$_2$] $\approx$

t_{Zn} [1.5 M $Zn(ClO_4)_2$] = 0.319 was used, taken from Ref. [2a]. The value of Λ(1.5 M $Cd(ClO_4)_2$] was determined by the author (cf. Section 3.2.1.3.). For the determination of the transport numbers, emf titrations were suggested by the author in Ref. [3].

The plot in question is shown in Fig. 3.1. As is seen, the deviations from additivity are rather small, $\leq 1\%$, and they are negative. They can be described with the help of two straight lines. As the deviations are a linear function of the c_B, they can be interpreted as the result of the presence of the Cd^{2+} ions. Therefore, $\lambda_{Cd}{}^{tr}$ will be smaller than its value in the pure solution of 1.5 M $Cd(ClO_4)_2$ and it changes its value at $c_B \approx 0.090$ M. Moreover, the negative intercept is most probably due to the decrease of λ_H value, compared to λ_H(3 M $HClO_4$).

The Plot of 10^3 κ Versus c_B at $[HClO_4] = 0.025$ M, Constant

This plot is presented in Fig. 3.2. The conductivity of these mixtures is given by Eq. (3.2). The validity of $\lambda_{Yadd(3)}$ was assumed (cf. Eq. (3.3)).

The intercept of this plot is

$$c_H\lambda_H{}^{tr} + c_A\lambda_A + c_Y\lambda_{Yadd(2)} = 169.15 \tag{3.8}$$

at $c_B = 0$ M. This represents the ionic molar conductivity in the two-component system 0.025 M $HClO_4$ + 3 M $NaClO_4$. As these concentrations are kept constant, this mixture is functioning as a constant ionic medium in this system. This mixture will be termed "actual medium". Here, λ_{Na} can be considered as constant, being equal to the value in 3 M $NaClO_4$. The ionic molar conductivity of the $ClO_4{}^-$ ions

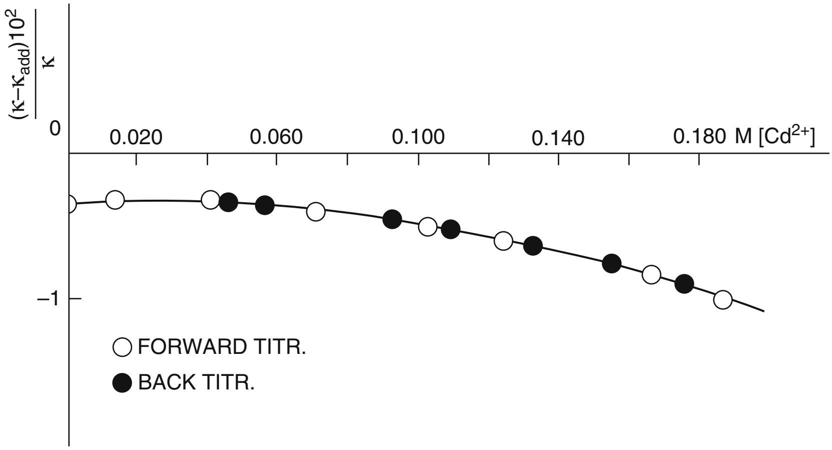

Fig. 3.1 Deviations of the measured conductivity ($10^3\kappa$) from additivity ($10^3\kappa_{add}$), in %, as a function of $[Cd^{2+}]$, in the system 0.025 M $HClO_4$, 3 M $NaClO_4$, $0 \leq [Cd(ClO_4)_2] \leq 0.18$ M at 25.000 ± 0.005°C. Reproduced by permission of the Royal Society of Chemistry from Néher-Neumann E (1998) Acta Chem Scand 52: 873–882 (Fig. 2)

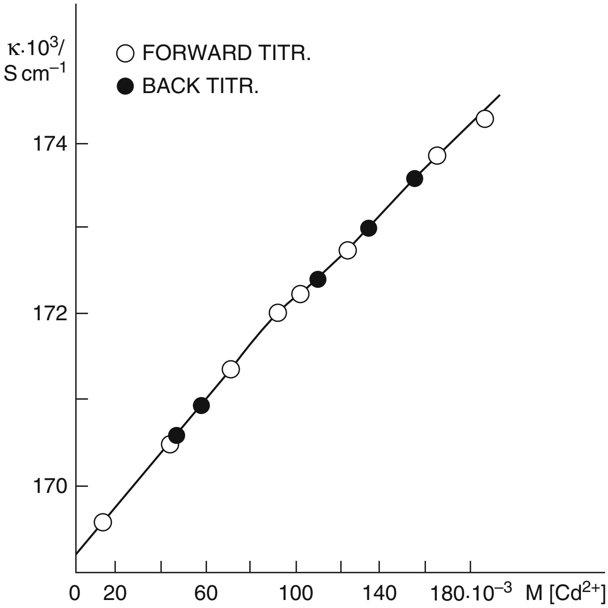

Fig. 3.2 $10^3\kappa$ versus [Cd^{2+}], for the determination of the ionic molar conductivities in the system 0.025 M $HClO_4$, 3 M $NaClO_4$, $0 \leq [Cd(ClO_4)_2] \leq 0.18$ M. (κ = the measured conductivity at 25.000 ± 0.005°C) Reproduced by permission of the Royal Society of Chemistry from Néher-Neumann E (1998) Acta Chem Scand 52: 873–882 (Fig. 3)

in this two-component system, $\lambda_{Yadd(2)} \equiv \lambda_Y{}^{MED}$, can be calculated due to additivity (cf. Eq. (3.3)). Therefore, we have

$$\lambda_A = 0.43 \times 54.60 = 23.48$$

$$\lambda_Y{}^{MED} = 31.19$$

In this case, $\lambda_H{}^{tr}$ can be obtained from the intercept

$$\lambda_{H(R)}{}^{tr} = 170.20 \pm 4.20$$

This value is the result (R) of two identical experiments, where the intercept differed by 0.1%.

The value of $\lambda_H{}^{tr}$ cannot be obtained with a very high accuracy using Eq. (3.8). This can partly depend on the fact that in the calculation, the difference between almost equal numbers was divided by a very small one. Therefore, a possible experimental uncertainty in the position of the intercept will be very much magnified. The result was obtained with an uncertainty of ± 2.46%. Now, only $\lambda_B{}^{tr}$ to be determined.

The Plot of the Deviation of $\lambda_{Cd}{}^{tr}$ from λ_{Cd} [1.5 M Cd(ClO$_4$)$_2$] Versus c_B

In the calculation of the deviation in question, λ_{Cd} [1.5 M Cd(ClO$_4$)$_2$] $= 23.6 \times 0.319 = 7.5$ was used. The deviation is defined as

$$\Delta(\lambda_B{}^{tr}) = 10^3\kappa - c_H\lambda_{H(1)}{}^{tr} - c_A\lambda_A - c_Y\lambda_{Yadd(3)} - z_Bc_B\lambda_B[C/z_B\,M\,BY_{z(B)}] = -z_Bc_Br_1 \tag{3.9}$$

and has been plotted as a function of c_B. Here, those values of λ_A and $\lambda_{H(1)}{}^{tr}$ should be used which have been determined in the previous section. This plot is shown in Fig. 3.3. The deviation, r_1, could be calculated from the slopes. The results are presented in Table 2.2.

We can conclude from these results that the concentration of the Cd^{2+} ions should be ≤ 0.086 M when this system is studied, in order to ensure the constancy of $\lambda_{Cd}{}^{tr}$. It is seen from Fig. 3.2 and Table 2.2 that the individual values of λ_J and the ratios of some ionic molar conductivities, which appear in the slope values determined in Chapter 2, are constant.

The data were also treated with the curve-fitting program MLAB [4]. Eq. (3.10) was fitted to the data using the values $\lambda_B{}^{tr}$, $\lambda_H{}^{tr}$ and λ_A as parameters.

$$F(c_B, c_H) \equiv 10^3\kappa - c_Y\lambda_{Yadd(3)} = z_Bc_B\lambda_B{}^{tr} + c_H\lambda_H{}^{tr} + C\lambda_A \tag{3.10}$$

The results are presented in Table 2.2.

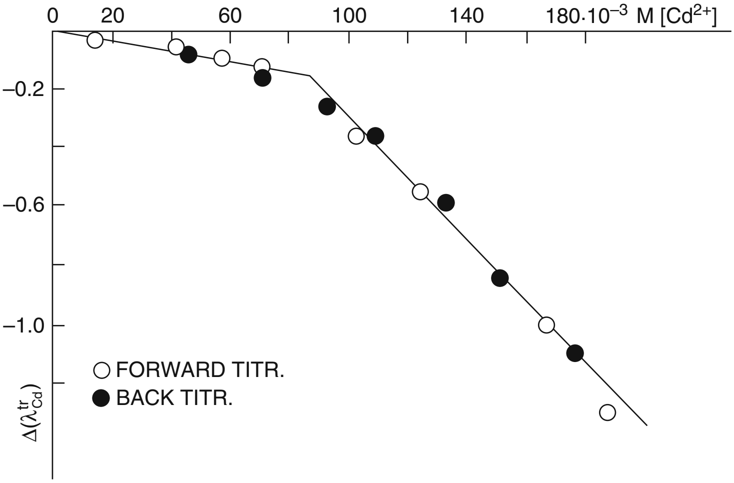

Fig. 3.3 The deviation of $\lambda_{Cd}{}^{tr}$ from its value in 1.5 M Cd(ClO$_4$)$_2$, as a function of [Cd^{2+}], in the system 0.025 M HClO$_4$, 3 M NaClO$_4$, $0 \leq$ [Cd(ClO$_4$)$_2$] ≤ 0.18 M at 25.000 ± 0.005°C. Reproduced by permission of the Royal Society of Chemistry from Néher-Neumann E (1998) Acta Chem Scand 52: 873–882 (Fig. 4)

3.2.1.2 Conductivity Measurements in Mixture 2 Where c_H is Varied While c_B is Kept Constant

The treatment of the data was similar to that used in Section 3.2.1.1.

The Percentage Deviations of Conductivity from Additivity

The deviation function defined in "The Percentage Deviations of Conductivity from Additivity" was plotted as a function of c_H. This plot is shown in Fig. 3.4. The presence of the H^+ ions causes negative deviations from additivity. The deviations are a linear function of c_H. This means that the ionic molar conductivities are either constant or a linear function of c_H.

The Plot of $10^3\kappa$ Versus c_H at $[Cd(ClO_4)_2] = 0.050$ M, Constant

This plot is presented in Fig. 3.5 which is a complete straight line. Mathematically it is described by Eq. (3.2). For this plot, we have

$$\text{The intercept} = c_A\lambda_A + z_B c_B \lambda_B{}^{tr} + c_Y\lambda_{Yadd(2)} = 166.45 \tag{3.11}$$

The intercept represents the properties of the two-component system 0.050 M $Cd(ClO_4)_2$ + 3 M $NaClO_4$. As these concentrations are kept constant, this mixture

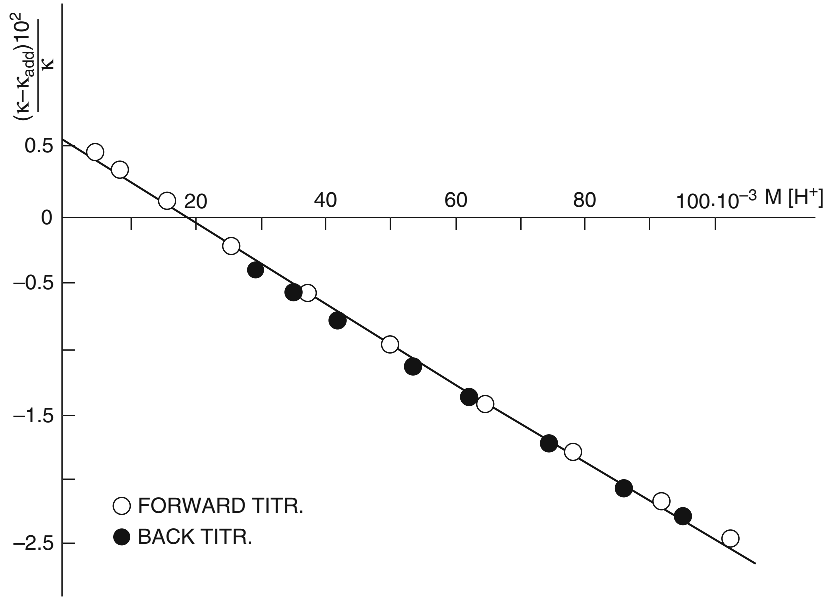

Fig. 3.4 Deviations of the measured conductivity ($10^3\kappa$) from additivity ($10^3\kappa_{add}$), in %, as a function of [H^+], in the system 0.050 M $Cd(ClO_4)_2$, 3 M $NaClO_4$, $0.005 \leq [HClO_4] \leq 0.10$ M at 25.000 ± 0.005°C. Reproduced by permission of the Royal Society of Chemistry from Néher-Neumann E (1998) Acta Chem Scand 52: 873–882 (Fig. 5)

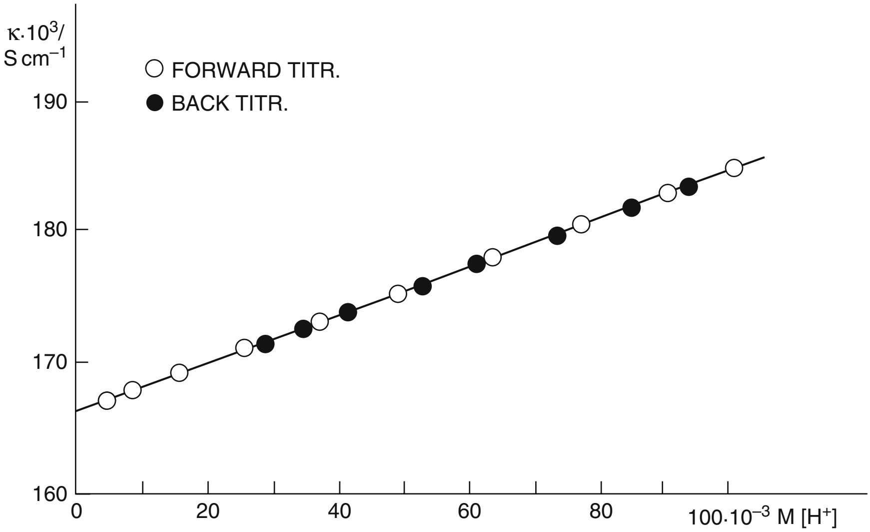

Fig. 3.5 $10^3\kappa$ versus [H$^+$], for the determination of the ionic molar conductivities in the system 0.050 M Cd(ClO$_4$)$_2$, 3 M NaClO$_4$ and $0.005 \leq [HClO_4] \leq 0.10$ M, at 25.000 ± 0.005°C. Reproduced by permission of the Royal Society of Chemistry from Néher-Neumann E (1998) Acta Chem Scand 52: 873–882 (Fig. 6)

can be considered as the actual medium used. Here, λ_A can be considered to have the same value as in 3 M NaClO$_4$ again. $\lambda_{Yadd(2)} = \lambda_Y{}^{MED}$, which can be calculated from Eq. (3.3). Then $\lambda_{Cd}{}^{tr}$ can be obtained from the intercept. Hence, we have:

$$\lambda_{Na} = 23.48, \lambda_Y{}^{MED} = 30.40 \quad \text{and} \quad \lambda_{Cd(R)}{}^{tr} = 18.68 \pm 1.12$$

This corresponds to ±6% uncertainty, which is caused by 0.12% deviation in the position of the intercept of two identical experiments.

Now, $\lambda_H{}^{tr}$ should be estimated.

The Plot of the Deviation of $\lambda_H{}^{tr}$ from λ_H(3 M HClO$_4$) Versus c_H

This deviation is defined as

$$\Delta\lambda_H{}^{tr} = 10^3\kappa - c_A\lambda_A - c_Y\lambda_Y - z_Bc_B\lambda_B - c_H\lambda_H(C\,M\,HY) = \pm c_Hr_2 \qquad (3.12)$$

For the value of λ_H (3 M HClO$_4$), we have: 233.1 × 0.83 = 193.5. Here, those values of λ_{Na} and $\lambda_{Cd(1)}{}^{tr}$ should be used which have been determined in the previous section. For the ionic molar conductivity of the ClO$_4{}^-$ ions, both $\lambda_Y{}^{MED}$, constant, and $\lambda_{Yadd(3)}$, varying and calculated according to Eq. (3.3), have been tried.

The plot in question, using $\lambda_Y{}^{MED}$, is presented in Fig. 3.6. The slope of this straight line is identical with the deviation r_2:

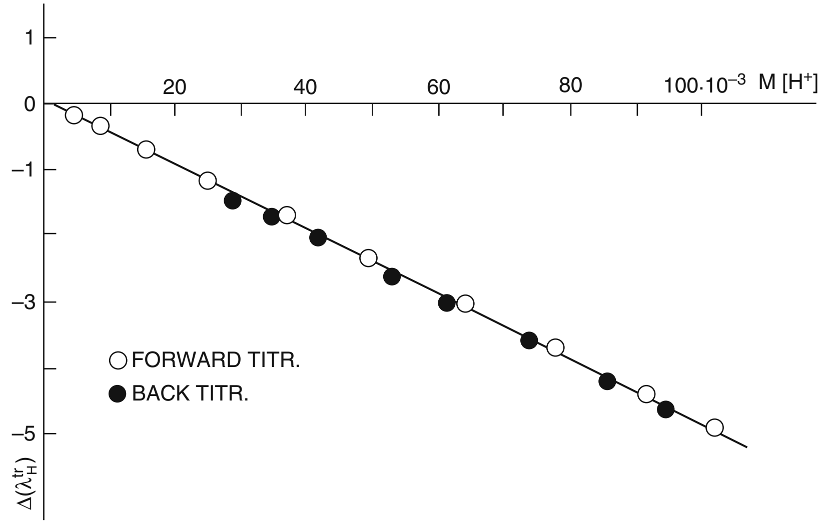

Fig. 3.6 The deviation of $\lambda_H{}^{tr}$ from its value in 3 M $HClO_4$, as a function of $[H^+]$, in the system 0.050 M $Cd(ClO_4)_2$, 3 M $NaClO_4$, $0.005 \leq [HClO_4] \leq 0.10$ M at 25.000 ± 0.005°C. Reproduced by permission of the Royal Society of Chemistry from Néher-Neumann E (1998) Acta Chem Scand 52: 873–882 (Fig. 7)

$r_2 = -48.41$ and $\lambda_H{}^{tr} = 193.5 - 48.41 = 145.0$. These results have been refined by using the curve-fitting computer program MLAB [4]. Substituting the concentration condition

$$c_Y = z_B c_B + c_A + c_H \tag{3.13}$$

into Eq. (3.2), we obtain, omitting the index MED,

$$10^3\kappa = z_B c_B(\lambda_B{}^{tr} + \lambda_Y) + c_H(\lambda_H{}^{tr} + \lambda_Y) + c_A(\lambda_A + \lambda_Y) \tag{3.14}$$

with

$$\text{the slope} = \lambda_H{}^{tr} + \lambda_Y = 177.0 \tag{3.15}$$

Eq. (3.14) was fitted to the data by adjusting $\lambda_H{}^{tr}$, λ_Y, $\lambda_B{}^{tr}$ and λ_A as parameters. The earlier results have been used as start values. The experimental slope (cf. Eq. (3.15)) was given as a condition "constraints" in the calculation. The results are presented in Table 3.1.

The same plot can also be investigated using the assumption that the ionic molar conductivity of the perchlorate ions can be described by $\lambda_{Yadd(3)}$, valid for the three-component system and calculated according to Eq. (3.3). In this case, the results given in Table 2.6 have been obtained. The data were also treated with the

Table 3.1 Survey of the values for the ionic molar conductivities in S cm^2 (mol ion)$^{-1}$ |charge|$^{-1}$, valid in the mixtures of 3.00 M $NaClO_4$, 0.050 M $Cd(ClO_4)_2$, $0.0046 \leq [HClO_4] \leq 0.100$ M at 25.000 ± 0.005°C. Presentation of the molar conductivities Λ_{CdY2}, Λ_{HY} and Λ_{NaY}, moreover, t_Y and t_A which appear in the potential functions. Eq. (26 b) in Ref. [1] was fitted to the experimental data using the program MLAB [4]. The validity of $\lambda_Y{}^{MED}$ was assumed, denoted λ_Y here. [Na$^+$] = 3.00 M, is kept constant

$\lambda_H{}^{tr} = 146.60$	$\Lambda_{CdY}{}^2 = \lambda_{Cd}{}^{tr} + \lambda_Y = 47.83$
$\lambda_{Na} = 23.48$	$\Lambda_{NaY} = \lambda_{Na} + \lambda_Y = 53.88$
$\lambda_Y = 30.39_8$	$t_Y = \dfrac{\lambda_Y}{\lambda_{Na} + \lambda_Y} = 0.56$
$\lambda_{Cd}{}^{tr} = 17.43$	
$\Lambda_{HY} = \lambda_H{}^{tr} + \lambda_Y = 177.0$	$t_{Na} = \dfrac{\lambda_{Na}}{\lambda_{Na} + \lambda_Y} = 0.43$

Source: Reproduced by permission of the Royal Society of Chemistry from Néher-Neumann E (1998) Acta Chem Scand 52: 873–882 (Table 6).

curve-fitting computer program MLAB [4]. Eq. (3.10) was fitted to the data using the values $\lambda_B{}^{tr}$, $\lambda_H{}^{tr}$ and λ_A as parameters. The results are shown in Table 2.6.

3.2.1.3 Conductivity Measurements in Mixture 3 Where Both c_B and c_H Are Varied

Conductivity measurements were carried out in Mixture 3 where both the concentrations c_B and c_H were varied equally in the range 0 – 0.110 M, using $NaClO_4$ ionic medium at [Na$^+$] = 3 M constant. The measured conductivity data, $10^3\kappa$, could be interpreted only with the help of a curve-fitting computer program, e.g. MLAB [4]. Eq. (3.10) was fitted to the data. The results given below have been obtained.

For $0 \leq [Cd(ClO_4)_2] \leq 0.060$ M:

$$\lambda_{Cd}{}^{tr} = 16.11,\ \lambda_H{}^{tr} = 122.72,\ \lambda_{Na} = 23.97$$

For $0.060 \leq [Cd(ClO_4)_2] \leq 0.109$ M:

$$\lambda_{Cd}{}^{tr} = 9.21,\ \lambda_H{}^{tr} = 117.52,\ \lambda_{Na} = 24.32$$

3.2.1.4 Conclusion Which Can Be Obtained from Tables 2.2 and 3.1

We can see from these tables that the ionic molar conductivities in Mixture 1 and Mixture 2 are rather constant. This constancy is valid for a given set of experimental conditions. The individual values of $\lambda_{Cd}{}^{tr}$ and $\lambda_H{}^{tr}$ differ greatly in the different mixtures. They cannot be interchanged. In the slope functions SL(B, c_B), SL(B, c_H) and SL(H, c_H), SL(H, c_B) *ratios of the ionic molar conductivities* appear. As we can see from Tables 2.2 and 3.1, these ratios are rather constant. The uncertainty of these values, due to the slight change in $\lambda_{\mathrm{Yadd}(3)}$ with composition, does not exceed the uncertainty of the transport numbers and molar conductivities of the $NaClO_4$ and $HClO_4$ solutions, obtained from separate experiments [5, 6], cf. Tables 2.10 and 2.11.

3.2.1.5 Measurement of the Molar Conductivity of Concentrated Aqueous $Cd(ClO_4)_2$ Solutions

In order to be able to calculate the deviations of conductivity from additivity in the mixtures studied, we must know the molar conductivity and the transport numbers of the pure components. Therefore, conductivity measurements have been carried out in aqueous solutions of $Cd(ClO_4)_2$, in the concentration range 0.76–1.5 M at $[H^+] = 8.891 \times 10^{-3}$ M, constant.

The conductivity of the test solution can be given as

$$10^3\kappa = z_B c_B \lambda_B + c_Y \lambda_Y + c_H \lambda_H \tag{3.16}$$

Introducing the concentration condition

$$c_Y = z_B c_B + c_H \tag{3.17}$$

we obtain

$$10^3\kappa = z_B c_B(\lambda_B + \lambda_Y) + c_H(\lambda_H + \lambda_Y) \tag{3.18}$$

Plotting 10^3 κ versus c_B, $(\lambda_{Cd} + \lambda_Y)$ can be calculated from the slope. This plot is presented in Fig. 3.7. The function obtained could be divided into three regions, each

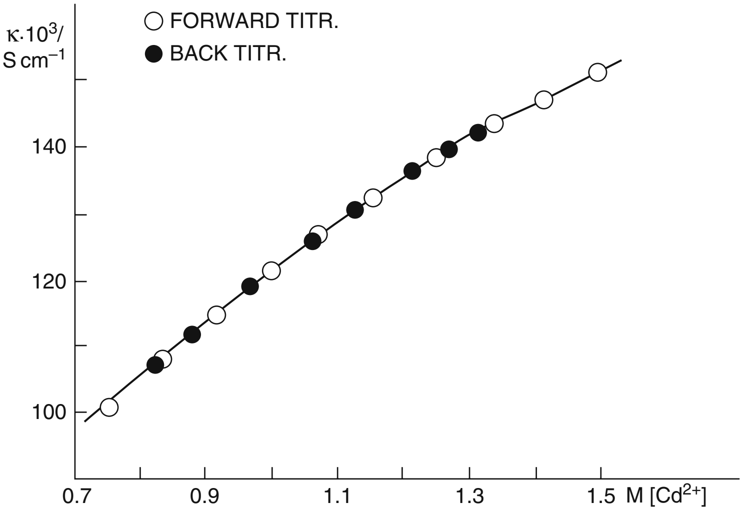

Fig. 3.7 Determination of the molar conductivity of the aqeous solutions of $Cd(ClO_4)_2$, Λ $Cd(ClO_4)_2$, in the concentration range $0.75 \leq [Cd(ClO_4)_2] \leq 1.54$ M at $[HClO_4] = 8.891.10^{-3}$ M, constant, and 25.000 ± 0.005°C. Reproduced by permission of the Royal Society of Chemistry from Néher-Neumann E (1998) Acta Chem Scand 52: 873–882 (Fig. 1)

Table 3.2 Molar conductivity of the aqeous solutions of pure $Cd(ClO_4)_2$ in the concentration range 0.75–1.5 M

$Cd(ClO_4)_2$ + 0.008891 $HClO_4$/M	$\Lambda Cd(ClO_4)_2$/S cm^2 mol^{-1}
0.75–1.03	41.1
1.03–1.29	32.3
1.29–1.50	23.6

Source: Reproduced by permission of the Royal Society of Chemistry from Néher-Neumann E (1998) Acta Chem Scand 52: 873-882 (Table 3).

of them could be described by a straight line. The results are given in Table 3.2. As is seen, we could obtain the quantity $\Lambda = (\lambda_{Cd} + \lambda_Y)$ accurately. In these solutions, the conductivity of the ClO_4^- ions can slightly be influenced by the presence of $HClO_4$ at a constant level. This can be estimated as follows.

In these solutions, λ_Y can be calculated according to additivity, in terms of the ionic strength fractions. The ionic strength is

$$I = c_H + c_B(z_B^2 + z_B)/2 \tag{3.19}$$

and therefore,

$$\lambda_Y = [(z_B^2 + z_B)/2]c_B\lambda_Y(BY_{z(B)})/I + c_H\lambda_Y(HY)/I \tag{3.20}$$

where the values of λ_Y (component) refer to the ionic molar conductivity of the Y^- ions in the pure solution of the components of the mixture in question, at the actual level of $[Y^-]_{total}$.

The order of magnitude of the last term in the previous equation was estimated at 0.75 and 1.5 M concentrations of the Cd^{2+} ions, using the values λ_Y (1 M HY) $= 329.3 \times 0.15 = 51.0$ and λ_Y (3 M HY) $= 233.1 \times 0.17 = 39.6$. The result is $\lambda_Y(HClO_4)[H^+]/ I = 0.20$ and 0.08, respectively. The molar conductivity (Λ) of $HClO_4$ at 1 M and 3 M levels and the corresponding transport numbers were taken from Tables 2.10 and 2.11.

As is seen, the first decimal place of the value $(\lambda_{Cd} + \lambda_Y) = \Lambda$ is influenced by the presence of 8.891×10^{-3} M $HClO_4$ in the solutions studied. If we give the results with one decimal place accuracy, no further correction is necessary. If higher accuracy is required, we should make the plot $10^3\,\kappa - c_H\,(\lambda_H + \lambda_Y)$ versus c_B.

3.2.2 Conductivity Measurements in Mixtures Where $[ClO_4^-] = 3$ M, Constant [7]

The ionic strength in these mixtures can be given, with the concentration condition

$$c_Y = z_Bc_B + c_H + c_A, \text{ as}$$

$$I = c_H + c_A + c_B(z_B^2 + z_B)/2 \tag{3.21}$$

3.2.2.1 Conductivity Measurements in Mixture 2 Where c_H Is Varied While c_B Is Kept Constant

The Percentage Deviations of the Conductivity from Additivity

These deviations have been investigated through a plot of 10^2 (10^3 κ – 10^3 κ_{add})/$10^3\kappa$ versus c_H (cf. Eq. (3.7). This plot is given in Fig. 3.8.

As is seen from this figure, the deviation function is linear, positive and almost constant. The deviations are small, <2.5 %. As the deviations, here, are practically of the same magnitude in the whole range of c_H studied, it means that they appear due to the presence of either the Cd^{2+} or the ClO_4^- ions, as the concentration of these ions is constant. Owing to the experiences gained in this laboratory during the study of the conductivity of the systems $HClO_4$ – $NaClO_4$ or $LiClO_4$ and HCl – NaCl and the authors' investigations made on the $Cd(ClO_4)_2$ – $HClO_4$ – $NaClO_4$ system, we can assume, first, that the ionic molar conductivity of the common anion follows the additivity. This can mean that the Cd^{2+} ions seem to be responsible for the noticed deviations, and $\lambda_{Cd}{}^{tr}$ is larger, here, than in 1.5 M $Cd(ClO_4)_2$. The linearity of the deviation function means that the ionic molar conductivities are either constant or a linear function of the composition, in this system.

The Plot of 10^3 κ Versus [H $^+$] at [$Cd(ClO_{4)2}$] = 0.050 M, Constant

This plot is presented in Fig. 3.9. The basic equation for this system is given by Eq. (3.2). For the values of $\lambda_{Yadd(3)}$, we obtained, according to additivity (cf. Eq. (3.3)) for the three-component mixture

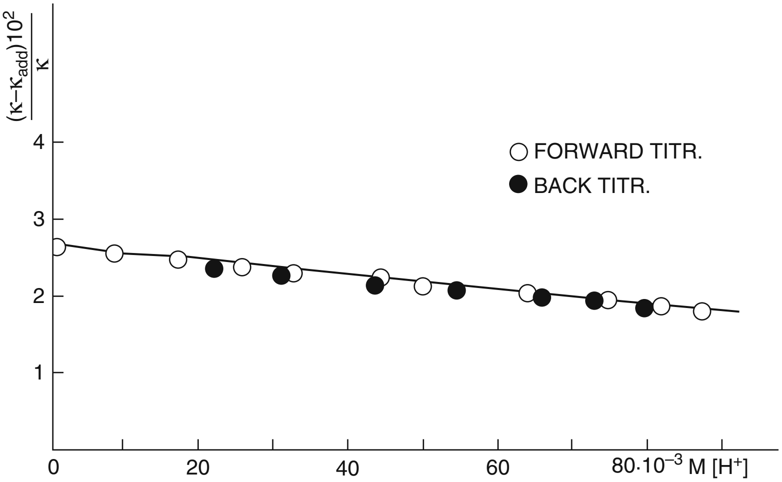

Fig. 3.8 The percentage deviation of the measured conductivity (10^3 κ) from additivity ($10^3\kappa_{add}$) as a function of [H^+], in the system 0.050 M $Cd(ClO_4)_2$, $0.002 \leq [HClO_4] \leq 0.1$ M, X M $NaClO_4$, using [ClO_4^-] = 3 M, constant, at 25.000 ± 0.005°C. Reproduced by permission of the Royal Society of Chemistry from Néher-Neumann E (1998) Acta Chem Scand 52: 1075–1080 (Fig. 1)

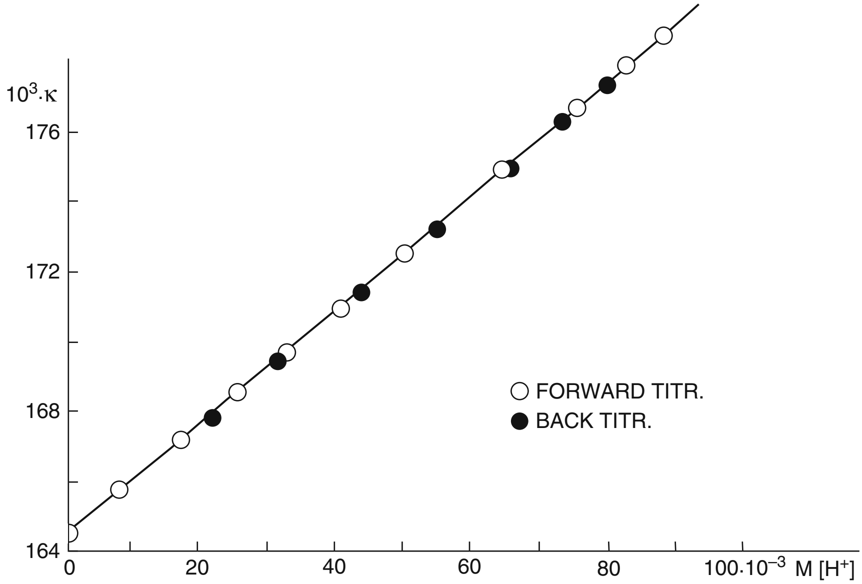

Fig. 3.9 $10^3\kappa$ versus $[H^+]$, for the determination of the ionic molar conductivities in the system 0.050 M $Cd(ClO_4)_2$, $0.002 \leq [HClO_4] \leq 0.10$ M, X M $NaClO_4$, using $[ClO_4^-] = 3$ M, constant, at 25.000 ± 0.005°C. Reproduced by permission of the Royal Society of Chemistry from Néher-Neumann E (1998) Acta Chem Scand 52: 1075–1080 (Fig. 2)

$$\lambda_{Yadd(3)} = 30.38 + 2.76\,c_H \cong 30.38 = \lambda_{Yadd(2)} \tag{3.22}$$

Here, the constant value of 30.38 represents the ionic molar conductivity of the perchlorate ions in the two-component system 0.050 M $Cd(ClO_4)_2$ constant and 2.900 M $NaClO_4$ ($=[Na^+]_2$) at $c_H = 0$. As the concentration of the ClO_4^- ions is constant and that of the H^+ ions is low ($c_H \leq 0.1$ M), it can be assumed that $\lambda_{Yadd(3)}$ is constant and is equal to $\lambda_{Yadd(2)}$. Inserting the concentration condition

$$c_Y = z_B c_B + c_H + c_A \tag{3.23}$$

into Eq. (3.2), we obtain

$$10^3\kappa = z_B c_B({\lambda_B}^{tr} + \lambda_{Yadd(2)}) + c_H({\lambda_H}^{tr} + \lambda_{Yadd(2)}) + c_A(\lambda_A + \lambda_{Yadd(2)}) \tag{3.24}$$

Hence, *the intercept* of this plot is

$$z_B c_B({\lambda_B}^{tr} + \lambda_{Yadd(2)}) + [Na^+]_2(\lambda_A + \lambda_{Yadd(2)}) = 164.30 \tag{3.25}$$

Hence, the first estimated value for ${\lambda_{Cd}}^{tr}$ can be obtained from the intercept:

$${\lambda_{Cd(1)}}^{tr} = 50.7$$

This value is much higher than λ_{Cd} in 1.5 M $Cd(ClO_4)_2$: $0.319 \times 23.6 = 7.5$.

The value of $\lambda_{Cd}{}^{tr}$ cannot be obtained with a high accuracy, due to a small uncertainty in the position of the intercept. This can be estimated, comparing the values of $10^3\ \kappa$ in the common points in Mixture 1 and Mixture 2. Namely, in $[Cd(ClO_4)_2] = 0.050$ M, and $[HClO_4] = 0.025$ M, which should be equal.

For these points, we have

$$10^3\kappa = 167.97 \text{ in Mixture 1 and}$$

$$10^3\kappa = 168.51 \text{ in Mixture 2.}$$

These numbers show that there is a 0.54 unit uncertainty in the position of the intercept, which denotes 0.3% deviation in the conductivity. Repeating the calculation with $10^3\ \kappa = 164.30{-}0.54 = 163.76$, we obtain,

$$\lambda_{Cd(2)} = 45.28.$$

Taking the average value as the result (denoted R), we have

$$\lambda_{Cd(R)} = 48.0 \pm 2.7$$

As is seen, this result includes ± 5.6% uncertainty.

For the estimation of $\lambda_H{}^{tr}$, we can use the value of the *slope* in question. For this purpose, Eq. (3.2) must be redefined by inserting into it the special concentration condition valid in this cell:

$$[A^+]_3 = C - z_Bc_B - c_H \tag{3.26}$$

Therefore, we have

$$10^3\kappa = z_Bc_B(\lambda_B{}^{tr} - \lambda_A) + c_H(\lambda_H{}^{tr} - \lambda_A) + C\lambda_A + C\lambda_{Yadd(3)} \tag{3.27}$$

Assuming that the constant value of $\lambda_{Yadd\ (2)}$ is valid in this system, the slope of the plot of $10^3\ \kappa$ versus c_H, at constant c_B, is

$$\lambda_H{}^{tr} - \lambda_A = 166.25 \tag{3.28}$$

This difference is very accurate. Hence, we can calculate

$$\lambda_H{}^{tr} = 166.25 + 23.48 = 189.73$$

Eq. (3.28) is not valid if λ_{Yadd} is not constant. The same value can also be obtained for $\lambda_H{}^{tr}$ through the interpretation of the plot $\Delta(\lambda_H{}^{tr})$ versus c_H (cf. Eq. (3.12)), if the constant value of $\lambda_{Yadd(2)}$ is used for the ionic molar conductivity of the perchlorate ions. This assumption, in this mixture, can be verified by the shape of the deviation function, shown in Fig. 3.8. Here, the function has essentially the same values through the entire $[H^+]$ range studied. Hence, we can assume that λ_A, λ_Y and $\lambda_{Cd}{}^{tr}$ have the same values as at $c_H = 0$ M. The negative sign of the almost flat slope we have shows that $\lambda_H{}^{tr}$ is slightly lower than in 3 M $HClO_4$: $\lambda_H{}^{tr}$ (3 M $HClO_4$) $= 233.1 \times 0.83 = 193.5$ (cf. Tables 2.10 and 2.11).

3.2.2.2 Conductivity Measurements in Mixture 1 Where c_B Is Varied While c_H Is Kept Constant

The Percentage Deviations of the Conductivity from Additivity

These deviations versus c_B are shown in Fig. 3.10. As is seen, the deviations are positive, a linear function of the concentration of the Cd^{2+} ions and are <4% in the concentration range studied.

In principle, both the Cd^{2+} and the perchlorate ions can be responsible for the noticed deviations in the range of c_B studied, as both $\lambda_{Cd}{}^{tr}$ and $\lambda_{Yadd(3)}$ are dependent on $[Cd^{2+}]$. However, on considering the data, given as a plot $10^3\,\kappa$ versus $[Cd^{2+}]$ in Fig. 3.11, it is seen that the measured conductivity decreases with the concentration of the Cd^{2+} ions. This is an unexpected result and it allows us to assume that the positive deviations of Fig. 3.10 are most probably due to the increase of $\lambda_{Yadd(3)}$.

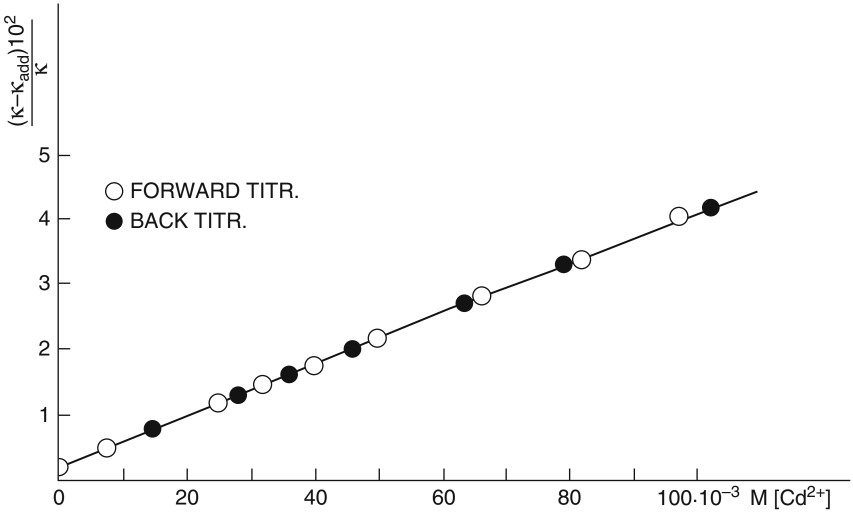

Fig. 3.10 The deviation of the measured conductivity ($10^3\kappa$) from additivity ($10^3\kappa_{add}$), in %, as a function of $[Cd^{2+}]$, in the system 0.025 M $HClO_4$, $0 \leq [Cd(ClO_4)_2] \leq 0.1$ M, X M $NaClO_4$, using $[ClO_4^-] = 3$ M, constant, at 25.000 ± 0.005°C. Reproduced by permission of the Royal Society of Chemistry from Néher-Neumann E (1998) Acta Chem Scand 52: 1075–1080 (Fig. 3)

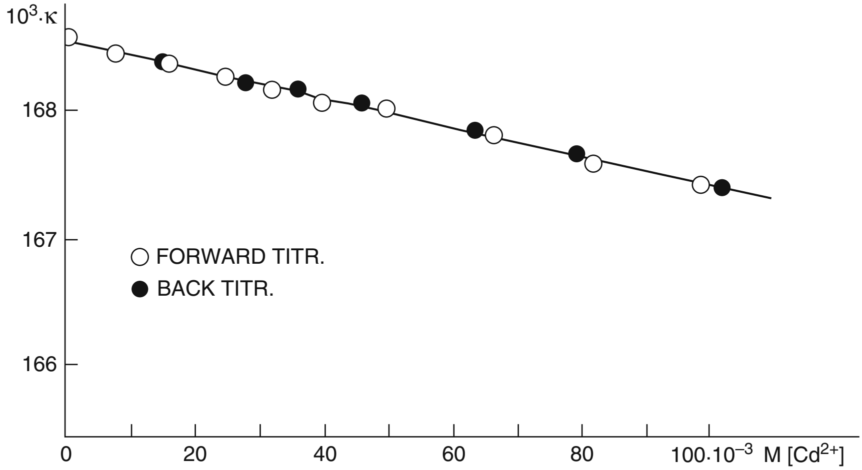

Fig. 3.11 $10^3\kappa$ versus [Cd^{2+}], for the determination of the ionic molar conductivities in the system 0.025 M $HClO_4$, $0 \leq [Cd(ClO_4)_2] \leq 0.1$ M, X M $NaClO_4$, using $[ClO_4^-] = 3$ M, constant, at 25.000 ± 0.005°C. Reproduced by permission of the Royal Society of Chemistry from Néher-Neumann E (1998) Acta Chem Scand 52: 1075–1080 (Fig. 4)

Such deviations have not been observed in the other systems studied (cf. Section 3.2.1. and Ref. [8]). The linearity of the deviation function shows that the ionic molar conductivities are either constant or a linear function of c_B.

The Plot of 10^3 κ Versus c_B at $c_H = 0.025$ M, Constant

This plot is presented in Fig. 3.11, which is a complete straight line. According to Eq. (3.2), the *intercept* of this plot is

$$c_H(\lambda_H{}^{tr} + \lambda_{Yadd(2)}{}') + c_A(\lambda_A + \lambda_{Yadd(2)}{}') = 168.55 \tag{3.29}$$

The intercept represents the conductivity of the two-component system: 0.025 M $HClO_4$, constant, and 2.975 M $NaClO_4$. This value can be used for the estimation of $\lambda_H{}^{tr}$. We can assume, again, that λ_{Na} has the same value as in 3 M $NaClO_4$. $\lambda_{Yadd(2)}{}'$ can be calculated due to the additivity, as before. Therefore, we have for this system

$$\lambda_{Na} = 23.48,\ \lambda_{Yadd(2)}{}' = 31.19,\ \lambda_{H(1)} = 205.1$$

Taking into account the 0.54 unit uncertainty in the position of the intercept, with 168.55 + 0.54 = 169.09, an alternative value can be calculated:

$$\lambda_{H(2)}{}^{tr} = 226.80$$

Taking the average value as the result,

$$\lambda_{\mathrm{H(R)}}{}^{\mathrm{tr}} = 215.9 \pm 10.9$$

This result includes ±5.0% uncertainty.

For the estimation of $\lambda_{\mathrm{Cd}}{}^{\mathrm{tr}}$, *the slope* of the plot in question can be used. On the basis of the deviation function presented before, we shall assume that $\lambda_{\mathrm{Yadd(3)}}$ is a linear function of the concentration of the $\mathrm{Cd^{2+}}$ ions and can be described as

$$\lambda_{\mathrm{Yadd(3)}} = 31.19 \pm f_1 z_B c_B \tag{3.30}$$

Inserting this expression into Eq. (3.27), we obtain

$$10^3\kappa = z_B c_B(\lambda_B{}^{\mathrm{tr}} - \lambda_A \pm Cf_1) + C\lambda_A + c_H(\lambda_H{}^{\mathrm{tr}} - \lambda_A) + C31.19 \tag{3.31}$$

Hence, *the slope* of the plot $10^3\,\kappa$ versus c_B, at $c_H = 0.025$ M, constant, is

$$z_B(\lambda_B{}^{\mathrm{tr}} - \lambda_A \pm Cf_1) = -11.60 \tag{3.32}$$

As is seen, now we have two unknown quantities, $\lambda_B{}^{\mathrm{tr}}$ and f_1, and only one equation. For the determination of these quantities, we can use Eq. (3.32) and the experimental slope function $\mathrm{SL(H,}\ c_B)_2$, as defined by Eq. (2.37) in Chapter 2, which was also determined in this mixture by emf measurements.

The slope of the plot $E_H - g\log_{10} c_H$ versus c_B, at $c_H = 0.025$ M, constant, was found to be in a forward and back titration

$$\mathrm{SL(H,}\ c_B)_{2,\mathrm{exp}} = 18.4\,\mathrm{mV\,M^{-1}\,Cd^{2+}}$$

as shown in Table 2.13. Here, exp denotes experimental. The estimation of $\lambda_{\mathrm{Cd}}{}^{\mathrm{tr}}$ and f_1 was done as follows.

As a first step, we assume that $\lambda_{\mathrm{Yadd(3)}}$ decreases with an increase in c_{Cd}. On the basis of the definition of $\lambda_{\mathrm{Yadd(3)}}$ (cf. Eq. (3.3), we can write

$$\lambda_{\mathrm{Yadd(3)}} = 31.19 - f_1 z_B c_B \tag{3.33}$$

$$= 31.19 - [(z_B + 1)/2] z_B \lambda_Y (C/z_B\,\mathrm{M\,BY}_{z(B)}) c_B/I \tag{3.34a}$$

$$= 31.19 - 7.25 \times 2[\mathrm{Cd^{2+}}] \tag{3.34b}$$

at $c_{\mathrm{Cd}} = 0.1$ M. The value $f_1 = 7.25$ results in

$$\lambda_{\mathrm{Yadd(3)}} = 29.74$$

$$\lambda_{\mathrm{Cd}}{}^{\mathrm{tr}} = 39.43$$

using Eq. (3.32) for the calculation. With these ionic molar conductivities, the slope function

$$\mathrm{SL(H,\ c_B)_2} = 11.8\,\mathrm{mV\,M^{-1}\,Cd^{2+}}$$

can be calculated from Eqs. (2.37) and (2.28) at $c_{Cd} = 0.1$ M. As is seen, this slope value differs very much from the experimental one. It seems that the conclusion of the deviation function is valid, namely that the deviations are positive in this system.

As a second step, it was assumed that the equation

$$\lambda_{Yadd(3)} = 31.19 + f_1 z_B c_B \tag{3.35}$$

describes correctly the ionic molar conductivity of the ClO_4^- ions. This means that the positive sign is valid in Eqs. (3.30) and (3.32). Then several values were assumed for $\lambda_{Cd}{}^{tr}$, and the corresponding f_1 values were calculated from Eq. (3.32). With these values of $\lambda_{Cd}{}^{tr}$ and $\lambda_{Yadd(3)}$, the corresponding slope values, SL(H, $c_B)_2$, were calculated at $c_B = 0.1$ M, using Eqs. (2.37) and (2.28, as $d_3 = d_1$), and were compared with the experimental one, as shown in Table 3.3. As is seen, assumption (c) gives the correct value. It means that

$$\lambda_{Cd}{}^{tr} = 0, \quad f_1 = 5.89, \quad \lambda_{Yadd(3)} = 32.37, \quad t_Y = 0.58$$

in this mixture. This is a very unusual result. The concentration condition $[ClO_4^-] =$ 3 M, constant, results in such a strong retardation of the Cd^{2+} ions in this mixture that they do not move at all to the anode. This result is consistent with the plot of $10^3\kappa$ versus c_B at $c_H = 0.025$ M, constant (cf. Fig. 3.11). In this Figure, the conductivity is decreasing, while the concentration of the Cd^{2+} ions is changing in the range 0 – 0.1 M. This can happen only if the Cd^{2+} ions do not contribute at all to the value of $10^3\kappa$.

In order to see the effect of the slight change of $\lambda_{Yadd(3)}$ with c_B on the value of the slope function, SL(H, $c_B)_2$ was calculated at $c_B = 0.050$ M also. The result is

$$\lambda_{Cd}{}^{tr} = 0, \quad \lambda_{Yadd(3)} = 31.78, \quad t_Y = 0.57, \quad \mathrm{SL(H,\ c_B)_2} = 18.17\,\mathrm{mV\,M^{-1}\,Cd^{2+}}$$

Table 3.3 Estimation of the value $\lambda_{Cd}{}^{tr}$ in Mixture 1

Assumption	$\lambda_{Cd}{}^{tr}$	f_1	SL(H,$c_B)_{calc.}$ / mV/ M Cd^{2+}
a	5.00	4.22	17.41
b	1.00	5.56	18.03
c	0	5.89	18.18

Note: Here, calc. denotes calculated.

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As is seen, we obtain the same result as at $c_B = 0.1$ M, because the ratios of the ionic molar conductivities in Eqs. (2.37) and (2.28) are constant, as was also noticed earlier (cf. Tables 2.2 and 2.6).

All ionic molar conductivities, which have been determined in this chapter, are collected in Table 2.12.

3.2.2.3 Conductivity Measurements in Mixture 3 Where Both c_B and c_H Are Varied

In this case, the measured conductivity data, $10^3\kappa$, can be interpreted in terms of the ionic molar conductivities only with the help of a curve-fitting computer program, e.g. MLAB [4]. In order to establish a suitable theoretical function which can be fitted to the data, we can assume, again, that λ_{Na} is constant and equal to its value in C M $NaClO_4$. Moreover, $\lambda_{Cd}{}^{tr}$ and $\lambda_{Yadd(3)}$ can be defined in general, as follows:

$$\lambda_B{}^{tr} = f_2 - f_3\,c_B \tag{3.36}$$

$$\lambda_{Yadd(3)} = \lambda_Y{}^0 - f_4\,c_B \tag{3.37}$$

where

$$\lambda_Y{}^0 = t_Y(C\,M\,AY)\Lambda(C\,M\,AY) \tag{3.38}$$

Hence, we can transform the data, on the basis of Eq. (3.2), to form the experimental function $F_{exp} = 10^3\,\kappa - c_A\,\lambda_A$. Then for the calculated one, we have

$$F_{calc} = z_B\,c_B(f_2 - f_3\,c_B) + c_H\lambda_H{}^{tr} + c_Y(\lambda_Y{}^0 - f_4\,c_B) \tag{3.39}$$

At the fitting, the four unknown parameters: f_2, f_3, f_4 and $\lambda_H{}^{tr}$ should be adjusted. As a starting value for f_2, we can take the value $\lambda_B{}^0$, valid in C/ z_B M $BY_{z(B)}$ solution:

$$\lambda_B^0 = t_B(C/z_B\,M\,BY_{z(B)})\Lambda(C/z_B\,M\,BY_{z(B)}) \tag{3.40}$$

For the calculation of $\lambda_{Cd}{}^0$, the value of $\Lambda[Cd(ClO_4)_2]$ was measured by the author in a broad concentration range (cf. Table 3.2). The transport number t_{Cd} can be determined with the help of an emf cell, as is described in Ref. [3]. Similarly, as a starting value for $\lambda_H{}^{tr}$, we can take that which is valid in 3 M $HClO_4$ (cf. Tables 2.10 and 2.11), Refs. [5, 6].

3.2.3 Conductivity Measurements in Mixtures Where I = C M, Constant [8]

Solutions, with this experimental condition, were prepared as it was discussed in Section 2.3. We measure $10^3\kappa$. The ionic strength in these mixtures can be given, with the concentration condition $c_Y = z_B\, c_B + c_H + c_A$, as

$$I = c_H + c_A + c_B(z_B^2 + z_B)/2 = C\,M \tag{3.41}$$

Moreover, for the ion concentration c_A and c_Y, we have

$$c_A = C - c_H - c_B(z_B^2 + z_B)/2\,M\,AY \tag{3.42}$$

$$c_Y = C + z_B c_B - c_B(z_B^2 + z_B)/2\,M \tag{3.43}$$

3.2.3.1 Conductivity Measurements in Mixture 1 Where c_B Is Varied While c_H Is Kept Constant

The Percentage Deviations of Conductivity from Additivity

These deviations have been investigated as before (cf. “The Percentage Deviations of the Conductivity from Additivity”). The plot in question is shown in Fig. 3.12. As is seen, the deviation function is linear, positive and at around $c_B = 0.1$ M reaches 6%. This mixture shows the highest deviation from additivity among all the mixtures of $HClO_4$ + $Cd(ClO_4)_2$ + $NaClO_4$ which were studied by the author.

The plot of 10^3 κ Versus c_B at $c_H = 0.025$ M, Constant

This plot is shown in Fig. 3.13. The fundamental equation, which is valid here, is

$$10^3\kappa = z_B\, c_B\, \lambda_B{}^{tr} + c_H\, \lambda_H{}^{tr} + c_Y\, \lambda_{Yadd} + c_A\, \lambda_A \tag{3.44}$$

For this plot,

$$\text{the intercept} = c_H\lambda_H{}^{tr} + c_Y\lambda_{Yadd(2)} + \lambda_A[A^+]_2 \tag{3.45}$$

which is equal to 168.88 in experiment 1 and 169.33 in experiment 2. The intercept represents the conductivity of the two-component system 0.025 M $HClO_4$ + 2.975 M $NaClO_4$. First, we can estimate the ionic molar conductivities valid in this system.

For this system, we have

$$\lambda_{Yadd(2)} = c_A\, \lambda_Y(3\,M\,NaClO_4)/I + c_H\lambda_Y(3\,M\,HClO_4)/I = 31.19 \tag{3.46}$$

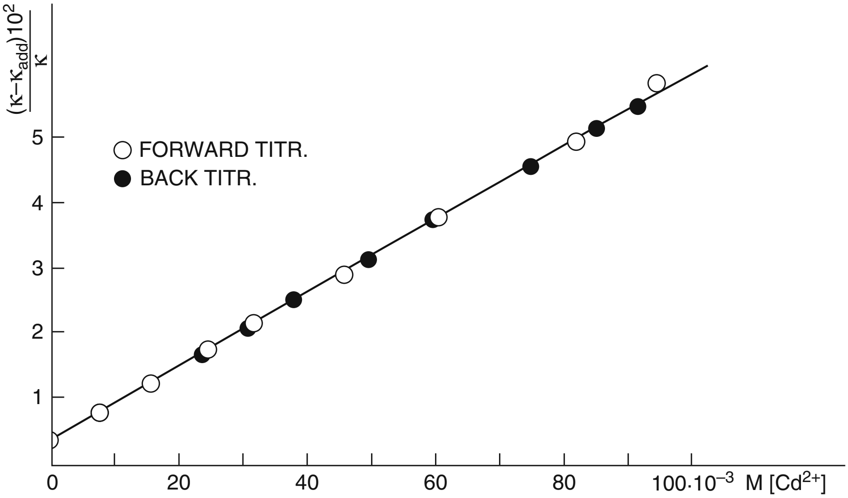

Fig. 3.12 The deviation of the measured conductivity ($10^3\kappa$) from additivity ($10^3\kappa_{add}$), in %, as a function of $[Cd^{2+}]$, in the system 0.025 M $HClO_4$, $0 \leq [Cd(ClO_4)_2] \leq 0.1$ M and X M $NaClO_4$, using I = 3 M, constant, at 25.000 ± 0.005°C. Reproduced by permission of the Royal Society of Chemistry from Néher-Neumann E (1999) Acta Chem Scand 53: 1–6 (Fig. 1)

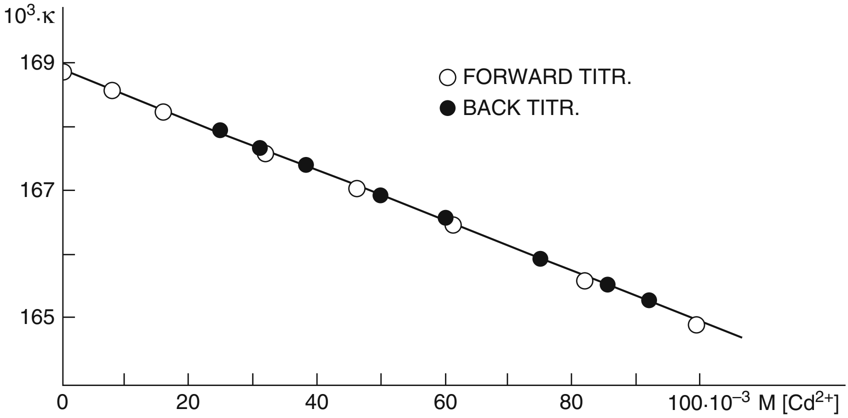

Fig. 3.13 $10^3\kappa$ versus $[Cd^{2+}]$, for the determination of the ionic molar conductivities in the system 0.025 M $HClO_4$, $0 \leq [Cd(ClO_4)_2] \leq 0.1$ M and X M $NaClO_4$, using I = 3 M, constant, at 25.000 ± 0.005°C. Reproduced by permission of the Royal Society of Chemistry from Néher-Neumann E (1999) Acta Chem Scand 53: 1–6 (Fig. 2)

This function can be calculated as in Section 3.1. Hence, $\lambda_H{}^{tr}$ can be obtained from the intercept = 168.88 as

$$\lambda_{H(1)}{}^{tr} = 218.28$$

As is seen, $\lambda_H{}^{tr}$ is slightly higher than its value in 3 M $HClO_4$:

$$\lambda_H(3\,M\,HClO_4) = 0.83 \times 233.1 = 193.5\,(\text{cf. Tables 2.10 and 2.11}).$$

A small uncertainty in the position of the intercept influences strongly the value of $\lambda_H{}^{tr}$, as discussed in "The Plot of 10^3 κ Versus $[H^+]$ at $[Cd(ClO_4)_2] = 0.050$ M, Constant". This can be estimated as follows. We have two experiments (expt) in Mixture 1 and one in Mixture 2. In the common points with the compositions $c_H = 0.025$ M and $c_B = 0.050$ M, the measured 10^3 κ values should be equal. We have

Mixture 1 Mixture 2

$10^3\kappa$ 166.93 (in expt 1)

$10^3\kappa$ 167.27 (in expt 2) 167.20

According to this comparison, –0.27 unit total uncertainty (0.18 %) appears between the corresponding 10^3 κ values for Mixture 1 (expt 1) and Mixture 2, due to some uncertainty in the position of the intercept in Fig. 3.13. Therefore, we choose expt 2 as the correct one (169.30 ± 0.07) for the calculation of the final value of $\lambda_H{}^{tr}$ from Eq. (3.45). Hence, we obtain

$$\lambda_{H(R)}{}^{tr} = 235.08 \pm 1.60$$

The uncertainty in this result is ±0.68%.

The Plot of 10^3 κ – c_Y $\lambda_{Yadd(3)}$ Versus c_B, at $c_H = 0.025$ M, Constant

The value of $\lambda_{Cd}{}^{tr}$ in this system was estimated as follows. Inserting the special concentration condition given by Eq. (3.42) into Eq. (3.44) and forming the difference given in the title, we obtain

$$10^3\kappa - c_y\lambda_{Yadd(3)} = c_B[z_B\lambda_B{}^{tr} - \lambda_A(z_B{}^2 + z_B)/2] + c_H(\lambda_H{}^{tr} - \lambda_A) + C\lambda_A \quad (3.47)$$

According to Section 3.1, we have

$$\begin{aligned}\lambda_{Yadd(3)} = {} & c_A\lambda_Y(3\,M\,NaClO_4)/I + c_H\lambda_Y(3\,M\,HClO_4)/I \\ & + [c_B(z_B^2 + z_B)/2]\lambda_Y[1.5\,M\,Cd(ClO_4)_2]/I\end{aligned} \quad (3.48)$$

The values obtained change linearly with composition, according to

$$\lambda_{Yadd(3)} = 31.19 - 15.03\,[Cd^{2+}] \quad (3.49)$$

The molar conductivity of 1.5 M $Cd(ClO_4)_2$ was measured by the author (cf. Section 3.2.1.5.). Moreover, the approximation t_{Cd} [1.5 M $Cd(ClO_4)_2$] ≅ t_{Zn} [1.5 m (molal) $Zn(ClO_4)_2$] = 0.319 [2a] was introduced.

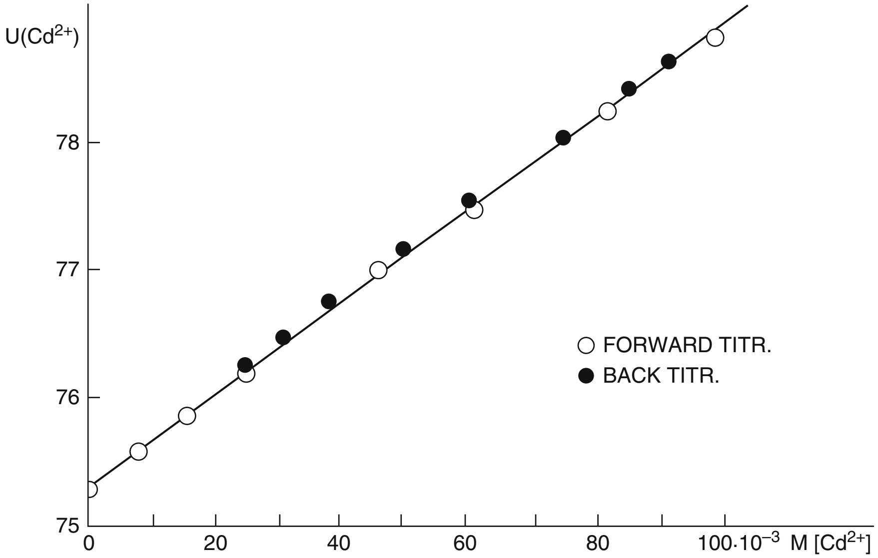

Fig. 3.14 $U(Cd^{2+}) = 10^3\kappa - [Y^-_{(3)}]\ \lambda_{Y(3)}$ versus $[Cd^{2+}]$, for the estimation of $\lambda_{Cd}{}^{tr}$ in the system 0.025 M $HClO_4$, $0 \leq [Cd(ClO_4)_2] \leq 0.1$ M and X M $NaClO_4$, using I = 3 M, constant, at 25.000 ± 0.005°C. Reproduced by permission of the Royal Society of Chemistry from Néher-Neumann E (1999) Acta Chem Scand 53: 1–6 (Fig. 3)

The plot in question is shown in Fig. 3.14. Here, the slope is equal to

$$z_B\lambda_B{}^{tr} - \lambda_A(z_B{}^2 + z_B)/2 = 35.10 \tag{3.50}$$

From this slope, value we can calculate

$$\lambda_{Cd}{}^{tr} = 52.77$$

As is seen, the Cd^{2+} ions are strongly accelerated in this mixture. Therefore, the deviations are positive in Fig. 3.12.

Having these results, we can check how the constancy of the ionic molar conductivities is fulfilled. As is seen, $\lambda_{Cd}{}^{tr}$, $\lambda_H{}^{tr}$ and λ_{Na} are constant, while $\lambda_{Yadd(3)}$ changes slightly with the composition of the test solution.

This mixture is generally used in E_0 titrations, where a $B^{z(B)+}$ ion-sensitive indicator electrode is used. Here, the potential function given below is valid [Part 5 in Ref. 9].

$$E_B' = E_B - (g/z_B)\log_{10} c_B = E_{0B} + g\, d_1\, c_B + g\, d_2\, c_H \tag{3.51}$$

The functions d_1 and d_2 are defined by Eqs. (2.49) and (2.50), respectively. In this function, E_B', ratios of the following ionic molar conductivities appear:

Table 3.4 The estimation of the uncertainties $\lvert d\,E_B \rvert$ in E_B (cf. Eq. (3–51)), in mV M^{-1} Cd^{2+} or H^+, caused by the change of $\lambda_{Y(3)}$ with the composition

$[Cd^{2+}]$ in M: 7.679×10^{-3}	99.508×10^{-3}
$31.08 \geq \lambda_{Y(3)} \geq$	29.70
$-0.0356 \geq R(B^{2+}) \geq$	−0.0334
$-2.10 \geq 59.16\ R(B^{2+})$ mV l/mol $Cd^{2+} \geq$	−1.97
$\lvert d\,E_B \rvert$ mV l/mol $Cd^{2+} = 0.13$	
$-0.5158 \leq R(H^+) \leq$	−0.5292
$-30.52 \leq 59.16\ R(H^+)$ mV l/mol $H^+ \leq$	−31.31
$\lvert d\,E_B \rvert$ mV l/mol $H^+ = 0.79$	

Source: Reproduced by permission of the Royal Society of Chemistry from Néher-Neumann E (1999) Acta Chem Scand 53: 1–6 (Table 1).

$$R(B^{z(B)+}) = -F_0[\lambda_B{}^{tr} - z_B\lambda_Y + (\lambda_Y - \lambda_A)(z_B{}^2 + z_B)/2] \tag{3.52}$$

$$R(H^+) = -F_0(\lambda_H{}^{tr} - \lambda_A) \tag{3.53}$$

$$\text{where } F_0 = 1/[2.303C(\lambda_A + \lambda_Y)]$$

Calculating these ratios at the beginning and at the end of the concentration range of the Cd^{2+} ions studied, we obtain the uncertainties given in Table 3.4. As it is seen from this table, the ratios of the ionic molar conductivities in question are constant. However, the function obtained for the total cell emf E_B is very sensitive to small changes in these ratios. The uncertainties in E_B, denoted $/dE_B/$, which appear due to changes in $\lambda_{Yadd(3)}$, are 0.13 mV/M Cd $^{2+}$, which gives 0.01 mV at $c_{Cd} = 0.1$ M, and 0.79 mV/M H^+, which gives 0.02 mV uncertainty at $c_H = 0.025$ M. As is seen, the uncertainties are of the same order of magnitude as those of the most accurate emf measurements. Hence, the potential functions derived in Ref. [9] are valid for these mixtures.

3.2.3.2 Conductivity Measurements in Mixture 2 Where c_H Is Varied While c_B Is Kept Constant

These conductivity data have been treated in a similar way as in Section 3.2.3.1.

The Percentage Deviations of Conductivity from Additivity

This deviation versus c_H is shown in Fig. 3.15. The deviations are positive, a linear function of c_H and decrease. At $c_H = 0$ M, we have large positive deviation due to the increase of $\lambda_{Cd}{}^{tr}$ in this mixture, too. The small and negative slope shows that $\lambda_H{}^{tr}$ is slightly lower than in 3 M $HClO_4$.

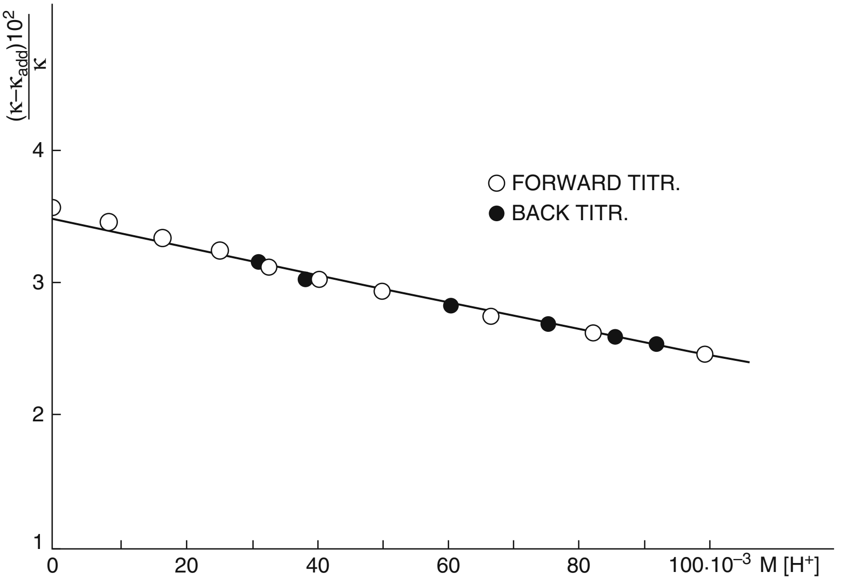

Fig. 3.15 The percentage deviation of the measured conductivity ($10^3\kappa$) from additivity ($10^3\kappa_{add}$) as a function of [H$^+$], in the system 0.050 M $Cd(ClO_4)_2$, $0.002 \leq [HClO_4] \leq 0.1$ M and X M $NaClO_4$, at I = 3 M, is kept constant, and 25.000 ± 0.005°C. Reproduced by permission of the Royal Society of Chemistry from Néher-Neumann E (1999) Acta Chem Scand 53: 1–6 (Fig. 4)

The Plot of 10^3 κ Versus c_H at $c_B = 0.050$ M, Constant

This plot is presented in Fig. 3.16 which is a straight line. According to Eq. (3.44), the intercept of this plot is

$$z_B c_B \lambda_B{}^{tr} + [A^+]_2 \lambda_A + c_Y \lambda_{Yadd(2)}{}^x = 163.1 \tag{3.54}$$

This equation describes the conductivity of the two-component system 0.050 M $Cd(ClO_4)_2$, is kept constant, and 2.850 M $NaClO_4$. The intercept can be used for the estimation of $\lambda_{Cd}{}^{tr}$, if we assume that λ_{Na} has the same value as in 3 M $NaClO_4$ and $\lambda_{Yadd(2)}{}^x$ is calculated according to additivity [cf. Eq. (3.48)]. Hence, we have for this system:

$$\lambda_{Na} = 23.48,\ \lambda_{Yadd(2)}{}^x = 30.37.$$

Thus, we can calculate from the intercept

$$\lambda_{Cd(1)}{}^{tr} = 65.93$$

It was found to be ±0.04 unit uncertainty in the position of the intercept. Hence, the following final result could be calculated:

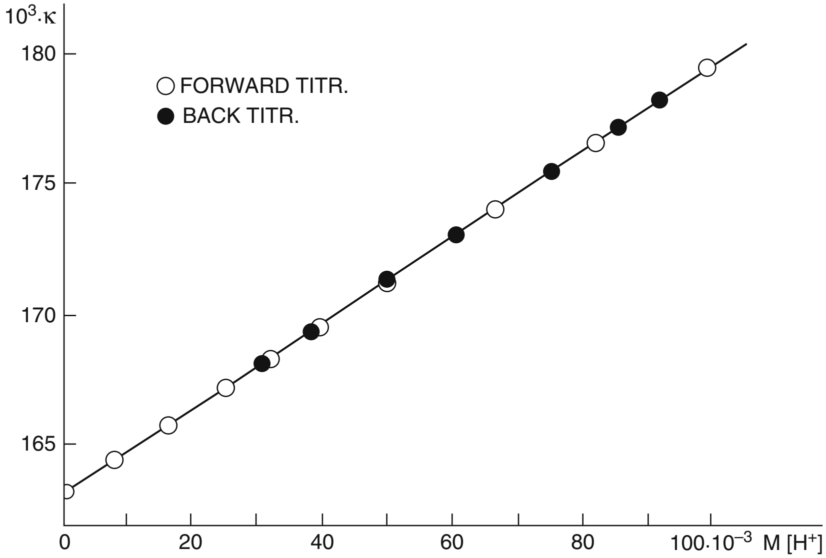

Fig. 3.16 $10^3\kappa$ versus $[H^+]$, for the determination of the ionic molar conductivities in the system 0.050 M $Cd(ClO_4)_2$, $0.002 \leq [HClO_4] \leq 0.1$ M and X M $NaClO_4$, using I = 3 M, is kept constant, at 25.000 ± 0.005°C. Reproduced by permission of the Royal Society of Chemistry from Néher-Neumann E (1999) Acta Chem Scand 53: 1–6 (Fig. 5)

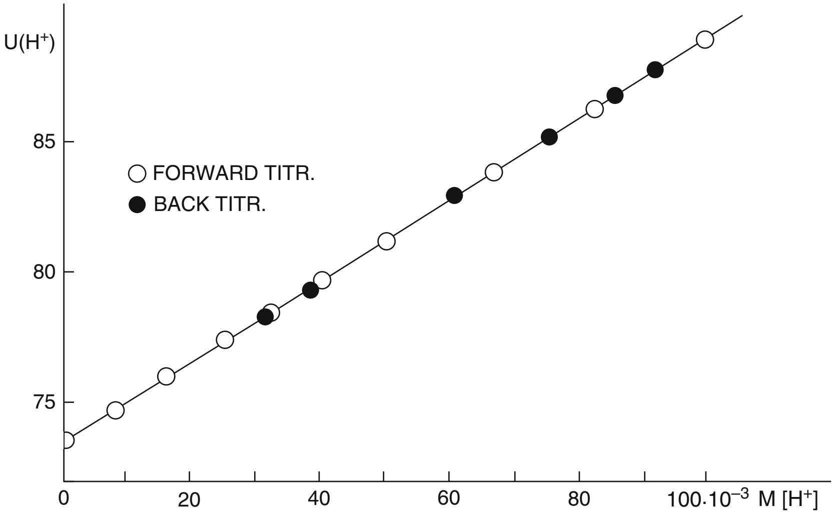

Fig. 3.17 $U(H^+) = 10^3\kappa - [Y^-_{(3)}]\lambda_{Y(3)}$ versus $[H^+]$, for the estimation of $\lambda_H{}^{tr}$ in the system 0.050 M $Cd(ClO_4)_2$, $0.002 \leq [HClO_4] \leq 0.1$ M and X M $NaClO_4$, at I = 3 M, is kept constant, and 25.000 ± 0.005°C. Reproduced by permission of the Royal Society of Chemistry from Néher-Neumann E (1999) Acta Chem Scand 53: 1–6 (Fig. 6)

$$\lambda_{Cd(R)} = 66.31 \pm 0.38$$

This corresponds to ± 0.57% uncertainty.

The Plot of 10^3 $\kappa - c_Y\ \lambda_{Yadd(3)}{}^x$ Versus c_H at $c_B = 0.050$ M, Constant

This plot is presented in Fig. 3.17. On the basis of this plot and Eq. (3.47), the slope is given by

$$\lambda_H{}^{tr} - \lambda_{Na} = 156.43 \tag{3.55}$$

From this, we can calculate

$$\lambda_H{}^{tr} = 179.91$$

The values of $\lambda_{Yadd(3)}{}^x$ have again been calculated due to the additivity. The values obtained can be described by the equation

$$\lambda_{Yadd(3)}{}^x = 30.37 + 2.83\,[H^+] \tag{3.56}$$

The slight change in these values with $[H^+]$ does not influence the constancy of the ratios R, which appear in the total cell emf E_H [cf. Eqs. (3.51) – (3.53)].

3.2.3.3 Conductivity Measurements in Mixture 3 Where Both c_B and c_H Are Varied

In this case, the measured conductivity data can be interpreted in terms of the ionic molar conductivities with the help of a curve-fitting computer program, e.g. MLAB [4]. This can be done in a similar way as suggested in Sections 3.2.1.3 and 3.2.2.3. In this treatment of the data, $\lambda_{Yadd(3)}$ can be used for the ionic molar conductivity of the $ClO_4{}^-$ ions. We assume that λ_{Na} has the same value as in 3 M $NaClO_4$.

Expressing $\lambda_{Cd}{}^{tr}$ in general as

$$\lambda_{Cd}{}^{tr} = f_1 + (or-)f_2c_B \tag{3.57}$$

we can transform the data into the following form:

$$\begin{aligned} F_{0\,exp} \equiv 10^3\kappa - c_Y\lambda_{Yadd(3)} - C\lambda_A = c_B\{z_B[f_1 + (or-)f_2c_B] \\ - \lambda_A(z_B^2 + z_B)/2\} + c_H(\lambda_H{}^{tr} - \lambda_A) \end{aligned} \tag{3.58}$$

on the basis of Eq. (3.47). Now, the function F_{0calc}, which consists of the right-hand side of Eq. (3.58), can be fitted to the data F_{0exp} by adjusting f_1, f_2 and $\lambda_H{}^{tr}$ as parameters. Here, we can use λ_{Cd} [1.5 M $Cd(ClO_4)_2$] as a starting value for f_1. The subscript calc stands for calculated.

Values of the ionic molar conductivities which were determined in this section are summarized in Table 2.16. All ionic molar conductivities which were determined in Chapter 3 are presented in Tables 3.5 and 3.6.

Table 3.5 Survey of the ionic molar conductivities in S cm^2 (mol ion)$^{-1}$. |charge|$^{-1}$ units in the mixtures of 0.025 M $HClO_4$, constant, X M $NaClO_4$ and $0 \le [Cd(ClO_4)_2] \le 0.10$ M at different experimental conditions and 25.000 ± 0.005°C (tr = trace)

Experimental conditions	$[A^+] = 3$ M, constant	$[Y^-] = 3$ M, constant	I = 3 M, constant
λ_{Na}	23.48	23.48	23.48
$\lambda(ClO_4)$	a	32.37	b
$\lambda_{Cd}{}^{tr}$	c	0	52.77
$\lambda_H{}^{tr}$	174.40	205.21	217.93

Note: a: $31.19 - 13.9\,[Cd^{2+}]$

b: $31.19 - 15.03\,[Cd^{2+}]$

c: $0 \le [Cd(ClO_4)_2] \le 86$ mM: $7.54 - 0.90 = 6.64$

$86 \le [Cd(ClO_4)_2] \le 187$ mM: $7.54 - 5.25 = 2.29$

Table 3.6 Survey of the ionic molar conductivities (λ_J) in S cm^2 (mol ion)$^{-1}$charge^{-1} unit in the mixtures of 0.050 M $Cd(ClO_4)_2$, constant, X M $NaClO_4$ and $1 - 2 \le [HClO_4] \le 100$ mM at different experimental conditions and 25.000 ± 0.005°C (tr = trace)

Experimental conditions	$[A^+] = 3$ M, constant	$[Y^-] = 3$ M, constant	I = 3 M, constant
λ_{Na}	23.48	23.48	23.48
λClO_4add	a	b	c
$\lambda_H{}^{tr}$	137.78	189.73	179.91
$\lambda_{Cd}{}^{tr}$	17.57	50.68	65.93
Alternative, obtained by curve-fitting with the computer program MLAB			
λ_{Na}	23.48		
$\lambda ClO_4{}^{MED}$	30.40		
$\lambda_H{}^{tr}$	146.60		
$\lambda_{Cd}{}^{tr}$	17.43		

a: $30.41 + 2.80\,[H^+]$

b: $30.38 + 2.76\,[H^+] \sim 30.38$

c: $30.37 + 2.83\,[H^+]$

3.3 Conclusion on Conductivity Measurements

For the use of the potential functions derived, it is very important to check the constancy of the ionic molar conductivities in the systems studied. Up to now, it was not known how this should be done.

The author has suggested methods to interpret specific conductance data in terms of the ionic molar conductivities in mixtures of strong electrolytes of constant ionic medium type. Two type of mixtures of $Cd(ClO_4)_2 + HClO_4 + NaClO_4$, Mixture 1 and Mixture 2, defined in Chapter 2, have been studied at three experimental conditions:

(1) $[Na^+] = 3$ M, constant,
(2) $[ClO_4^-] = 3$ M, constant,
(3) $I = 3$ M, constant.

The most important results of these measurements can be given as follows.

(1) The ionic molar conductivities are constant in most of the cases or a linear function of the composition. But the slight change of for example $\lambda(ClO_4)$ with the composition does not influence the constancy of the *ratios* of the ionic molar conductivities which appear in the potential functions, if $[Cd(ClO_4)_2] \leq 0.1$ M.
(2) The ionic molar conductivities *are rather constant within one type of mixture, but differ very much from those existing in another type. Therefore, they must be determined in every test solution studied and they cannot be interchanged.*

The constancy of the ionic molar conductivities is a surprising result. This is the first investigation presented for the determination of the ionic molar conductivities, with high accuracy, in concentrated electrolyte solutions, which include three components and ions of higher charges than 1.

3.4 Experimental Details

The conductivity measurements were carried out according to Ref. [6]. A Wien bridge of the Shedlovsky type [10] manufactured by the LKB Company, Stockholm, was used. A calibration certificate supplied by this company made it possible to attain an accuracy of 0.01%. A dual-beam oscilloscope, type DM 64 from Telequipment, was used as a zero instrument. The cells were calibrated as suggested by Jones and Bradshaw [11]. The potassium chloride preparation was purified by recrystallizations, until no trace of Mg^{2+} could be detected. When the same solution was in rapid succession measured with two or three of our cells, we have usually obtained resistance values differing less than one part in 5.10^4.

To minimize the adsorption error, we always employed lightly platinized platinum electrodes. They have shown at the two frequencies available with the LKB bridge, 1 and 2 kHz, identical resistance values.

The conductance measurements have been carried out with the flask cells of the type developed by Shedlovsky [10] in 1932 for the study of the millimolar concentration range. Biedermann and Douhéret have simplified somewhat Shedlovsky's original design [10] by using ring-shaped electrodes [6], which are fastened to the wall of the cell vessel by four glass rods sealed to the platinum surface. This electrode construction makes the cell manufacturing much easier without resulting in any appreciable loss of precision. Indeed, their cell constants changed less than 0.1% in several years.

The accuracy of conductivity measurements can be increased by using properly designed conductivity cells with large cell constants. The cathode and anode compartment should be connected by a ca. 13 cm long capillary tube of about 3 mm inner diameter.

The flask cell offers great advantages not only when efficiency is sought but also for precision work in general.

Employing paraffin coated flasks, one can get in this way even with alkaline solutions satisfactory conductivity data.

During the conductivity measurements, the temperature fluctuations in the bath were kept below ±0.005° C.

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Chapter 4

Studies on Emf Cells Where Complex Formation Takes Place Using Liquid Junctions of the Type AY | AY + HY + $BY_{z(B)}$ + A_yL and $-\log_{10}[H^+] \leq 7$

4.1 Deduction of the General Equations [1]

4.1.1 Introduction

Emf cells containing equilibrium solutions are in principle quite different from those containing mixtures of strong electrolytes. Therefore, we use different notations in these two types of cells.

In emf cells with mixtures of strong electrolytes, *all ion concentrations can be calculated by the mixing rule.* There, the notations c_B, c_H, c_Y and c_A were used for the concentrations of the corresponding ions. The correction factors in the total potential anomalies (ΔE_B and ΔE_H) have been denoted by d_1 and d_2 for Cell B and by d_3 and d_4 for Cell H, moreover, by the different slope functions.

In emf cells containing equilibrium systems, *the equilibrium concentrations are defined by the law of mass action.* These will be denoted differently, e.g. $V = b$, h, l, etc. for the $B^{z(B)+}$, H^+ and the ligand (L^{y-}) ions, respectively. The correction factors in the total potential anomalies *are fundamentally different also*; these will be denoted Q(B, V) and Q(H, V) for Cells B and H, respectively. *These potential functions cannot be interchanged with the slope functions, valid in mixtures of strong electrolytes.*

In the recent curve-fitting computer programs, they do not distinguish between these two types of correction factors, because they do not have a special, well-defined theory to calculate them.

The concentrations of the ions of the ionic medium (A^+, Y^-), c_A and c_Y, and the different total, analytical concentrations (B_T, H_T, L_T, AY_T for the $B^{z(B)+}$, H^+, L^{y-} ions and the ionic medium, respectively) will be calculated by the mixing rule.

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E. Néher-Neumann, *Advanced Potentiometry*,
DOI 10.1007/978-1-4020-9525-2_4,

In the derived theoretical equations, *the composition changes of the ionic medium appear.* These will be denoted as $\Delta c_A = c_A - C$ for the cation of the ionic medium and $\Delta c_Y = c_Y - C$ for the anion of the ionic medium. The corresponding correction terms, $Q(B,\Delta c_A)\Delta c_A$ or/and $Q(B,\Delta c_Y)\Delta c_Y$ for Cell B and $Q(H,\Delta c_A)\Delta c_A$ or/and $Q(H,\Delta c_Y)\Delta c_Y$ for Cell H, *do not exist in curve-fitting computer programs. This is a serious, principal error in them. These correction terms are dominating ones.*

The functions Q(B, V) and Q(H, V) include *the contribution of the activity factors* f_{BTS2} and f_{HTS2} *to the ideal electrode potentials* E_B *and* E_H, respectively, also. The corresponding terms *are also missing* in the curve-fitting computer programs. This is another serious error in them. These potential contributions *are also dominating.*

The third serious source of systematic errors in recent curve-fitting computer treatment is *the use of the conditional constants* $E_{0B1} = E_{0B} + g\, d_2\, c_H$ and $E_{0H1} = E_{0H} + g\, d_3\, c_B$. It was already shown in Chapter 2 that the neglection of the later contribution results in the suggestion of polynuclear complexes which do not exist. Also, this does the neglect of the potential contributions caused by the composition changes of the ionic medium. Hence, we can conclude that the curve-fitting criterion widely used in the present practice, E (experimental) – E (calculated) = 0.01 mV, is completely wrong. The real potential anomalies must be taken into account. These will be derived in this chapter.

4.1.2 Definitions and Symbols Used in Equilibrium Systems

We shall study the following complex formation reactions:

$$qH + rL^{y-} \rightleftharpoons H_q\, L_r \tag{I}$$

$$pB + qH + rL^{y-} \rightleftharpoons B_p\, H_q\, L_r \tag{II}$$

$$pB + qH_2O \rightleftharpoons B_p(OH)_q + qH \tag{III}$$

with the equilibrium constant (concentration constant)

$$\beta_{pqr} = [\text{complex}]/(b^p\, h^q\, l^r), \tag{IV}$$

where $BY_{z(B)} + HY + A_yL$ are the reacting compounds and AY is the ionic medium. Here, p, q, r are integers. Ionic charges in the chemical formulas are generally omitted for simplicity. In reactions (I)–(III), the reaction product will be denoted as (i) $N_j^{z(Nj)-}$, if it is a negatively charged metal containing complex ion, and (ii) $P_i^{z(Pi)+}$, if it is a positively charged metal containing complex ion. Uncharged species cannot be considered in this theory.

We shall use Cells H and B, defined in Section 1.2. The total cell emf for Cells B and H is

$$E_B = E_{0B} + (g/z_B)\log_{10} b\, f_{BTS2} + E_D + E_{Df} \quad (4.1)$$

$$E_H = E_{0H} + g \log_{10} h\, f_{HTS2} + E_D + E_{Df} \quad (4.2)$$

where

$$E_{j(1,2)} = E_D + E_{Df} \quad (4.3)$$

is the liquid junction potential, defined by Eq. (9) in the Definitions…

The composition of the test solution (TS2) at equilibrium can be given, if strong complexes are formed with a ligand from a weak acid, as

$$h = [H^+]\,M = H_T^+ - \Sigma_{pqr}\, q\, \beta_{pqr}\, b^p\, h^q\, l^r \quad (4.4)$$

the equilibrium concentration of the H^+ ions in M, where $H_T{}^+$ is the total, analytical concentration of the H^+ ions in M, β_{pqr} is the equilibrium constant for the formation reaction of the complexes (conditional, so-called concentration constant),

$$l = [L^{y-}]\,M = L_T - \Sigma_{pqr}\, r\, \beta_{pqr}\, b^p\, h^q\, l^r \quad (4.5)$$

the equilibrium concentration of the ligand, where $L_T = [A_yL]$ M, the total, analytical concentration of the ligand used,

$$\Sigma_k l_k = \Sigma_k[L_k{}^{z(Lk)-}] = \Sigma_{qr}\, \beta_{qr}\, h^q\, l^r \text{ with } k \geq 2 \quad (4.6)$$

equilibrium concentration of the species of the protolysis of the acid H_yL with k $\geq$2,

$$b = [B^{z(B)+}]\,M = B_T - \Sigma_{pqr}\, p\, \beta_{pqr}\, b^p\, h^q\, l^r \quad (4.7)$$

equilibrium concentration of the central metal ion, where $B_T = [B^{z\,(B)+}]$ M is the total, analytical concentration of the central metal ion,

$$\Sigma_j n_j = \Sigma_j[N_j{}^{z(Nj)-}]\,M = \Sigma_{pqr}\, \beta_{pqr}\, b^p\, h^q\, l^r, \text{ with } j = 1, 2, \ldots \quad (4.8)$$

equilibrium concentration of the complex ions noted,

$$\Sigma_i\, p_i = \Sigma_i[P_i{}^{z(Pi)+}]\,M = \Sigma_{pqr}\, \beta_{pqr}\, b^p\, h^q\, l^r, \text{ with } i = 1, 2, \ldots \quad (4.9)$$

equilibrium concentration of the complex ions noted. In the equations above, β_{pqr} $b^p\, h^q\, l^r$ = [complex], equilibrium concentration.

Potentiometric titrations are generally carried out at three different experimental conditions: (i) $[A^+] = C$ M, is kept constant, (ii) $[Y^-] = C$ M, is kept constant and (iii) $I = C$ M, is kept constant. These conditions will result in different total potential anomalies.

For the concentration of the ions of the ionic medium in the test solution, c_A and c_Y, the following fundamental functions are valid, if the complexing agent A_yL is used for the increase of the pH of the test solution during the main titration. For Cell

H, the constant E_{0H} is assumed to be determined through an acid–base titration with NaOH.

$$c_A = [AY] + AOH_T + yL_T \tag{4.10}$$

$$c_Y = [AY] + z_B\, B_T + HY_T = c_A - AOH_T - yL_T + HY_T + z_B B_T \tag{4.11}$$

If $[A^+] = C$ M, is kept constant,

$$c_Y = C - AOH_T - yL_T + HY_T + z_B B_T = C + \Delta c_Y \tag{4.12}$$

If $[Y^-] = C$ M, is kept constant,

$$c_A = C - HY_T - z_B B_T + yL_T + AOH_T = C + \Delta c_A \tag{4.13}$$

If $I = C$ M, is kept constant, we have for the ionic strength

$$I = C = (1/2)\,(HY_T + c_A + c_Y + z_B{}^2\, B_T + y^2\, L_T) \tag{4.14}$$

Inserting c_Y from the left-hand side of Eq. (4.11) into Eq. (4.14), and also c_A from Eq. (4.10), we have

$$I = C = HY_T + [AY] + (1/2)\,(z_B{}^2 + z_B)\, B_T + (1/2)\,(y^2 + y)\, L_T + (1/2)\, AOH_T \tag{4.15}$$

From Eq. (4.15), we can get, for the concentration of the ionic medium to be used,

$$[AY] = C - HY_T - (1/2)\,(z_B{}^2 + z_B)\, B_T - (1/2)\,(y^2 + y)\, L_T - (1/2)\, AOH_T \tag{4.16}$$

According to Eq. (4.10), we have

$$\begin{aligned} c_A &= C - HY_T - (1/2)\,(z_B{}^2 + z_B)\, B_T - (1/2)\,(y^2 + y)\, L_T + y\, L_T + (1/2)\, AOH_T \\ &= C + \Delta c_A \end{aligned} \tag{4.17}$$

and from Eq. (4.11), we have

$$c_Y = C + z_B\, B_T - (1/2)\,(z_B{}^2 + z_B)\, B_T - (1/2)\,(y^2 + y)\, L_T - (1/2)\, AOH_T \tag{4.18}$$

In the equations above [cf. Eqs. (4.12), (4.13), (4.14), (4.15), (4.16), (4.17) and (4.18)], $\Delta c_A = c_A - C$ is the changes in the composition of the ionic medium, $\Delta c_Y = c_Y - C$ is the changes of the composition of the ionic medium, and $HY_T = [HY]$ M is the total analytical concentration of the strong acid used.

In the test solution, we have $[H_yL]$ which denotes the equilibrium concentration of the non-dissociated acid corresponding to the ligand L^{y-}, in M, h, b, l, $\Sigma_k\, l_k$, $\Sigma_j\, n_j$, $\Sigma_i\, p_i$ are the free, equilibrium concentrations as defined above.

The equilibrium concentrations depend upon each other through the equilibrium constants β_{pqr} defined by the mass action law. As is seen from the cell composition, all the equilibrium concentrations are depending upon h, among other parameters. h, which is considered to be the main variable, can always be measured (Cell H). b can be either measured, e.g. with the help of an amalgam or an ion-selective electrode (Cell B), or calculated as given in the composition of the cell. The different equilibrium concentrations, such as h, b, l, l_k,n_j and p_i with k = 2, 3, 4,. . ., j = 1, 2, 3, . . . , i = 1, 2, 3, . . . , can be calculated from the corresponding equilibrium constants determined at the preliminary interpretation of the data, using an incomplete ΔE_J function, and from the known, actual total concentrations. Preliminary equilibrium constants can be obtained by standard methods [2–4] or by a suitable computer program [5]. The total, analytical concentrations can be calculated on the basis of the mixing rule.

The concentration terms Δc_Y and Δc_A appear due to the changes in the composition of the ionic medium; consequently, they are different for each of the experimental conditions (i)–(iii). These terms depend only on total, analytical concentrations.

As we can see from the functions given for c_Y and c_A in the cell composition [cf. Eqs. (4.10), (4.11), (4.12), (4.13), (4.14), (4.15), (4.16), (4.17) and (4.18)], here, the free, equilibrium concentrations of the potential-determining ions (h, b) have no direct relationships with the concentrations of the anion or cation of the ionic medium, c_Y and c_A, respectively. The situation was quite different in cells with mixtures of strong electrolytes. Now, e.g. c_Y is a function of the change in the composition of the medium, Δc_Y. Hence, ΔE_J will be the function of the changes in the composition of the ionic medium, Δc_Y and Δc_A.

It should be mentioned that the presence of the undissociated molecules in the test solution, H_yL, can also have an effect on E_H and E_B owing to different possible reasons. These should be kept under control by carrying out the titrations in appropriate ways as it will be discussed later on. However, this contribution depends on the equilibrium concentration of the undissociated acid, $[H_yL]$, and not on its total concentration.

The total potential anomalies depend on (among other properties) all the concentrations of the ions present in the mixture of the two terminal solutions. Consequently, ΔE_J depends on the experimental condition chosen and also on the type of chemical processes taking place in the test solution.

4.1.3 Deduction of the Potential Functions E_D, E_{Df}, E_B and E_H

The ion concentrations at some intermediate plane of the transition layer will be established by the mixing of the equilibrium solution (TS2) and the bridge solution, C M AY (TS1). The preliminary equilibrium concentrations of the complexes and the ligand in the test solution is supposed to be known and can be obtained from a preliminary treatment of the data as described below. If equilibrium has already been reached in the test solution, it seems to be reasonable to assume that the equilibrium concentrations of the reacting species, according to Eqs. (I) (II) and (III), are affected in the same way by the dilution occurring in the transition layer. Therefore, it will be assumed that these concentrations in the transition layer can be calculated according to the model of linear mixing

$$c_J{}^* = [c_J{}^*] = x\ c_{JTS2} + (1 - x)\ c_{JTS1} \tag{4.19}$$

Hence, we have $b^* = x\,b$, $h^* = x\,h$ and $l^* = x\,l$.

Consequently, the equilibrium concentration of the complexes in the transition layer, [cpx*], with the general composition $B_pH_qL_r$, can be written in general, according to the mass action law. In equilibrium studies, in general, first the so-called concentration constants are determined in the cell which are valid on the concentration scale, at a constant C level of the ionic medium. These β_{pqr} values include the contribution of the activity coefficients which are considered to be constant at constant C and will be taken into account in a second step when the β_{pqr} values found are extrapolated to zero ionic strength [6]. Hence, we can write

$$\begin{aligned}[\mathrm{cpx}^*] = {} & \beta_{pqr}\, b^{*p}\, h^{*q}\, l^{*r} = \beta_{pqr}\,(xb)^p\,(xh)^q\,(x\,l)^r \equiv \beta_{pqr}\, b^p\, h^q\, l^r\, x^{(p+q+r)} \\ & \equiv [\mathrm{cpx}]\, x^{(p+q+r)}\end{aligned} \tag{4.20}$$

where [cpx] is the preliminary equilibrium concentration of the complex species in the test solution. Considering our special notation used for the description of the concentration of the complexes, we can write

$$\Sigma_i\, p_i^* = \Sigma_i\, p_i\, x^{(p+q+r)\,(i)} \equiv \Sigma_i\, p_i\, x^{u(i)} \tag{4.21}$$

$$\Sigma_j\, n_j^* = \Sigma_j\, n_j\, x^{(p+q+r)(j)} \equiv \Sigma_j\, n_j\, x^{u(j)} \tag{4.22}$$

$$\Sigma_k\, l_k^* = \Sigma_k\, l_k\, x^{(q+r)\,(k)} \equiv \Sigma_k\, l_k\, x^{u(k)} \tag{4.23}$$

where $u(i) = (p + q + r)(i)$ is the sum of the integers in the chemical formula for the species $P_i^{z(Pi)+}$, $u(j) = (p + q + r)(j)$ is the same kind of sum for the species $N_j^{z(Nj)-}$ and $u(k) = (\,q + r)(k)$ is the same kind of sum for the species $L_k^{z(Lk)-}$.

According to the concentration model suggested above for the transition layer, the mass action law is fulfilled too. Therefore, we can expect very real ΔE_J values even for cells with the formation of strong complexes.

The concentration of the ions of the ionic medium in the transition layer can be expressed according to Eq. (4.19), again. For example, for the experimental condition $[A^+] = C$ M, constant, we have

$$c_A^* = C\ \mathrm{M}$$

$$c_Y^* = C + x\,(HY_T + z_B\,B_T - y\,L_T) \equiv C + x\Delta c_Y \tag{4.24}$$

4.1.4 Calculation of the Ideal Diffusion Potential, E_D, in Cells with Complex Formation

We can rewrite the definition of E_D, given by Eq. (7) in Definitions and symbols, as

$$E_D = -g \int_{TS1}^{TS2} \Sigma_J(1/z_J)\, t_J^*\, d\log_{10} c_J^* \tag{4.25a}$$

by making the substitution $d \log_{10} c_J = (1/2.303)\, d \ln c_J$. Moreover, we have, for the transport numbers in the transition layer, $t_J{}^*$, cf. Eq. (15) in Definitions and symbols

$$t_J{}^* = |z_J|\lambda_J^*\, c_J{}^*/\{\Sigma_J|z_J|\lambda_J^*\, c_J{}^*\} \tag{4.25b}$$

and introducing the approximation $\lambda_J^* = \lambda_J$, the ionic molar conductivities in the text solution (TS2)

$$N = \Sigma_J\lambda_J\, c_J{}^*|z_J| = \Sigma_J(\lambda_J\, c_J{}^*|z_J|)_{cat} + \Sigma_J(\lambda_J\, c_J{}^*|z_J|)_{an} \tag{4.25c}$$

where cat = cation, an = anion.
Considering

$$d \ln c_J{}^* = d\, c_J{}^*/c_J{}^* \tag{4.26}$$

the function E_D can be written as

$$E_D = -(g/2.303) \int_{TS1}^{TS2} (1/N)[\Sigma\lambda_{cat}\, d\, c_{cat}{}^* - \Sigma_{an}\, \lambda_{an}\, d\, c_{an}*] \tag{4.27}$$

Substituting the derivatives of the ion concentrations in the transition layer into Eq. (4.27), we obtain

$$\begin{aligned} E_D = -(g/2.303) \int_{TS1,x=0}^{TS2,x=1} (1/N) \\ \times[\lambda_H\, h + \lambda_B\, b + \Sigma_i\lambda_{Pi}\, u(i)\, p_i\, x^{u(i)-1} - \lambda_L\, l - \Sigma(_k \geq 2)\, \lambda_{Lk}\, u(k)\, c_k\, x^{u(k)-1} \\ -\Sigma_j\lambda_{Nj}\, u(j) n_j\, x^{u(j)-1} + \lambda_A\, dc_A{}^* - \lambda_Y\, dc_Y{}^*]\, dx \end{aligned} \tag{4.28}$$

The last two terms under the integral in Eq. (4.28) concern the ions of the ionic medium, different for every experimental condition used out of (i)–(iii), e.g. for $[A^+] = C$ M, constant, $\lambda_A\, dc_A{}^* = 0$, and $-\lambda_Y\, dc_Y{}^* = -\lambda_Y\, \Delta c_Y$. Similarly, the function N [cf. Eq. (4.25c)] should also be expressed in terms of the ion concentrations in the transition layer. This function can always be written in the form

$$N = wx + a + \Sigma(_k \geq 2)\, \lambda_{Lk}|z_{Lk}|l_k x^{u(k)} + \Sigma_i\lambda_{Pi}|z_{Pi}|p_i x^{u(i)} + \Sigma_j\lambda_{Nj}|z_{Nj}|n_j x^{u(j)} \tag{4.29a}$$

where for $[A^+] = C$ M, constant, we have

$$w = \lambda_H h + \lambda_L|z_L|l + \lambda_B z_B b + \lambda_Y \Delta c_Y \tag{4.29b}$$

$$a = C(\lambda_A + \lambda_Y) \tag{4.29c}$$

Hence, Eq. (4.28) can be integrated graphically. This should be done for every titration point, as the potential term E_D is a function of the actual ion concentrations. Hence,

$$E_H \text{ (or } E_B) = f\,(h,\ b,\ l,\ \Sigma_{(k\geq 2)}\, l_k,\ \Sigma_i\, p_i,\ \Sigma_j\, n_j,\ \Delta c_Y \text{ or/and } \Delta c_A).$$

4.1.5 The Suggested Function for E_D for the Preliminary Treatment of Emf Data

For the establishment of the preliminary chemical model and equilibrium constants, we can use an approximate function for E_D, taking into account only the dominating species, L^{y-}, Y^-, A^+, $B^{z(B)+}$, and the H^+ ions. Therefore, a simplified version of the function, given by Eq. (4.28), can be integrated in the following form:

$$E_D = -(g/2.303) \int_{x=0}^{x=1} (\theta_2/N)\, dx \tag{4.30}$$

where N can be approximated by

$$N = wx + a \tag{4.31}$$

The content of the function θ_2 will be given in forthcoming chapters for every special cell studied. Equation (4.30) can be integrated according to Eq. (18) in Part 2 of Ref. [7]:

$$-\,g \int_{x=0}^{x=1} [\theta/(wx + a)]dx = -(g\theta/w)\ln[(w/a) + 1] \tag{4.32a}$$

The result is

$$E_D = -(g\theta_2/2.303w \ln[(w/a) + 1] \tag{4.32b}$$

For small values of w/a, we obtain

$$E_D = -g\theta_2/(2.303a) \tag{4.33}$$

As an alternative method for the integration of Eq. (4.30), we can use the formulas of Hendersson [8–10]:

$$E_D = -(g/2.303)[(U_{TS2} - U_{TS1})/(S_{TS2} - S_{TS1})]\ln(S_{TS2}/S_{TS1}) \tag{4.33a}$$

where the functions U and S are defined in Definitions and Symbols Often Used... We obtain

$$E_D = -(g/2.303)[(U_{TS2} - U_{TS1})/w] \ln[(w/a) + 1] \tag{4.33b}$$

For small values of w/a, we can write, using the approximation $\ln[(w/a)+1] \cong w/a$,

$$E_D \cong -(g/2.303)(U_{TS2} - U_{TS1})/a \tag{4.33c}$$

4.1.6 Calculation of the Contribution of the Activity Coefficients to the Ideal Diffusion Potential, E_{Df}, in Cells with Complex Formation

According to the definition of E_{Df} given by Eq. (8) in Definitions and symbols often used, we have

$$E_{Df} = -g \int_{TS1}^{TS2} \Sigma_J \, (t_J{}^*/z_J) \, d \log_{10} f_J{}^* \tag{4.34a}$$

$$E_{Df} = -g \int_{x=0}^{x=1} (1/N)[xh\lambda_H \, d \log_{10} f_H^* + xb\lambda_B \, d \log_{10} f_B^* + c_A{}^*\lambda_A \, d \log_{10} f_A^* - xl\lambda_L \, d \log_{10} f_L^* - c_Y{}^*\lambda_Y \, d \log_{10} f_Y^* + \Sigma_{ipi} x^{u(i)} \lambda_{Pi} \, d \log_{10} f_{Pi}^* - \Sigma(_k \geq 2) \, l_k x^{u(k)} \lambda_{Lk} \, d \log_{10} f_{Lk}^* - \Sigma_j \, n_j x^{u(j)} \lambda_{Nj} \, d \log_{10} f_{Nj}^*] \tag{4.34b}$$

Here, the functions denoting the ion concentrations $c_A{}^*$ and $c_Y{}^*$ are different in cells with different experimental conditions. The values of $\log_{10} f_J$ can be estimated, again, with the help of the specific interaction theory [6, 11–17]. These functions will be given in forthcoming chapters for every cell with the chosen experimental condition out of (i)–(iii) [7, 18, 19]. Substituting the corresponding d $\log_{10} f_J$ values into Eq. (4.34b), the integral can be evaluated graphically for every experimental point.

4.1.7 The Suggested Function for E_{Df} for the Preliminary Treatment of Emf Data

We can suggest a simplified function for $E_{Df,}$ again, taking into account only the dominating species, $B^{z(B)+}$, L^{y-}, Y^-, A^+, and the H^+ ions. In this case, the approximate function for E_{Df} can always be integrated in the form

$$E_{Df} \cong \text{corr} - g \int_{x=0}^{x=1} [\Phi_3 x \, dx/(wx + a) + \theta_3 dx/(wx + a)] \tag{4.35a}$$

where the term “corr” is defined by Eq. (1.23). The value of the integral is given by Eq. (31) in Ref. [10]. The content of the functions $\Phi_1(x)$ (appearing in corr), Φ_3 and θ_3 will be given for every experimental cell with the chosen condition out of (i)–(iii) in forthcoming chapters.
Hence, we have

$$\mathrm{corr} = -g \int_{x=0}^{x=1} [\mathrm{d\,D\,(I^*)/dx}]\Phi_1(x)\,\mathrm{dx}/(\mathrm{wx} + \mathrm{a}) \tag{4.35b}$$

$$E_{Df} = \mathrm{corr} - (g\Phi_3/w) + \{g[\Phi_3 a - \theta_3 w]/w^2\}\ln[(w/a) + 1] \tag{4.35c}$$

For small values of w/a, we obtain

$$\begin{aligned} E_{Df} &\cong \mathrm{corr} - g\theta_3/a \\ &= f_2(h,\ b,\ l,\ \Delta c_A\ \text{or/and}\Delta c_A, C). \end{aligned} \tag{4.36}$$

4.1.8 The Total Cell Emf in Cells with Complex Formation

4.1.8.1 The Total Emf of Cell B with an Amalgam Indicator Electrode

The total emf of Cell B can be described by Eq. (4.1). The total potential anomalies, ΔE_B, are

$$\Delta E_B = E_B - (g/z_B)\log_{10} b = (g/z_B)\log_{10} f_{BTS2} + E_D + E_{Df} \tag{4.37}$$

The approximate function of E_B can always be written in the following form, for the preliminary treatment of emf data and for small values of w/a:

$$E_B \cong E_{0B} + (g/z_B)\log_{10} b - g\ z_B\ [D(I) - D(C)] + \Sigma_V\ Q\,(B,\ V)\ V + \mathrm{corr} \tag{4.38a}$$

where Q(B, V) is a function which defines a constant in terms of some interaction coefficients and ionic molar conductivities measured in the equilibrium solution studied, and V is h, b, l, Δc_Y or/and Δc_A, the ion concentrations taken into account in the equilibrium solution. D(I), the Debye–Hückel term, is given by Eq. (2) in Ref. [10] as

$$D(I) = 0.5115\ I^{1/2}/(1 + 1.5\ I^{1/2}) \tag{4.38b}$$

D(C) is the Debye–Hückel term in C M AY (TS1).

The terms Σ_v Q(B, V)V give the potential contributions of the ions present in the transition layer, to ΔE_J, reduced by the Debye–Hückel terms. They cannot be determined experimentally, in contrast to the slope functions, e.g. SL(B, c_B) and SL(B, c_H), valid in mixtures of strong electrolytes, but they can be calculated. The term “corr” includes the Debye–Hückel terms of the activity factors for the considered ions in the transition layer.

If it was found in a separate experiment that the undissociated molecules of H_yL also influence the potential of the measuring electrode, Eq. (4.38a) should be extended with a proper term, e.g. $SL(B, H_yL)$ $[H_y L]$. The slope function $SL(B, H_yL)$ denotes the slope of the plot $E_B - (g/z_B) \log_{10} b$ versus $[H_yL]$, at constant [HY], e.g. 50 mM, and $[BY_{z(B)}]$, and varying $[H_yL]$.

From Eq. (4.38a), b can be calculated by successive approximations, from the constant E_{0B} and the terms $\Sigma_V\, Q\,(B,\ V)\, V$. The functions Q(B, V) will be given in forthcoming chapters for every special cell studied.

4.1.8.2 The Total Emf of Cell H with a H^+-Sensitive Indicator Electrode

The total emf of this cell can be described by Eq. (4.2). The total potential anomaly, ΔE_H, is given by

$$\Delta E_H = E_H - g \log_{10} h = g \log_{10} f_H + E_D + E_{Df} \tag{4.39}$$

The approximate function for E_H can always be written in the following way, for the preliminary treatment of the emf data and for small values of w/a:

$$E_H \cong E_{0H} + g \log_{10} h - g\, [D(I) - D(C)] + \Sigma_V\, Q(H,\ V)\, V + \text{corr} \tag{4.40}$$

where Q(H, V) is the same type of function as Q(B, V) and represents a constant.

From Eq. (4.40), h can be calculated by successive approximations from the constant E_{0H} and the terms $\Sigma_V\, Q\,(H,\ V)\, V$. The functions Q(H, V) will be given in forthcoming chapters for every special cell studied.

If it was found in a separate experiment that the undissociated molecules of H_yL also influence E_H, Eq. (4.40) should be extended with a proper term, again, e.g. $SL(H, H_yL)[H_yL]$. Here, $SL(H, H_yL)$ denotes the slope of the plot $E_H - g\ \log_{10} c_H$ versus $[H_yL]$, at constant [HY], e.g. 50 mM, and $[BY_{z(B)}]$, and at varying $[H_yL]$.

4.1.9 The Validity of the Equations

(1) The different functions are derived on the molar concentration scale and are valid there.

(2) The equations used for the calculation of the activity factor contribution to the total cell emf assume constant interaction coefficients. These have experimentally been proved to be true in the range $0.5 \leq I \leq 3$ M for cationic charges ≤ 3 (cf. the Section "On the difficulties…" in Part 1 of Ref. [7]). If these interaction coefficients prove to be functions of the ionic strength, new ΔE_J functions have to be derived using Pitzer's model (cf. the above-mentioned section in Part 1 of Ref. [7]) for the estimation of the ionic activity factors. Hence, the constant concentration of the ionic medium used, or I, denoted C, should be equal to or higher than 0.5 M.

(3) In the integration of the ideal diffusion potential term, E_D (the Henderson term) and E_{Df}, the ionic molar conductivities have been assumed to be constants. This can be tested experimentally from the slope functions. The constancy of λ_Y, λ_A, λ_B^{tr}, λ_H^{tr} and λ_L^{tr} (here, tr = trace) can be tested by determining the experimental slope functions, e.g. SL(H, c_H) and SL(H, c_B), presented in Ref. [10] and in forthcoming chapters, and SL(H, l). Alternatively, the slopes SL(B, c_H) and SL(B, c_B) can also be tested. The slope of the plots given below define the slope functions:

   (a) $E_H - g\ \log_{10} c_H$ versus c_H, at constant c_B, defines SL(H, c_H)$_2$.
   (b) $E_H - g \log_{10} c_H$ versus c_B, at constant c_H, defines SL(H, c_B)$_2$.
   (c) $E_B - (g/z_B) \log_{10} c_B$ versus c_B, at constant c_H, defines SL(B, c_B)$_2$.
   (d) $E_B - (g/z_B) \log_{10} c_B$ versus c_H, at constant c_B, defines SL(B, c_H)$_2$.
   (e) $E_H - g\ \log_{10} c_H$ versus $l = [L^{y-}]$, at constant or very low $[H^+]$, defines SL(H, l).

   The slope functions depend only on some of the ionic molar conductivities of the system studied. If they are constant in the concentration range investigated, we obtain a straight line for the slope functions summarized under (a)–(e).

   The magnitude of the ionic molar conductivities mentioned above can also be accurately determined by conductivity measurements.

(4) The value of $-\log_{10}[H^+]$ of the test solution is supposed to be ≤ 7. In alkaline solutions, new interaction coefficients should be introduced for the interactions between the cations of the test solution and the OH^- ion. Therefore, the following terms will appear in the $\log_{10} f_J$ values and in the potential functions:

   (i) $\varepsilon''(A, OH)[OH^-]$, in $\log_{10} f_A$
   (ii) $\varepsilon''(A, OH)\Delta c_A$, in $\log_{10} f_{OH}$, if $[Y^-] = CM$, constant, and $I = CM$, constant,
   (iii) $\varepsilon''(P_i, OH)[OH^-]$, in $\log_{10} f_{Pi}$
   (iv) $\varepsilon''(P_i, OH)\ p_i$ and $\varepsilon''(B, OH)\ b$ in $\log_{10} f_{OH}$.

   If the concentrations $[OH^-]$, p_i and b are $\leq 10^{-3}$ M, these interaction terms are probably negligible. If the value for the interaction term $\varepsilon''(A, OH)\Delta c_A$ is equal or less than 0.01, then this is negligible as well. In this case, the equations derived for the acid range are valid in alkaline solutions as well, leaving out the terms $\varepsilon''(H, Y)\ h$, $\varepsilon''(H, L)\ l$ and $\varepsilon''(H, Nj)\ h$, of course. Moreover, $\log_{10}[H^+]$ should be replaced by $\log_{10} K_w - \log_{10}[OH^-]$. Here, K_w is the ionic product of water. However, if the composition change of the ionic medium is large, new potential functions must be derived.

(5) The highest value that can be used for $[BY_{z(B)}]$ in connection with the use of the functions ΔE_J is limited by the requirement that λ_B should be constant. This can be verified from the experimental slope functions SL(H, c_B) or SL(B, c_B), as discussed under point (3).

(6) The highest total ligand concentration recommended, L_T, is limited by the requirement that λ_L should be constant. This can also be tested from the

experimental slope function SL(H, 1), as discussed under point (3). The constancy of λ_L^{tr} can also be investigated by conductivity measurements in the mixtures of AY $+A_y$ L at the experimental conditions $[A^+] = C$ M, constant, $[Y^-] = C$ M, constant, and $I = C$ M, constant, respectively.

(7) The constancy of the ionic molar conductivities in the test solution (λ_J), used as approximations for the λ_J^* values in the transition layer, is proved to be true only in junctions of constant ionic medium type, as was shown in Refs. [20–22]. Therefore, the equations to be presented in this series are valid only for these cases.

The usefulness of the model for the calculation of the total potential anomalies in the preliminary data treatment will be tested in Section 4.2.1.3 in the protolysis of the acetic acid and in the first step of the protolysis of ascorbic acid.

4.2 Emf Cells Where $[A^+] = C$ M, Is Kept Constant [23]

In this chapter, the appearance of the total potential anomalies will be studied in cells where complex formation takes place in the system AY-HY-$BY_{z(B)}$-A_yL. We assume that the equilibrium processes I–III occur in the cells, as given in Section 4.1. Definitions and Symbols used in equilibrium systems are also defined there. Emf cells of the same construction can be used as in Chapter 1. The composition of the test solution is given in Section 4.1.

The titrations can be carried out in different ways. Some possibilities are summarized in Appendix 1 of this chapter. It is important to realize that the different ways of making the titration will result in different data sets. The total potential anomalies depend on the experimental conditions used. The equilibrium concentration of the undissosiated acid H_yL is different in different titrations. These uncharged molecules isolate the ions from each other differently in the test solution. Therefore, the ionic molar conductivities can be very different in the different titrations resulting in systematic errors of varying magnitude. The proof of this hypothesis will be given in a forthcoming chapter.

The determination of the constants E_{0B} and E_{0H} should be done as described in Chapter 2. We derive the equations for the case when A_yL is used as a complexing agent at constant or varied total concentrations. For other cases (using H_yL and AOH), the term yL_T should be replaced by c_{AOHT}, the total concentration of the alkali metal hydroxide used. In this case, E_{0B} should be determined in a solution where c_H is kept constant, and in the presence of the ligand HL respective H_2L at constant concentration.

According to the newest results obtained by the author, potentiometric titrations should be carried out by using a buffer solution as a titrating solution, where the concentration of the acid component (HL, H_2L or AHL) should be kept constant during the titration. In the case of HL, H_2L, E_{0H} should also be determined in the presence of the ligand, $c_{acid} = X$ M, is kept constant.

The original deduction of the equations was done in Refs. [7, 23]. Here, only the final results are given for the total cell emf.

4.2.1 Potential Functions for the Formation of Strong Complexes

4.2.1.1 The Study of the Formation of Metal Ion Complexes

The Total Emf of Cell B for Small Values of w/a

Here, an amalgam or an ion-selective indicator electrode is used.

Equations have been derived for the total cell emf, E_B, partly without approximations (Section 4.1) and partly assuming only the presence of the H^+, $B^{z(B)+}$ L^{y-}, A^+ and Y^- ions [23]. The later case is used *for the preliminary data treatment.* We obtained in Section 4.1

$$E_B \cong E_{0B} + (g/z_B)\log_{10} b - g\, z_B\, [D(I) - D(C)] + \Sigma_V\, Q\,(B, V)V + \text{corr} \quad (4.41)$$

where

$$V = b,\ h,\ l,\ \Delta c_Y$$

$$w \equiv S_{TS2} - S_{TS1} = h\lambda_H^{tr} + b\, z_B\lambda_B^{tr} + \lambda_Y\Delta c_Y + |z_L| l\lambda_L^{tr} \quad (4.42a)$$

$$a = C(\lambda_A + \lambda_Y) \quad (4.42b)$$

and corr is given by Eqs. (1.23), (1.24) and (1.25).

The activity coefficients in the transition layer, $\log_{10} f_J{}^*$, and in the non-ideal electrode potential term, were calculated according to the specific interaction theory, SIT [6, 11–17], cf. Eqs. (12), (13). The reference state is chosen in such a way that the trace activity coefficients $f_J{}^{tr} \rightarrow 1$ as $c_J \rightarrow 0$ in C M AY as solvent. Hence, we can write for some intermediate plane in the transition layer

$$\log_{10} f_J{}^* = -z_J{}^2[D(I^*) - D(C)] + [\Sigma_k\varepsilon''(J, L_k)\, l_k{}^* + \Sigma_j\varepsilon''(J, N_j)\, n_j{}^* + \varepsilon''(J, Y)\, (c_Y{}^* - C)]_{ca} + [\varepsilon''(J, H)\, h^* + \varepsilon''(J, B)\, b^* + \Sigma_i\varepsilon''(J, P_i)\, p_i{}^*]_{an} \quad (4.43)$$

cf. Eqs. (12)–(14b) in Ref. [23]. Here, $[\ldots]_{ca}$ = the terms to be used if J is a cation + $[\ldots]_{an}$ = the terms to be used if J is an anion. D (I*) is the Debye–Hückel term in the transition layer. (I*) is defined by Eq. (1.24).

In Cell B, the different Q(B, V) functions have the following values:

$$Q\,(B, h) = -g\, F_0\lambda_H^{tr} + g\, t_Y\varepsilon''(H, Y) \quad (4.44)$$

$$Q(B, b) = -g\, F_0\lambda_B^{tr} + g\, t_Y\varepsilon''(B, Y) \quad (4.45)$$

$$Q(B, l) = (g/z_B)\varepsilon''(B, L) + g\, F_0\lambda_L^{tr} - g\, t_A\varepsilon''(A, L) \quad (4.46)$$

$$Q(B, \Delta c_Y) = (g/z_B)\varepsilon''(B, Y) + g\,F_0\lambda_Y - g\,t_A\varepsilon''(A, Y) \tag{4.47}$$

$$\Delta c_Y = c_Y - C = -y\,L_T + HY_T + z_B\,B_T \tag{4.48}$$

from Eq. (4.12). This term gives the composition change of the ionic medium.

If it was found in a separate experiment that the potential of the measuring electrode, E_B, is influenced by the presence of the H_yL molecules also, due to e.g. adsorption, Eq. (4.41) should be extended by the term SL(B, acid) $[H_yL]_T$. In this case, we have

$$\Delta E_B = -g\,z_B[D(I) - D(C)] + \Sigma_V\,Q(B, V)\,V + SL(B, \text{acid})[H_yL] + \text{corr} \tag{4.49}$$

The slope function SL(B, acid) can be determined by titrating solution S of the composition 50 mM HY + 0.1 M $BY_{z(B)}$ + C M AY with solution T of the composition 50 mM HY + 0.100 M $BY_{z(B)}$ + 0.1 M H_yL + C M AY. The slope of the plot $E_B - (g/z_B)\log_{10} b + gz_B[D(I) - D(C)]$ versus $[H_yL]_T$, at constant c_H, c_B and c_A, gives SL(B, acid).

According to these results, Eqs. (4.41), (4.49) are the correct functions for the calculation of the free, equilibrium concentration of the metal ion, b, for small values of w/a. This can be done by successive approximations in the knowledge of E_{0B} and the functions Q(B, V). It is important to remember that a conditional constant, denoted E_{0B1} or E_{0B2} in Chapter 2, cannot be used here. The estimation of the functions Q(B, V) will be presented in a following chapter.

As is seen, the total potential anomalies, ΔE_B, *depends on the ion concentrations and the deviation* of the anion concentration of the ionic medium from the composition of the ionic medium, *and not on total concentrations.*

In Eq. (4.41), the term "corr" gives only a minor contribution to ΔE_B, if the composition of the ionic medium is not changed drastically. It has been proved to be negligible [7, 10], e.g. in the cell containing mixtures of strong electrolytes with the experimental condition $[A^+] = 3$ M, constant. For the estimation of the term "corr", the knowledge of the trace (tr) ionic molar conductivities for the dominating species in the equilibrium solution, such as λ_B^{tr}, λ_H^{tr} and λ_L^{tr}, is necessary. How to get this information will be discussed in a following chapter. This estimation has to be made for a titration where C, B_{Tmax} and L_{Tmax} are used, as in the complex formation.

When using the functions presented above for the estimation of ΔE_B and E_B, the poles of the cell must be considered. For cells which have poles opposite to those defined here, for Cells B and H, the function E_B and E_H must be taken with the opposite sign.

The Total Emf of Cell H for Small Values of w/a

Here, a H^+ ion sensitive indicator electrode is used.

For the preliminary treatment of emf data, we can derive an approximate function for E_H using the same reasoning and conditions as in Section 4.2.1.1. Hence, we obtain for the total cell emf

$$E_H \cong E_{0H} + g \log_{10} h - g[D(I) - D(C)] + \Sigma_v Q(H, V)V + \text{corr}, \tag{4.50}$$

where $V = b, h, l$ and Δc_Y. Moreover,

$$Q(H, h) = -g\, F_0 \lambda_H^{tr} + g\, t_Y \varepsilon''(H, Y) \tag{4.51}$$

$$Q(H, b) = -g\, F_0 \lambda_B^{tr} + g\, t_Y \varepsilon''(B, Y) \tag{4.52}$$

$$Q(H, l) = g\varepsilon''(H, L) + g\, F_0 \lambda_L^{tr} - g\, t_A \varepsilon''(A, L) \tag{4.53}$$

$$Q(H, \Delta c_Y) = g\varepsilon''(H, Y) + g\, F_0 \lambda_Y - g\, t_A \varepsilon''(A, Y) \tag{4.54}$$

Moreover, we have

$$\Delta E_H = -g\, [D(I) - D(C)] + \Sigma_v\, Q(H, V)V + \text{corr} \tag{4.55}$$

For the composition change of the ionic medium, we have, from Eq. (4.12),

$$\Delta c_Y = c_Y - C = -AOH_T - y\, L_T + HY_T + z_B B_T \tag{4.56}$$

We calculated

$$Q(H, \Delta c_Y) = 14.77 \text{ mV } M^{-1} \Delta c_Y \text{ for NaClO}_4 \text{ ionic medium.}$$

If it was found in some separate experiments that the cell emf is influenced by the presence of the H_yL molecules as well, Eq. (4.50) should be extended as follows.

$$E_H \cong E_{0H} + g\, \log_{10} h - g\, [D(I) - D(C)] + \Sigma_v\, Q(H, V)V + SL(H, \text{acid})[H_yL] + \text{corr} \tag{4.57}$$

where $[H_yL]$ denotes equilibrium and not total concentration. The slope function SL(H, acid) stands for the slope of the plot $E_H - g \log_{10} h + g\, [D(I) - D(C)]$ versus c_{acid} , at constant [HY], e.g. 0.050 M $HClO_4$, and $c_A = C$ M, constant.

In this case, we have for the total potential anomalies:

$$\Delta E_H = -g\, [D(I) - D(C)] + \Sigma_v\, Q(H, V)V + SL(H, \text{acid})[H_yL] + \text{corr} \tag{4.58}$$

It should be noted that the magnitude of this slope depends on the way the titration is carried out.

According to this result, Eq. (4.50) or (4.57) is the correct function for the calculation of the free, equilibrium concentration of the H^+ ions, h, for small values of w/a. This can be done by successive approximations, knowing E_{0H} and the functions Q(H, V). E_{0H} should be determined at the beginning of the titration, as it was discussed in Chapter 2.

We should remember that a conditional constant, denoted either E_{0H1} or E_{0H2} in Chapter 2, cannot be used here. The functions Q(B, V) and Q(H, V) can be estimated as it will be discussed in the next section.

The term “corr” is given by Eqs. (1.23), (1.24) and (1.25), where the function $\Phi_1(x)_1$ is included. This is defined as (cf. Eq. (15) in Ref. [23])

$$\Phi_1(x) \cong x(-h\lambda_H - z_B^2\, b\lambda_B + \Delta c_Y\lambda_Y + y^2\, l\lambda_L) + C(\lambda_Y - \lambda_A) \tag{4.59}$$

The term “corr” can be neglected here [7, 10].

The Estimation of the Functions Q(H, b) Respective Q(B, b)

We have two possibilities.

Estimation Through Conductivity Measurements of λ_H^{tr}, λ_B^{tr}, λ_A and λ_Y

These ionic molar conductivities are included in the functions in question. The conductivity of the electrolyte mixture given below should be measured by accurate measurements:

$$0 \le c_B \le B_{T\,\max}$$

$1 \le c_H \le 5$ mM, constant, or a level should be used which prevents the hydrolysis and complex formation of the $B^{z(B)+}$ ions,

$$[H_yL] \text{ M undissociated acid, constant,}$$

$$\text{C M AY, keeping } [A^+] = \text{C M, constant.}$$

Here, $B_{T\max}$ denotes the maximum level of the total, analytical concentration used for $BY_{z(B)}$ during the study of the equilibrium system. It is important to mention that the same levels of the complexing agent H_yL should be studied as those used in the study of complex formation. As is seen, both c_B and c_H are varied during this titration. The conductivity data can be interpreted in terms of the ionic molar conductivities only with the help of a curve-fitting computer program, e.g. MLAB [24], and using the unknown λ_J values as parameters. This treatment has already been described in Chapter 3.

Estimation by Slope Functions

We should measure the experimental slope function $SL(H, c_B)_{1\exp}$ in the mixture in question, using constant level for c_H. This is the slope of the plot 1: $E_H - g \log_{10} c_H + g\,[D(I) - D(C)] -$ corr versus c_B, at constant c_H. Hence, we have

$$SL(H, c_B)_1 = g\, d_3 \tag{4.60a}$$

where d_3 is given by Eq. (2.14a). Then we should form and calculate the difference function $Q(H, b) - SL(H, c_B)_1$. Hence, we obtain

$$Q(H, b) = SL(H, c_B)_{1\,\exp} + \text{the difference function} \tag{4.60b}$$

where the difference function is

$$- \mathrm{g}\, z_B \varepsilon''(\mathrm{H, Y}) - \mathrm{g}\, z_B\, F_0 \lambda_Y + \mathrm{g}\, z_B\, t_A \varepsilon''(\mathrm{A, Y}) \tag{4.60c}$$

and exp denotes experimental.

The function Q(B, b) can be estimated similarly, through the slope function SL(B, $c_B)_1 = gd_1$, where d_1 is given by Eq. (2.3).

The Estimation of $\lambda_L{}^{tr}$, λ_A and λ_Y in Mixtures of Strong Electrolytes

The function Q(H, 1) includes the term $\lambda_L{}^{tr}$. This can be estimated in two ways.

Estimation Through Conductivity Measurements

The conductivity, $10^3\kappa$, can be measured in the mixtures of

$$0 \leq [A_yL] \leq L_{Tmax}$$

$$[H_yL] \text{ M undissociated acid, constant,}$$

$$\text{AY, keeping } [A^+] = \text{C M, constant.}$$

From this data, $\lambda_L{}^{tr}$ can be estimated in a similar way as it was used for the estimation of $\lambda_{Cd}{}^{tr}$, discussed in Section 3.2.1. We assume that λ_Y has the same value as in C M AY solution. λ_A should be calculated in terms of the ionic strength fractions.

The ionic strength in this mixture is

$$I = [AY] + L_T(y + y^2)/2 \tag{4.61a}$$

Hence, we have

$$\lambda_A^{Mix} = \lambda_A(\text{C M AY})[AY]/I + \lambda_A(\text{C/y M } A_yL)L_T(y + y^2)/2\, I \tag{4.61b}$$

According to the additivity, we have

$$10^3\kappa = C\lambda_A^{Mix} + c_Y\lambda_Y\, (\text{C M AY}) + y\, L_T\lambda_L(\text{C/y M } A_yL) \tag{4.62}$$

We assume that the deviations from additivity are due to the deviation of $\lambda_L{}^{tr}$ from its value in C/y M A_yL solution, denoted as

$$\Delta(\lambda_L^{tr}) = \pm\, y\, L_T\, r_1 \tag{4.63}$$

This deviation is described by the following function:

$$\Delta(\lambda_L^{tr}) = 10^3\kappa - C\lambda_A^{Mix} - c_Y\lambda_Y(\text{C M AY}) - y\, L_T\lambda_L(\text{C/y M } A_yL) = \pm\, y\, L_T\, r_1 \tag{4.64}$$

Here, $10^3\kappa$ denotes the measured conductivity of the mixture studied. Plotting $\Delta(\lambda_L{}^{tr})$ versus L_T, r_l can be calculated from the slope. Then we have

$$\lambda_L^{tr} = \lambda_L(C/y \text{ M } A_yL) - r_l \tag{4.65}$$

where

$$\lambda_L(C/y \text{ M } A_yL) = t_L(C/y \text{ M } A_yL)\Lambda(C/y \text{ M } A_yL) \tag{4.66}$$

The transport numbers in C/y M solution of the pure electrolyte A_yL, t_L and t_A, can be determined with the help of an emf cell (cf. Ref. [25]), if the pK_a values of the corresponding acid are well separated.

The Estimation of $\lambda_L{}^{tr}$ or Q(H, l) by Using Slope Functions

An approximate value can be obtained for the ligand L^- or HL^- from the experimental slope function SL(H, l). This is defined by Eq. (4.89) for the ligand L^-, determined by emf measurements, as it will be discussed in "Titration by Adding a Buffer Solution". Having the experimental slope function, we can act in two ways.

(a) Using the definition of the slope function, the value of $\lambda_L{}^{tr}$ can directly be calculated from the known function.
(b) We form and calculate the difference function Q(H, l) – SL(H, l) on the basis of the definitions. Then Q(H, l) = $SL(H, l)_{exp}$ + the difference function.

This estimation requires the assumption that the ionic molar conductivities have the same values in both functions, namely, in the two solutions which they have been determined in. Therefore, the experiments, done for obtaining SL(H, l) and to study the complex formation, must be carried out practically in the same way. In these calculations, for the values of λ_A and λ_Y, we can use those which are valid in C M ionic medium AY.

During the study of the equilibrium system, the equilibrium concentration of the ligand, $l = [L^-]$, is changed while $[A^+] = C$ M, is kept constant, and $10^{-7} < [H^+] < 10^{-3}$ M. During the determination of the slope function SL(H, l), the $[H^+]$ is kept at a constant or negligible level, by using the buffer system HL - L^- , and $[A^+] = C$ M, constant, while $[L^-]$ is changed in the range 0 – L_T M. Therefore, we can hope that $\lambda_L{}^{tr}$ has the same value in both systems.

It is important to emphasize that Q(H, L) and SL(H, l) are two different functions and they cannot be interchanged.

The Effect of the Composition Changes of the Ionic Medium on the Total Potential Anomalies and on the Equilibrium Constants

This effect will be investigated in both mV and in $\log_{10} \beta_{pqr}$ units.

The Effect on the Total Potential Anomalies ΔE_B and on $\Delta \log_{10} \beta_{pqr}$

The function $Q(B, \Delta c_Y)$ can be calculated according to its definition [cf. Eq. (4.47)]. Δc_Y for Cell B is given by Eq. (4.48).

For $NaClO_4$ ionic medium and $B = Cd^{2+}$, we can calculate, in mV M^{-1} Δc_Y:

$$Q(B, \Delta c_Y) = 11.83 + 4.88 - 0.76 = 15.95$$

This value is the sum of the following terms

$$(g/z_B)\varepsilon''(B, Y) = 11.83$$

$$g\lambda_Y/[2.303\ C(\lambda_A + \lambda_Y)] = 4.88$$

$$-\ g\ t_A\varepsilon''(A, Y) = -0.76,$$

due to the introduction of the approximations for the transport numbers

$$t_Y = \lambda_Y/(\lambda_A + \lambda_Y) \cong t_Y(3\ M\ NaClO_4) = 0.57$$

and

$$t_A = \lambda_A/(\lambda_A + \lambda_Y) \cong t_A(3\ M\ NaClO_4) = 0.43$$

These transport numbers are given in Table 2.10. As is seen, this potential contribution is a dominating term, and it cannot be neglected, as it is done in the curve-fitting computer programs.

According to the definition of Δc_Y, given by Eq. (4.48), this concentration term *depends on B_T and L_T*. This means that the equilibrium constants calculated contain a systematic error which depends on B_T and L_T. *This looks like the formation of polynuclear complexes,* with the composition $B_pH_qL_r$, and *the emf data will be interpreted according to this.*

The composition change of the ionic medium can be estimated in advance, when planning the titration.

The systematic errors in the equilibrium constants, $\Delta \log_{10} \beta_{pqr}{}^{(2)}$, caused by the composition change of the ionic medium, and e.g. for Cell B, can be estimated from the equations given below.

$$\log_{10} \beta_{pqr} = \log_{10}[\text{complex}] - q \log_{10} h - p \log_{10} b - r \log_{10} l \qquad (4.67a)$$

$$\log_{10} b = (E_B - E_{0B})(z_B/g) + z_B{}^2\ [D(I) - D(C)] - (z_B/g)\Sigma_v\ Q(B, V)V - (z_B/g)\ \text{corr} \qquad (4.67b)$$

$$\Delta \log_{10} \beta_{pqr}^{(2)} = -p\Delta \log_{10} b = p(z_B/g)\ Q\ (B, \Delta c_Y)\Delta c_Y \qquad (4.67c)$$

This effect is z_B times higher than in Cell H.

The Effects on the Total Potential Anomalies ΔE_H and on $\Delta\ \log_{10}\beta_{pqr}$

The function $Q(H, \Delta c_Y)$ can be calculated according to its definition (cf. Eq. (4.54). It is $= 14.77\ \text{mV}\ M^{-1}\ \Delta c_Y$ for $NaClO_4$ ionic medium. The composition change of the ionic medium for Cell H, Δc_Y, is given by Eq. (4.56). For the change of the equilibrium constants with the composition change of the ionic medium, we have

$$\log_{10} h = (E_H - E_{0H})/g + [D(I) - D(C)] - (1/g)\Sigma_v\, Q(H, V)V - \text{corr}/g \quad (4.68a)$$

where

$$V = b,\ h,\ l,\ \Delta c_Y \text{ and}$$

$$\Delta \log_{10} \beta_{pqr}{}^{(2)} = -q\Delta \log_{10} h = q(1/g)Q(H, \Delta c_Y)\Delta c_Y \quad (4.68b)$$

due to Eqs. (4.50) and (4.67a). It is assumed that E_{0H} was determined in the absence of the metal ions.

The effect of the composition changes in mV, $Q(H,\Delta c_Y)\ \Delta c_Y$, and that on the equilibrium constants for Cell H, was estimated for four titrations, *generally used in potentiometric titrations.* The complexing agent AL is assumed to be used with B $= Cd^{2+}$. Moreover, the approximation

$$\Delta c_Y \cong z_B\, B_T - y\, L_T$$

was introduced, as $HY_T \cong AOH_T$ at the end of the E_0 titration. The results are presented in Table 4.1.

As is seen from this table, *the systematic errors are not 0.01 mV, for $z_B = 2$, and they are changing with B_T, as well as it does* $\Delta\log_{10}\beta_{pqr}{}^{(2)}$ *also.* Consequently, this error will be interpreted as the formation of polynuclear complexes.

Table 4.1 The effect of the composition changes of 3 M $NaClO_4$ on the equilibrium constants, when strong complexes are formed in cell H, for two sets of usual emf titrations, at 25°C and $[Na^+] = 3$ M, constant

B_T M	L_T M	$\sim\Delta c_Y$ M	$Q(H,\Delta c_Y)\Delta c_Y$ mV	$\Delta\log_{10}\beta_{pqr}{}^{(2)}$ q=1	q=2	q=3
For $z_B = 2$						
0.01	0.05	−0.03	−0.44	−0.007	−0.014	−0.021
0.03	0.10	−0.04	−0.59	−0.010	−0.020	−0.030
0.05	0.15	−0.05	−0.74	−0.012	−0.024	−0.036
0.10	0.30	−0.10	−1.48	−0.025	−0.050	−0.075
For $z_B = 3$						
0.01	0.05	−0.02	−0.29	−0.005	−0.010	−0.015
0.03	0.10	−0.01	−0.15	−0.002	−0.004	−0.006
0.05	0.15	0	0	0	0	0
0.10	0.30	0	0	0	0	0

In order to reach the level of uncertainty of $\Delta E_H = 0.01$ mV for the total potential anomalies, besides the contributions of the composition change of the ionic medium, Q(H, b) b and Q(H, l) l, must be also taken into account. The term Q(H, h) h is probably negligible, as $[H^+] < 10^{-3}$ M. These terms can be estimated as it was discussed earlier in this chapter.

4.2.1.2 Survey of the Potential Functions for the Protolysis of the Weak Acid HL

The following protolysis equilibrium is studied:

$$HL \rightleftharpoons H^+ + L^-, \text{ with the protolysis constant } K_1 = [H^+][L^-]/[HL]. \tag{4.69}$$

We shall use the same cell as before, with a glass or $H_2(g)$ indicator electrode. First, the constant E_{0H} should be determined, in the presence of the acid HL of constant level. V_0 ml solution S_0 with the composition

$$S_0 : HY_0 \cong 25 \text{ mM strong acid, } HClO_4$$

$$c_{HL} = [HL] \text{ M weak acid, to be kept constant}$$

$$c_{AY0} = [AY] = C \text{ M}$$

should be titrated with $v_1 = v_2$ ml solutions S_1 and S_2 of the composition

$$S_1 : HY_1 = [H^+] \text{ M, is present in trace amounts}$$

$$2\ c_{HL}\text{M weak acid}$$

$$c_{AY1} = C \text{ M AY}$$

$$S_2 : c_{AOH2} = [AOH]$$

$$c_{AY2} = [AY] = C - c_{AOH2}$$

Here, the following potential function is valid

$$E_H = E_{0H} + g \log_{10} H^+] - g[D(I) - D(C)] + SL(H, c_H)[H^+] + SL(H, \text{acid})[HL]_T + \text{corr} \tag{4.70}$$

The intercept of the plot $E_H^x = E_H - g \log_{10} [H^+] + g [D(I) - D(C)] - SL(H, \text{acid}) [HL]_T - \text{corr}$ versus $[H^+]$ will result in E_{0H}. The slope of this plot is $SL(H, c_H)$.

The E_{0H} determination should be evaluated with the help of a Gran plot [26], in order to determine the equivalence point and to check the acidity level of the starting solution, H_0. The concentration of the H^+ ions can be calculated during this titration as

$$[H^+] = (v_0H_0 + v_1H_1 - v_2\, c_{AOH2})/v_T \equiv (V_E - v_2)c_{AOH2}/v_T \qquad (4.71)$$

where $v_T = v_0 + v_1 + v_2$ ml.

If V_E ml solution S_2 is added in the equivalence point, then we have

$$v_0\, H_0 + v_1\, H_1 = V_E\, c_{AOH2} \text{ mmol } OH^- \text{added} \qquad (4.72)$$

Defining

$$\begin{aligned} E_H{}^x &= E_H + g\,[D(I) - D(C)] - SL(H, \text{acid})[HL]_T - SL(H, c_H)\,[H^+] \\ &= E_{0H} + g\log_{10}[H^+] \equiv E_{0H} + g\log_{10}[(V_E - v_2)/v_T] + g\log_{10} c_{AOH2} \end{aligned} \qquad (4.73)$$

Dividing this equation by g and taking the antilogarithm of it, we obtain the Gran function:

$$F_1 = v_T \text{ antilog}_{10}(E_H{}^x/g) = \text{antilog}_{10}(E_{0H}/g) \times c_{AOH2} \times (V_E - v_2) \qquad (4.74)$$

If the function F_1 is plotted against v_2, the straight line obtained should be extrapolated to $F_1 = 0$ on the v_2 axel. In the cross point,

$$V_E - v_2 = 0, \text{ hence, } V_E = v_2 \text{ ml AOH2 added.}$$

From this value for V_E and Eq. (4.72), H_0 can be calculated.

The protolysis of the weak acid HL can be studied in two ways.

a) We titrate with dilute NaOH solution and the concentration of the weak acid is kept constant.
b) We carry out the titration by adding a buffer solution HL – AL.

Titration by Adding Dilute NaOH Solution

We continue with the addition of $v_1 = v_2$ ml solution S_1 and S_2; after that we decreased the volume of the test solution to $v_0{}^x$ by sucking out a portion of it with a calibrated pipette. We have the species H^+, L^-, HL, A^+ and Y^- in the test solution. The knowledge of the functions given below is useful.

$$c_A = C\text{ M} = c_{AY} + AOH_T \qquad (4.75a)$$

$$c_Y = C + HY_T - AOH_T = C + \Delta c_Y \qquad (4.75b)$$

$$\Delta c_Y = HY_T - AOH_T \qquad (4.75c)$$

$$I = C + (1/2)(h + \Delta c_Y + l\, y^2) \tag{4.75d}$$

$$w = h\lambda_H + \lambda_Y \Delta c_Y + y\, l\lambda_L \tag{4.75e}$$

$$\Phi_1(x) = x[-h\lambda_H + \lambda_Y \Delta c_Y + l\lambda_L\, y^2] + C(\lambda_Y - \lambda_A) \tag{4.75f}$$

$$a = C(\lambda_A + \lambda_Y) \tag{4.76}$$

We obtained for the total cell emf for small values of w/a

$$E_H \cong E_{0H} + g \log_{10} h + SL(H, \text{acid})[HL] + \Delta E_H, \tag{4.77}$$

where

$$\Delta E_H = g \log_{10} f_{HTS2} + E_D + E_{Df} = -g[D(I) - D(C) + Q(H, l)l + Q(H, \Delta c_Y)\Delta c_Y + \text{corr} \tag{4.78}$$

Here, [HL] denotes equilibrium concentration.
h can be calculated from Eqs. (4.77) and (4.78) by successive approximations, knowing E_{0H} and the potential functions involved.

Titration by Adding a Buffer Solution

The experimental constant E_{0H} should be determined, first, in the absence of the weak acid HL. This should be done as described in the previous section. When the $[H^+] \cong 10^{-3}$

M in the test solution, the E_{0H} titration is considered to be fulfilled. Then we titrate with solution S_2^x of the composition: 0.1 M HL, 1.8 M AL $\equiv L_T$ and 1.2 M AY.

The concentration of the acid component HL, in the solution S_2^x, has to be chosen in such a way that $3 \leq -\log_{10}[H^+] \leq 9$ in the test solution. Hence, neither the H^+ nor the OH^- ions are present in dominating concentration, and they can be neglected when calculating the potential contributions of the different ions present, to ΔE_H. The influence of the HL molecules on the potential of the measuring electrode has to be taken into account. If the pH of the test solution studied is less than 9, then a glass electrode can be used. Otherwise, a hydrogen gas electrode is necessary.

The following functions can be useful to know:

$$c_A = C\text{ M},\ \text{constant} = c_{AY} + AOH_T + L_T \tag{4.79}$$

$$c_Y = C - AOH_T - L_T + HY_T \tag{4.80}$$

$$\Delta c_Y = c_Y - C = HY_T - AOH_T - L_T = -L_T \tag{4.81}$$

as $HY_T - AOH_T \cong 0$ at the end of the E_0 titration.

$$\mathrm{I} = \mathrm{C} + (1/2)(\mathrm{h} \cong 0) \tag{4.82}$$

$$\mathrm{w} = \mathrm{h}\lambda_{\mathrm{H}} + (\lambda_{\mathrm{L}} - \lambda_{\mathrm{Y}})\mathrm{L_T} \tag{4.83}$$

$$\log_{10} \mathrm{f_{HTS2}} = -[\mathrm{D(I)} - \mathrm{D(C)}] + \varepsilon''(\mathrm{H, L})\mathrm{L_T} - \varepsilon''(\mathrm{H, Y})\mathrm{L_T} \tag{4.84}$$

$$\Phi_1(\mathrm{x}) = \mathrm{x}[-\mathrm{h}\lambda_{\mathrm{H}} + (\lambda_{\mathrm{L}} - \lambda_{\mathrm{Y}})\mathrm{L_T}] + \mathrm{C}(\lambda_{\mathrm{Y}} - \lambda_{\mathrm{A}}) \tag{4.85}$$

According to the earlier treatment of the problem, we obtain [cf. Eqs. (4.77), (4.78)] for the total cell emf, $\mathrm{E_H}$, and for small values of w/a:

$$\mathrm{E_H} = \mathrm{E_{0H}} + \mathrm{g}\log_{10}\mathrm{h} + \mathrm{SL(H, acid)[HL]} + \mathrm{SL(H, l)l} - \mathrm{g[D(I)} - \mathrm{D(C)]} + \mathrm{corr} \tag{4.86}$$

and

$$\begin{aligned} \Delta\mathrm{E_H} &\equiv \mathrm{g}\log_{10}\mathrm{f_{HTS2}} + \mathrm{E_D} + \mathrm{E_{Df}} \\ &= -\mathrm{g[D(I)} - \mathrm{D(C)]} + \mathrm{SL(H, acid)[HL]} + \mathrm{SL(H, l)l} + \mathrm{corr} \end{aligned} \tag{4.87}$$

where SL(H, l) is the slope of the plot $\mathrm{E_H}''$ versus $\mathrm{l} = [\mathrm{L}^-] = \mathrm{L_T}$. Considering Eqs. (4.77) and (4.78), we have

$$\begin{aligned} \mathrm{E_H}'' &\equiv \mathrm{E_H} - \mathrm{g}\log_{10}\mathrm{h} + \mathrm{g[D(I)} - \mathrm{D(C)]} - \mathrm{SL(H, cacid)[HL]} - \mathrm{corr} \\ &= \mathrm{E_{0H}} + \mathrm{Q(H, l)l} + \mathrm{Q(H, \Delta c_Y)\Delta c_Y} \end{aligned} \tag{4.88}$$

Considering Eqs. (4.53), (4.54) and $\Delta\mathrm{c_Y}$, we obtain for the *calculated slope function*

$$\begin{aligned} \mathrm{SL(H, l)} &= \mathrm{d\,E_H''/d\,l} \\ &= \mathrm{g}[\varepsilon''(\mathrm{H, L}) - \varepsilon''(\mathrm{H, Y})] - \mathrm{g\,F_0}(\lambda_{\mathrm{Y}} - \lambda_{\mathrm{L}}) - \mathrm{g\,t_A}[\varepsilon''(\mathrm{A, L}) - \varepsilon''(\mathrm{A, Y})] \end{aligned} \tag{4.89}$$

In order to get *the experimental slope function* SL(H, l), the expression

$$\log_{10}[\mathrm{H}^+] = \log_{10}\mathrm{K_1} - \log_{10}(\mathrm{c_{salt}/c_{acid}}) \tag{4.90}$$

obtained for the buffer system (cf. Section 1.1) should be inserted into Eq. (4.86). Then we obtain

$$\begin{aligned} \mathrm{E_H}'' &\equiv \mathrm{E_H} + \mathrm{g[D(I)} - \mathrm{D(C)]} - \mathrm{SL(H, acid)c_{acid}} - \mathrm{corr} + \mathrm{g}\log_{10}(\mathrm{c_{salt}/c_{acid}}) \\ &= \mathrm{constant} + \mathrm{SL(H, l)L_T} \end{aligned} \tag{4.91}$$

where

$$\mathrm{constant} = \mathrm{E_{0H}} + \mathrm{g}\log_{10}\mathrm{K_1} \tag{4.92}$$

As is seen, the slope of the plot $\mathrm{E_H}''$ versus $\mathrm{L_T}$ gives SL(H, l) and from the intercept = constant, the protolysis constant $\log_{10}\mathrm{K_1}$ can be obtained with high accuracy, in a broad concentration range. This graphical method is the correct way for the determination of $\log_{10}\mathrm{K_1}$, and this treatment does not result in the suggestion of non-existing dimer, trimer, etc. species. If we treat the data with a curve-fitting computer program, without giving the correct value for SL(H, l), we cannot explain the titrations without the suggestion of dimer, trimer, etc. species.

It is important to emphasize that Eqs. (4.91) and (4.92) are valid only in the case when a buffer solution of a suitable concentration was used as a titrating solution. In this case, the approximations $[HL] \cong c_{acid}$ and $[L^-] = l \cong c_{salt}$ are valid, if $c_{salt} \gg c_{acid}$. This is not the case when we titrate with dilute NaOH and a solution containing HL. In this case, the function Q(H, l) describes the potential contribution of the ligand in the preliminary data treatment. Therefore, the function SL(H, l) must be recalculated to Q(H, l). For this treatment, the difference function given below should be formed, first.

$$\begin{aligned} Q(H, l = L^-) - SL(H, l = L^-) &= Eq.(4.53) - Eq.(4.89) \\ &= g\varepsilon''(H, Y) + g\,F_0\lambda_Y - g\,t_A\varepsilon''(A, Y) \end{aligned} \qquad (4.93a)$$

Then using the known value for the experimental slope function, we can calculate

$$Q(H, l) = SL(H, l)_{exp} + \text{the difference function.} \qquad (4.93b)$$

Some of the interaction coefficients which are needed can be found in Table 2.3. A more extended summary of them, on the molal concentration scale, is given in Table 4.2. In Ref. [25], emf cells are suggested for the determination of some interaction coefficients.

Table 4.2 Survey of some molal interaction coefficients, ε(i, k), between the species i and k. Unknown ε (i, k) values have been approximated with the interaction coefficients between the ions j and l in the second column. ε is assumed constant in the ionic strength range 0.5 m≤I≤3.5 m [6]

i, k	j, l	ε
(Ho^{3+},ClO_4^-)		0.49
$(La^{3+},ClO_4^-)-(Lu^{3+},ClO_4^-)$		0.47−0.52
(Y^{3+},Cl^-)		0.28
(Y^{3+},HCO_3^-)	(Y^{3+},Cl^-)	
(Y^{3+},ClO_4^-)	(Ho^{3+},ClO_4^-)	
(Fe^{3+},ClO_4^-)		0.56
(H^+,ClO_4^-)		0.14
(YCO_3^+,ClO_4^-)		0.17
$(HgCl^+,ClO_4^-)$		0.20
$(CdCl^+,ClO_4^-)$		0.19
$(CdSCN^+,ClO_4^-)$		0.24
(CdI^+,ClO_4^-)		0.23
(Cd^{2+},ClO_4^-)	$[(Ca^{2+},Mg^{2+},Co^{2+},Cu^{2+},Zu^{2+},Hg^{2+}),ClO_4^-]$	0.27−0.34
$(YHCO_3^{2+},ClO_4^-)$		0.39
$(FeSCN^{2+},ClO_4^-)$		0.45
$(FeOH^{2+},ClO_4^-)$		0.38
$(Y_2CO_3^{4+},ClO_4^-)$		0.80
$(Fe_2(OH)_2^{4+},ClO_4^-)$		0.82
$(Pb_4(OH)_4^{4+},ClO_4^-)$		0.02
(Pb^{2+},ClO_4^-)		0.16

4.2.1.3 Experimental Studies

The Study of the H^+ - Hascorbate$^-$ System

After the determination of the constant E_{0H}, as it is described in Section 4.2.1.2., the protolysis of the ascorbic acid was studied by potentiometric titration with a buffer system (cf. "Titration by Adding a Buffer Solution"). The equilibrium system studied is

$$H_2Asc \rightleftharpoons Hasc^- + H^+, K_1 = [Hasc^-][H^+]/[H_2Asc]$$

We used a glass electrode as indicator electrode. $NaClO_4$ ionic medium was used in all experiments at $[Na^+] = 3$ M, constant.

Studies at Constant Level of H_2Asc

In one experiment, we chose $[H_2Asc]_F = 0.29749$ M, is kept constant. Here, H_2Asc denotes ascorbic acid, F formal, analytical concentration. The buffer system 0.29749 M H_2Asc, 1.6 M NaHAsc and 1.4 M $NaClO_4$ was used in the burette. The concentration of the $HAsc^-$ ions was varied in the test solution within the range 0 – 0.7 M. The graphical treatment of the data is shown in Fig. 4.1, based upon Eqs. (4.91), (4.92). Here, we obtained the slope function from the slope of this plot

$$SL(H, HAsc) = -7.6 \text{ mV } M^{-1} \text{ HAsc}^-$$

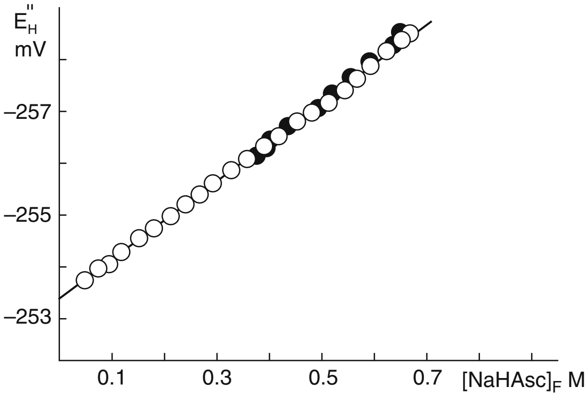

Fig. 4.1 The determination of the slope function SL(H, HAsc) and the first protolysis constant of the ascorbic acid, $\log_{10} K_1$, at $[H_2Asc]_F = 0.29749$ M, is kept constant, and $[Na^+] = 3$ M, is kept constant. The plot of E_H'' vs. $[NaHAsc]_F$ is based upon Eq. (4.91). Filled symbols denote back titration. Reproduced by permission of the Royal Society of Chemistry from Néher-Neumann E (1999) Acta Chem Scand 53: 557–574 (Fig. 1)

valid in the buffer system. From the intercept of the plot given in Fig. 4.1, the following value was obtained for the protolysis constant

$$\log_{10} K_1 = -4.348 \pm 0.002$$

This slope function was recalculated to the function Q(H, l), according to Eqs. (4.93 a, b). We obtained

$$Q(H, l) = SL(H, l)_{exp} + \text{difference function} = -7.6 + 14.8 = 7.2\text{mV M}^{-1}\text{Hasc}^{-}$$

Here, the notation l = $[HAsc^{-}]$ M is valid.

This function is valid if we titrate with dilute NaOH and a solution containing H_2Asc. In this case, we must take into account the potential contributions given in Table 4.3. Hence, the total systematic error at [NaHAsc] = 1 M is – 7.6 mV. If we do not take into account these effects, we must suggest the formation of dimer, trimer, etc. species, in order to explain the data.

In another experiment, we chose $[H_2Asc]_F = 0.1$ M, is kept constant. We titrated with the buffer solution 0.1 M H_2Asc, 1.8 M NaHAsc and 1.2 M $NaClO_4$. The concentration of the salt, NaHAsc, in the test solution was varied within the range 0 – 0.8 M. The evaluation of this titration is shown in Fig. 4.2. The graphical treatment of the data resulted in

$$SL(H, HAsc) = -8.1 \text{ mV M}^{-1} \text{ NaHAsc}$$

$$\log_{10} K_1 = -4.359 \pm 0.002$$

As we can see, 0.011 unit difference appears between the protolysis constants obtained up to now. This can be the result of some changes in the contribution of the H_2Asc molecules, and/or the change of the value of E_{0H}.

Table 4.3 Survey of the potential contributions to the total potential anomalies in the $H^{+} - HAsc^{-}$ system, when dilute NaOH and H_2 Asc solutions were used in the burette

a) The effect of the undissociated molecules H_2Asc
at $[H_2Asc] = 1$ M $[H_2Asc] = 0$ M
13 mV $\longleftarrow$ 13 × $[H_2Asc]$ [27] ——— 0 mV
b) The effect of the ligand $HAsc^{-}$
at [NaHAsc] = 0 M [NaHAsc] = 1 M
0 mV——— Q(H, HAsc)[HAsc] $\longrightarrow$ 7.2 mV
c) The effect of the composition change of the ionic medium
0 mV——— $Q(H,\Delta c_Y)\ \Delta c_Y$ $\longrightarrow$ −14.77 mV

Source: Reproduced by permission of the Royal Society of Chemistry from Néher-Neumann E (1999) Acta Chem Scand 53: 557–574 (Table 3).

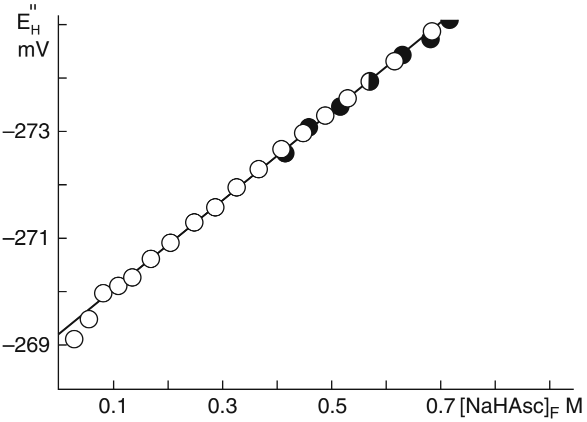

Fig. 4.2 The determination of the slope function SL(H, HAsc) and the first protolysis constant of the ascorbic acid, $\log_{10} K_1$, at $[H_2Asc]_F$ = 0.100 M, is kept constant, and $[Na^+]$ = 3 M, is kept constant. The plot of E_H'' vs. $[NaHAsc]_F$ is based upon Eq. (4.91). Filled symbols denote back titration. Reproduced by permission of the Royal Society of Chemistry from Néher-Neumann E (1999) Acta Chem Scand 53: 557–574 (Fig. 2)

Study at Constant Ratio of c_{acid}/c_{salt}

A titration was carried out at constant c_{acid}/c_{salt} ratio, too, which was equal to 0.18620. The constant E_{0H} was determined in the absence of H_2Asc. During the main titration, we used the following solution in the burette: 0.29941 M H_2Asc, 1.60799 M NaHAsc and 1.39201 M $NaClO_4$. The salt concentration in the test solution was varied within the range 0 – 0.7 M. The evaluation of this titration is shown in Fig. 4.3. The graphical treatment of the data resulted in the following results:

$$SL(H, HAsc) = -9.6 \text{ mV M}^{-1} \text{ HAsc}^-$$
$$\log_{10} K_1 = -4.359 \pm 0.002$$

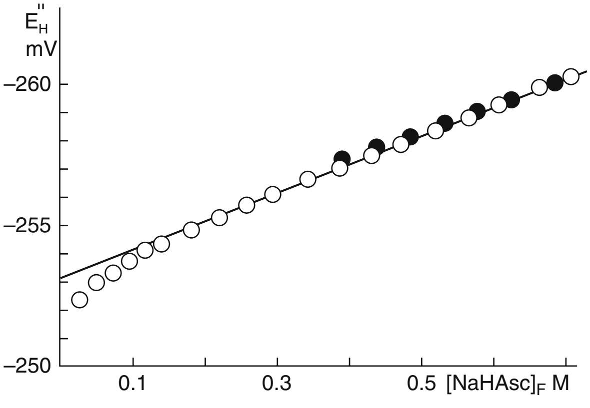

Fig. 4.3 The determination of the slope function SL(H, HAsc) and the first protolysis constant of the ascorbic acid, $\log_{10} K_1$, at constant (c_{acid}/c_{salt}) ratio, which was equal to 0.18620, and $[Na^+]$ = 3 M, is kept constant. The plot E_H'' vs. $[NaHAsc]_F$ is based upon Eq. (4.91). Filled symbols denote back titration. Reproduced by permission of the Royal Society of Chemistry from Néher-Neumann E (1999) Acta Chem Scand 53: 557–574 (Fig. 3)

As is seen, all data could be explained by the equilibrium

$$\mathrm{H_2Asc} \rightleftharpoons \mathrm{H^+} + \mathrm{Hasc^-},\ \log_{10}\mathrm{K_1} = -4.359 \pm 0.002$$

which could be obtained in a broad concentration range, without the suggestion of dimer, trimer, etc. species.

These titration data were also treated with *linear regression analysis.* Equation (4.91) was fitted to the data. We obtained very similar results to those discussed above.

For the forward titration:

$$\mathrm{SL(H, HAsc)} = -9.8\ \mathrm{mV\ M^{-1}\ HAsc^-}$$

$$\log_{10}\mathrm{K_1} = -4.356$$

For the back titration we obtained:

$$\mathrm{SL(H, HAsc)} = -8.8\ \mathrm{mV\ M^{-1}\ HAsc^-}$$

$$\log_{10}\mathrm{K_1} = -4.366$$

The average of $\log_{10}\mathrm{K_1}$ = - 4.361 ± 0.005

This system was also studied by Whalberg and Ulmgren [27] in the concentration range $0 \leq [\mathrm{H_2Asc}]_\mathrm{T} \leq 1$ M. The data were explained by assuming the following equilibrium processes:

(i) for $[\mathrm{H_2Asc}]_\mathrm{T} \leq 0.1$ M

$$\mathrm{Hasc^-} + \mathrm{H^+} \rightleftharpoons \mathrm{H_2Asc},\ \log_{10}\beta_1 = 4.359 \pm 0.006$$

$$\mathrm{Hasc^-} \rightleftharpoons \mathrm{Asc^2} + \mathrm{H^+},\ \log_{10}\beta_{11} = -11.342 \pm 0.007$$

(ii) for $[\mathrm{H_2Asc}]_\mathrm{T} \geq 0.25$ M

$$2\mathrm{Hasc^-} + \mathrm{H^+} \rightleftharpoons \mathrm{H_3Asc_2^-},\ \log_{10}\beta_{12} = 4.45 \pm 0.04$$

$$2\mathrm{Hasc^-} + 2\mathrm{H^+} \rightleftharpoons \mathrm{H_4Asc_2},\ \log_{10}\beta_{22} = 8.56 \pm 0.05$$

As is seen, our result for $\log_{10}\mathrm{K_1}$ is exactly the same as that obtained in Ref. [27] at a low concentration of $\mathrm{H_2Asc}$, namely ≤ 0.1 M. Hence, we can conclude that the species $\mathrm{H_3Asc_2}^-$ and $\mathrm{H_4Asc_2}$ are artefacts. They appear due to the neglect of important potential contributions at the explanation of the data. In Table 4.3, all the potential contributions to the total potential anomalies are gathered which are important in this system.

The $\log_{10}\mathrm{K_1}$ value in this system should be correctly calculated as given below [cf. Eq. (4.91)]

$$\begin{aligned}\log_{10} K_1 = (1/g)\{E_H - E_{0H} - SL(H, HL)[HL]_F - SL(H, L)[AL]_F - \text{corr}\} \\ + [D(I) - D(C)] - \log_{10}[c_{acid}/c_{salt}]\end{aligned} \tag{4.94}$$

By the neglect of the effect of the ligand ions on $\log_{10} K_1$, $SL(H, L)\,[AL]_F$, the caused systematic error in $\log_{10} K_1$ will be for the acid $H_q L$

$$\Delta \log_{10} K_1 = q\Delta \log_{10} h = q(1/g)SL(H, L)[AL]_F \tag{4.95}$$

This will result in monotonously increasing equilibrium constant, as is seen from Table 4.4. This effect will be interpreted as the formation of dimer, trimer, etc. species, which are artefacts.

As is seen, the value of the slope function $SL(H, HAsc^-)$ changes slightly with the experimental conditions. This is probably due to the influence of the undissociated molecules H_2Asc, which is not constant. Therefore, the titrations for the determination of SL(H, l) and the study of metal complex formation must be carried out in the same way.

Checking the Value of the Slope Function SL(H, H_2Asc)

The slope function $SL(H, H_2Asc) = 13$ mV M^{-1} H_2Asc was determined in Ref. [27], on the basis of the change of E_{0H} with $[H_2Asc]_T$. This slope function was checked by the author in the following mixture: 10 mM $HClO_4$, 0.100 M $Cd(ClO_4$ and 3 M $NaClO_4$. All of these concentrations were kept constant and H_2Asc was varied in the range 0.15 – 0.3 M. Here, we obtained

Table 4.4 The estimation of the systematic error in the first dissociation constant of the ascorbic acid ($\log_{10}K_1$) caused by the neglection of the potential contribution of the Hascorbate$^-$ ions to ΔE_H: $SL(H, HAsc^-)[HAsc^-]_F$ in mV and $\log_{10}$ units, using $NaClO_4$ ionic medium at $[Na^+] = 3$ M, constant. The slope $SL(H, HAsc^-) = -8.1$ mVM^{-1} was used

$[NaHAsc]_F$ / M	the neglected effect / mV	$\Delta\log k_1$ [cf. Eq. (4. 95)]
0.028 299	−0.23	−0.004
0.055 720	−0.45	−0.007
0.082 305	−0.66	−0.010
0.108 089	−0.87	−0.015
0.203 915	−1.65	−0.028
0.328 867	−2.66	−0.045
0.410 435	−3.32	−0.056
0.527 949	−4.27	−0.072
0.614 539	−4.98	−0.084
0.741 072	−6.00	−0.101

The correct value is at $[NaHAsc]_F = 0$ M: −4.359± 0.002
Wahlberg and Ulmgren found at low concentrations: −4.359± 0.006. [27]
Source: Reproduced by permission of the Royal Society of Chemistry from Néher-Neumann E (1999) Acta Chem Scand 53: 557–574 (Table 4).

$$SL(H, H_2Asc) = 22.9\ \text{mV}\ M^{-1}\ H_2Asc.$$

As is seen, the value of this slope function changes with the experimental conditions.

The Study of the H^+–Acetate$^-$ System

Study at Constant Ratio of c_{acid}/c_{salt}

A potentiometric titration was carried out at constant ratio of c_{acid}/c_{salt} , which was equal to 0.100. The buffer solution 0.3 M HAc (denotes acetic acid) and 3.000 M NaAc was used in the burette. The salt concentration in the test solution was varied within the range 0 – 1.3 M. The data were evaluated graphically, on the basis of Eq. (4.91). For the slope function SL(H, HAc), the value 6.7 mV M^{-1} HAc was used, determined by the author in a cell free from liquid junctions and at $[HClO_4]$ = 50 mM kept constant. The plot is shown in Fig. 4.4. The results given in Table 4.5 were obtained. The slope values SL(H, Ac) are valid in the buffer system used, while the function Q(H, Ac) in the case when dilute NaOH and HAc solutions are used in two burettes. From the intercept of the plot in question [cf. Eq. (4.91)], the following constant was obtained for the protolysis of acetic acid in 3 M $Na(ClO_4)$:

$$\log_{10} K_1 = -5.026 \pm 0.002$$

In the "Stability Constants" [28], the following values can be found:

$$\begin{aligned}\log_{10} K_1 &= -5.02 \pm 0.01\ [29]\\ &= -5.01\ [30]\end{aligned}$$

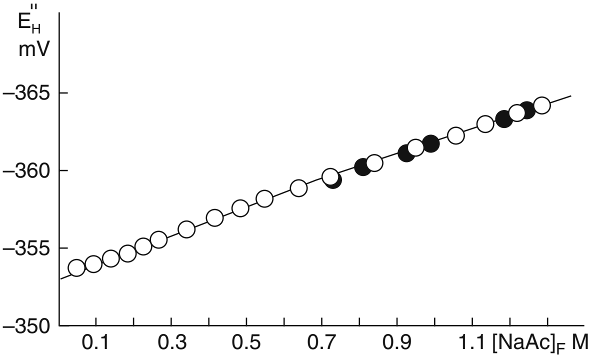

Fig. 4.4 The determination of the slope function SL(H, Ac) and the protolysis constant of the acetic acid, $\log_{10} K_1$, at constant ratio of (c_{acid}/c_{salt}) which was equal to 0.1000, and $[Na^+]$ = 3 M, is kept constant. The plot E_H'' vs. $[NaAc]_F$ is based upon Eq. (4.91). Filled symbols denote back titration. Reproduced by permission of the Royal Society of Chemistry from Néher-Neumann E (1999) Acta Chem Scand 53: 557–574 (Fig. 4)

Table 4.5 The determination of the slope function SL(H, Ac) and the function Q(H, Ac), using the plot defined by Eq. (4.91)

$[NaAc]_F$ M	SL(H, Ac) mV/M NaAc	Q(H, Ac) mV/M NaAc
0 – 0.58	−9.1	5.6
0.58 − 1.3	−7.7	7.1

Source: Reproduced by permission of the Royal Society of Chemistry from Néher-Neumann E (1999) Acta Chem Scand 53:557–574 (Table 5).

This titration data were also treated by linear regression analysis. Equation (4.91) was fitted to the data. The following results were obtained.

For the forward titration:

$$0 \le [\text{NaAc}] \le 0.58 \text{ M}$$

$$\text{SL(H, Ac)} = -9.3 \text{ mV M}^{-1} \text{ Ac}^-$$

$$\log_{10} K_1 = -5.024$$

$$0.58 \le [\text{NaAc}] \le 1.3 \text{ M}$$

$$\text{SL(H, Ac)} = -7.8 \text{ mV M}^{-1} \text{ Ac}^-$$

$$\log_{10} K_1 = -5.039$$

For the back titration:

$$\text{SL(H, Ac)} = -8.0 \text{ mV M}^{-1} \text{ Ac}^-$$

$$\log_{10} K_1 = -5.035$$

For the average value we obtained: $\log_{10} K_1 = - 5.033 \pm 0.006$.

As is seen, the same $\log_{10} K_1$ value was obtained as it was published by other scientists for low concentrations of HAc_T. No dimers or trimers were found, even though such species were reported in the literature. The neglection of the effect of the acetate ions on $\log_{10} K_1$ will result in monotonously increasing equilibrium constant, as is seen from Table 4.6. This can be interpreted as the formation of dimer species, which are artefacts.

Persson has investigated [30] this system in $NaClO_4$ ionic medium at $I = 3$ M, constant, in an emf cell with poles opposite to those discussed here. For the $[NaAc]_T$, the following values were used: 1000, 500, 250, 100, 50, 25, and 10 mM. The given constant was found in both a cell without and with liquid junction. In both cases, the author could describe the measurements by assuming the presence of the species HAc, Ac^-, HAc_2^- and $(HAc)_2$. However, he pointed out that the formation of the

Table 4.6 The estimation of the systematic error in the dissociation constant of the acetic acid ($\log_{10}K_1$)caused by the neglection of the potential contribution of the Acetate$^-$ ions to E_H: SL(H, Ac)$[Ac^-]_F$ in mV and $\log_{10}$ units, using $NaClO_4$ ionic meduim at $[Na^+] = 3$ M, constant

$[NaAc]_F$ / M	The neglected effect / mV	$\log K_1 + \Delta \log K_1$ [cf. Eqn. (66)]
0.047 408	−0.43	−5.036
0.093 341	−0.85	−5.039
0.264 822	−2.41	−5.060
0.552 207	−5.02	−5.112
1.069 835	−8.24	−5.180
1.322 198	−10.18	−5.212

The correct value is at $[NaAc]_F = 0$ M: −5.026±0.002. Reproduced by permission of the Royal Society of Chemistry from Néher-Neumann E (1999) Acta Chem Scand 53:557–574 (Table 6).

dimers is the result of the neglected diffusion potential and the changes of the activity factors. This conclusion is correct. The potential anomalies given below have existed in his system, in a cell with liquid junction:

$$\mathrm{SL(H, HAc)} = -6.7\ \mathrm{mV\ M^{-1}HAc}\ \ \text{and}\ \ \mathrm{SL(H, Ac)} = 7.7\ \mathrm{mV\ M^{-1}\ NaAc}$$

As is seen, the maximum value of the systematic error, at $[NaAc]_T = 1$ M, is 7.7 mV in this study. This is the explanation for the formation of the dimers.

In Persson's cell, free from liquid junctions, the following potential contributions have existed, which he neglected.

$$\begin{aligned} E_H = {} & E_{0H} - g\ \log_{10}[H^+] - g\ \log_{10} f_H - g\ \log_{10}[Cl^-] - g\ \log_{10} f_{Cl} \\ & - \mathrm{SL(H, HAc)[HAc]} \end{aligned} \tag{4.96a}$$

We can write according to the specific interaction theory [6, 11–17]

$$\begin{aligned} \log_{10} f_H = {} & -[D(I) - D(3)] + \varepsilon''(H,\ ClO_4)(c_Y - 3) \\ & + \varepsilon''(H, Ac)[NaAc]_T + \varepsilon''(H, Cl)[Cl^-] \end{aligned} \tag{4.96b}$$

$$\log_{10} f_{Cl} = -[D(I) - D(3)] + \varepsilon''(Na, Cl)(c_{Na} - 3) + \varepsilon''(H, Cl)[H^+] \tag{4.96c}$$

As is seen, these activity factors are not constant. Here, ε'' (H, ClO_4) = 0.18 liter solution mol^{-1} solute, ε''(H, Ac) = 0.12 liter solution mol^{-1} solute and $\varepsilon''(Na, Cl) \cong$ 0.03 liter solution mol^{-1} solute, determined by the author [31].

As is seen, the systematic errors are of different kinds and magnitudes in the two cells studied by Persson. Consequently, he has found different equilibrium constants for the dimers in the two different cells.

Study at Constant Level of HAc

Some titrations were carried out at constant level of acetic acid too, where the slope function SL(H, Ac) was studied. The purpose of these experiments was to show how the magnitude of this slope function changes with the experimental conditions.

In one case, we chose $[\mathrm{HAc}]_F = 0.010$ M, is kept constant. Here, we obtained the following slope functions.

$$0 \leq [\mathrm{NaAc}]_F \leq 90\ \mathrm{mM},$$

$$\mathrm{SL(H, Ac)} = -28.2\ \mathrm{mV\ M^{-1}\ Ac^-}$$

$$90 \leq [\mathrm{NaAc}]_F \leq 215\ \mathrm{mM},$$

$$\mathrm{SL(H, Ac)} = -11.2\ \mathrm{mV\ M^{-1}\ Ac^-}$$

$$215 \leq [\mathrm{NaAc}]_F \leq 450\ \mathrm{mM},$$

$$\mathrm{SL(H, Ac)} = -8.3\ \mathrm{mV\ M^{-1}\ Ac^-}$$

In another titration, we chose $[\mathrm{HAc}]_F = 1.000$ M, is kept constant. The slope function

$$\mathrm{SL(H, Ac)} = -9.5\ \mathrm{mV\ M^{-1}\ Ac^-}$$

was obtained in the concentration range $0 \leq [\mathrm{NaAc}]_F \leq 250$ mM. These variations in the slope correspond to the change of the ionic molar conductivities. This should be checked by conductivity measurements. According to the opinion of the author, this phenomenon can be connected either to the different isolation effects of the undissociated molecules HL in the different titrations or to the change of the activity factor of these molecules.

It can be noted that Olin and Svanström have also studied [32] the appearance of the liquid junction potential in the H^+-Acetate$^-$ system, using buffer solutions at different c_{acid}/c_{salt} ratios, which were kept constant during the titrations of one series. They evaluated the data graphically, in a similar way as we did. It is seen from their plots, also, that the slope function SL(H, Ac) is different at the different ratios studied. Moreover, they have modelled the influence of varying liquid junction potentials and activity coefficients on calculated stability constants of the Pb^{2+}-benzoate, Cd^{2+}-benzoate and Pb^{2+}-acetate complexes. They found that "liquid junction potentials and activity coefficient changes can have considerable effect on the numerical values of stability constants obtained from emf measurements of central ion concentrations. Realistic estimates of the uncertainties in these constants can therefore be obtained only by a study of these influences".

Checking the Value of the Slope Function SL(H, HAc)

The value of the slope function SL(H, HAc) was also checked in two different cells.

(a) In a cell with liquid junction, the test solution contained $[HClO_4] = 50$ mM, kept constant, 3 M $NaClO_4$, kept constant, and $[HAc]_F$ was varied in the range: 0 – 0.45 M. Here, we obtained

$$0 \leq [HAc]_F \leq 180 \text{ mM},$$

$$SL(H, HAc) = 2.2 \text{ mV M}^{-1} \text{ HAc}$$

$$180 \leq [HAc]_F \leq 450 \text{ mM},$$

$$SL(H, HAc) = 3.0 \text{ mV M}^{-1} \text{ HAc}$$

(b) In the cell given below, free from liquid junctions,
Ag, AgCl | Test solution | glass electrode
at $[HClO_4] = 50$ mM, kept constant, and $[Cl^-] = 10$ mM, kept constant, the following results were obtained:

$$0 \leq [HAc]_F \leq 90 \text{ mM},$$

$$SL(H, HAc) = 7.4 \text{ mV M}^{-1} \text{ HAc}$$

$$90 \leq [HAc]_F \leq 390 \text{ mM},$$

$$SL(H, HAc) = 8.4 \text{ mV M}^{-1} \text{ HAc}$$

As is seen, *the potential contribution of the undissociated molecules HL to ΔE_H is not clear and not constant.* Therefore, experiments in which slope functions and the protolysis constant of HL are determined, and the formation of metal ion complexes are studied, *must be carried out under the same experimental conditions. The author suggests that one should carry out potentiometric titrations in such a way that a buffer solution is used as a titrating solution, in which the concentration of the HL molecules is kept constant during the titration.*

4.2.1.4 Survey of the Potential Functions for the Calculation of the Second Protolysis Constant of the Weak Acid H_2L

Deduction for $pK_2 - pK_1 \geq 5$

The treatment which is going to be described, here, is valid for the case when the protolysis constants $\log_{10} K_1$ and $\log_{10} K_2$ are *well separated,* namely, by at least 5 $\log_{10}$ units.

We shall study the equilibrium

$$HL^- \rightleftharpoons H^+ + L^{2-}, \quad K_2 = [H^+]\,[L^{2-}]/[HL^-] \tag{4.97}$$

in the ionic medium AY at the experimental condition that $[A^+] = C$ M, is kept constant. First, we determine the constant E_{0H} in the absence of the ligand, as discussed in Section 4.2.1.2, for the case when a buffer titrating solution is used in the main titration. The composition of this can be: 0.2 M AHL + 1 M A_2L + 0.8 M AY. In our equilibrium solution, the following ions are present: H^+, $[HL^-] \cong c_{acid}$, $l = [L^{2-}] \cong c_{salt} = L_T$, Y^- and A^+ both at the concentration of C M. The acidity of the test solution can be calculated as

$$\log_{10}[H^+] = \log_{10} K_2 - \log_{10}(c_{salt}/c_{acid}) \tag{4.98}$$

The composition of the test solution is also described in Section 4.1. In the deduction, the species H^+ and L^{2-} are considered as components, and HL^- as a complex denoted $L_{k=2}$ in the general treatment.

Two deductions were made:

a) according to the "Deduction of the general equations" (cf. Section 4.1.),
b) using the known slope functions SL(H, HL^-) and SL(H, L^{2-}), the later to be presented here.

Deduction According to the General Theory

The potential functions E_D , E_{Df} and the total cell emf, E_H , were derived. Knowing these functions, we have

$$\log_{10} K_2 = (1/g)\,[E_H - g\ \log_{10}(c_{acid}/c_{salt}) - g\ \log_{10} f_{HTS2} - E_D - E_Df - E_0H] \tag{4.99}$$

As these functions are rather complicated, we prefer the determination of $\log_{10} K_2$ through the slope functions.

Determination of $\log_{10} K_2$ Using Known Slope Functions

$\log_{10} K_2$ can also be determined in the buffer system AHL – A_2L given above, from the known slope function SL(H, HL^-) and SL(H, L^{2-}). The potentiometric titration can be carried out at the constant ratio of c_{acid}/c_{salt}. In this case, the test solution is essentially a mixture of the strong electrolytes AHL, A_2L and AY. We have the same species present as given above. The total cell emf in this system is

$$\begin{aligned} E_H = {} & E_0H + g\ \log_{10} h - g\,[D(I) - D(C)] + SL(H, HL^-)\ c_{acid} \\ & + SL(H, L^{2-})\ c_{salt} + corr \end{aligned} \tag{4.100}$$

Inserting $\log_{10}h$ from Eq. (4.98) into this equation, we can form the function E_H'' and neglect corr

$$\begin{aligned} E_H'' \equiv\ & E_H + g\ \log_{10}(c_{salt}/c_{acid}) + g\ [D(I) - D(C)] - SL(H, HL^-)c_{acid} \\ & = E_{0H} + g\ \log_{10} K_2 + SL(H, L^{2-})\ c_{salt} \end{aligned} \quad (4.101)$$

The slope $SL(H, HL^-)$ can be determined as in the buffer system H_2Asc – NaHAsc, described in "Titration by Adding a Buffer Solution", according to Eq. (4.91). Plotting the function E_H'' versus c_{salt}, $\log_{10} K_2$ can be calculated from the intercept. The slope of this plot is $SL(H, L^{2-})_{exp}$.

For the calculation of the theoretical slope function SL (H, L^{2-}), the potential function for the total cell emf has been derived. For the system AHL + A_2L + AY and small values of (w/a), we have

$$w = h\lambda_H + \Delta c_Y\lambda_Y + HL_T{}^-\lambda_{HL}|z_{HL}| + yL_T\lambda_L \quad (4.102)$$

$$\log_{10} f_{HTS2} = -[D(I) - D(C)] + \varepsilon''\ (H, L)\ L_T + \varepsilon''\ (H, HL)\ HL_T{}^- + \Delta c_Y\ \varepsilon''(H, Y) \quad (4.103)$$

$$\Phi_1\ (x) = x\ [-h\lambda_H + HL_T{}^-\lambda_{HL} + L_T\lambda_L\ y^2 + \Delta c_Y\lambda_Y] + C\ (\lambda_Y - \lambda_A) \quad (4.104)$$

For the total cell emf in Cell H, we obtain Eq. (4.100), where the function $SL(H, HL^-)$ is defined by Eq. (4.89) and the theoretical function $SL(H, L^{2-})$ is

$$\begin{aligned} SL(H, L^{2-}) = g\ [\varepsilon''(H, L) - y\ \varepsilon''(H, Y)] + g\ (\lambda_L - y\lambda_Y)/ \\ [2.303\ C\ (\lambda_A + \lambda_Y)] - g\ t_A\ [\varepsilon''(A, L) - y\ \varepsilon''(A, Y)] \end{aligned} \quad (4.105)$$

Here, y = absolute value of z_L. These equations are valid for the buffer system studied. If we use AOH and H_2L or A_2L titrating solutions, we have to recalculate $SL(H, L^{2-})$ into $Q(H, L^{2-})$. We form the difference function $Q(H, L^{2-}) - SL(H, L^{2-})$ = Eq. (4.53) – Eq. (4.105). From here, we obtain

$$Q(H, L^{2-}) = SL(H, L^{2-})_{exp} + g\ y\ \varepsilon''(H, Y) + g\ y\ F_0\ \lambda_Y - g\ t_A y\ \varepsilon''\ (A, Y) \quad (4.106)$$

where

exp denotes experimental, F_0 is given by Eq. (2.5), t_A by Eq. (2.6).

Deduction for $pK_2 - pK_1 < 5$

If the two steps of the protolysis of H_2L are not well separated, only a brutto dissociation constant can be calculated:

$$\beta_{qr} = K_1.K_2 = [H^+]^2\ [L^{2-}]/[H_2L] \quad (4.107a)$$

If this is the case, it can be seen from the shape of a titration curve obtained from a titration with dilute NaOH solution. The jumps in the plot of E_H versus v ml NaOH added show the number of equivalence points we have in the system. If we have only one, then only β_{qr} can be determined. This can be done as to be described in "Deduction for pK_2 - $pK_1 < 5$" in Section 4.3.1.4. In this case, we should use a buffer titrating solution of the composition, e.g.:

$$c_{acid} \cong [H_2L] = 0.1 \text{ M } H_2L,$$

$$c_{salt} \cong [L^{2-}] = L_T = 1 \text{ M } A_2L,$$

$$C - 2\, L_T \text{ M AY}.$$

4.2.2 *Emf Studies on Weak Complex Formation at $[A^+] = C$ M, Constant*

Such studies include investigations on both mixtures of strong electrolytes (for the determination of the experimental constants E_{0B} and E_{0H}) and equilibrium systems. This means emf studies on the strong electrolyte mixtures HY – AY – $BY_{z(B)}$ and on the equilibrium systems HY – $BY_{z(B)}$ – AY – A_yL. These studies were described in the previous chapters, concerning formation of strong complexes.

Weak complex formation means that the average number of moles of H^+ or OH^-groups bound per B_T, defined as $Z = (H_T - h)/B_T$ or $Z = (h - H_T)/B_T$, respectively, is very low. For example, $0 \leq Z \leq 0.02$ at the hydrolysis of the La^{3+} ion [33]. It is assumed that the species $B_p(OH)_q$ are formed. These species bound only 1–2 % of the total metal ion concentration, B_T, in weak metal ion complexes. In order to measure such small effects accurately, it is necessary to use high metal ion concentrations. Such method was developed by Hietanen and Sillén [34], the so-called "self-medium method" for the experimental condition $[Y^-] = C$ M, constant. This will be discussed in the next chapter.

If we want to use this experimental condition, $[A^+] = C$ M, constant, $B_T = 0.1 - 0.2$ M can be used for the concentration of the central metal ion. In these cases, the approximation $b = [B^{z(B)+}] \cong [BY_{z(B)}] = B_T = c_B$ M can be used, first. This means that the formation of weak metal ion complexes is neglected, at first. But we cannot neglect the contribution of the total potential anomalies. Especially important are, e.g. with Cell H, the composition change of the inert ionic medium, the potential term $Q(H,\Delta c_Y)\Delta c_Y$, the terms gd_3c_B at the determination of E_{0H}, and $Q(H, c_B)B_T$. As conductivity data are generally not available, E_{0H} should be determined in the absence of the $B^{z(B)+}$ ions. Conditional experimental constants, E_{0B1} and E_{0H1}, cannot be used.

With the approximation mentioned above, the system is reduced to be the mixture of strong electrolytes. Only the species $B^{z(B)+}$, L^{y-}, A^+ and Y^- are considered. This is the same condition as used at the formation of strong complexes for the preliminary data treatment. The derived equations for E_B and E_H are valid here, as well.

For example, for a titration with Cell B, where weak complexes are formed with a ligand from a weak acid, if H_yL and AOH are used in separate burettes, the following potential functions are valid.

The composition of the test solution (TS2) is:

$$h = [H^+]\ M;\ b = [B^{z(B)+}] \cong B_T\ M;\ l = [L^{y-}]\ M$$

$$c_A = [A^+] = C = [AY] + AOH_T \tag{4.107b}$$

$$c_Y = C - AOH_T + z_B\ c_B + HY_T \tag{4.107c}$$

$$\Delta c_Y = c_Y - C = z_B\ c_B + R^x \tag{4.107d}$$

where

$$R^x = HY_T - AOH_T \tag{4.107e}$$

For the total cell emf, we have

$$E_B = E_{0B} + (g/z_B)\ \log_{10} c_B + \Sigma_V\ Q(B, V)V$$

where $V = b = c_B$, h, l, andΔc_Y

The function $Q(B, c_B)$ is given by Eq. (4.45) and $Q(B, \Delta c_Y)$ by Eq. (4.47). The total potential contribution of the $B^{z(B)+}$ ions to E_B is:

$$Q(B, c_B)\ c_B + Q(B, \Delta c_Y)\ z_B\ c_B = Q(B, c_B)^x\ c_B \tag{4.107f}$$

Considering Eqs, (4.45), (4.47) and (4.107 d), we obtain

$$Q(B, c_B)^x = g\varepsilon''(B, Y) + g\ F_0(z_B\lambda_Y - \lambda_B) + g\ t_Y\varepsilon''(B, Y) - g\ z_B\ t_A\varepsilon''(A, Y) \qquad (4.107)g$$

Moreover, we have

$$Q(B, \Delta c_Y)\ R^x = Q(B, R^x)\ R^x = [(g/z_B)\varepsilon''(B, Y) + g\ F_0\lambda Y - g\ t_A\varepsilon''\ (A, Y)]\ R^x, \qquad (4.107)h$$

Q(B, l) is given by Eq. (4.46).

Hence, the total potential anomalies are

$$\Delta E_B = -g\ z_B\ [D(I) - D(C)] + Q(B, c_B)^x\ c_B + Q(B, l)l + Q(B, R^x)R^x + \text{corr} \tag{4.107i}$$

In Ref. [18], a number of titrations were investigated by the author, where weak complexes are formed, using Cells B and H, respectively. Potential functions are derived. Conditional E_{0H} is supposed to be determined. This is wrong. *The statement that the potential contributions of the B $^{z(B)+}$ ions to E_H,* gd$_3$ c_B *and the term* Q(H, c_B)c_B, *can be incorporated into E_{0H}, is the result of a misunderstanding. The reported formation of polynuclear complexes is erroneous.* These terms are constant in a given titration, but are different in another. These contributions are a function of b$\cong$ B_T. This causes a large systematic error in E_{0H} and in the equilibrium constants.

4.3 Emf Cells Where [Y$^-$] = C M, Constant [35]

We study the equilibrium processes

$$\mathrm{q\,H + r\,L^{y-} \rightleftharpoons H_q\,L_r} \tag{I}$$

$$\mathrm{p\,B + q\,H + r\,L^{y-} \rightleftharpoons B_p\,H_q\,L_r} \tag{II}$$

$$\mathrm{p\,B + q\,H_2O \rightleftharpoons B_p\,(OH)_q + q\,H} \tag{III}$$

in the system $BY_{z(B)}$- HY – A_yL – AY using Cells B and H. We consider, first, only the presence of the H^+, $B^{z(B)+}$, L^{y-} , A^+ and Y^- ions, for the preliminary data treatment. The composition of the test solution in equilibrium is given in Section 4.1. Definitions and symbols used in equilibrium solutions are also given there. The ion concentrations of the ionic medium in the test solution are, after the determination of the constants E_{0B} and E_{0H}, respectively,

for CELL B:

$$c_Y = C\,M = [AY] + HY_T + z_B\,B_T \tag{4.108a}$$

$$[AY] = C - HY_T - z_B\,B_T \tag{4.108b}$$

$$c_A = [AY] + y\,L_T = C - HY_T - z_B\,B_T + y\,L_T \tag{4.108c}$$

$$\Delta c_A = c_A - C = -HY_T - z_B\,B_T + y\,L_T \tag{4.108d}$$

For CELL H:

$$c_A = [AY] + y\,L_T + AOH_T = C - HY_T - z_B\,B_T + y\,L_T + AOH_T \tag{4.109}$$

$$\Delta c_A = c_A - C = AOH_T - HY_T - z_B\,B_T + y\,L_T \cong -z_B\,B_T + y\,L_T \tag{4.110}$$

We follow the same treatment as in Section 4.2.

For the activity factors we have, at some intermediate plane in the transition layer without approximation,

$$\log_{10} f_J^* = -z_J^2\,[D(I^*) - D(C)] + [\Sigma_k \varepsilon''(J, L_k)\, l_k^* + \Sigma_j \varepsilon''(J, N_j) n_j^*]_{ca} + [\varepsilon''(J, H)h^* + \varepsilon''(J, B)b^* + \varepsilon''(J, A)\,(c_A^* - C) + \Sigma_i \varepsilon''(J, P_i) p_i^*]_{an} \quad (4.110a)$$

where $[\ldots]_{ca}$ = the terms to be used if J is a cation,

$[\ldots]_{an}$ = the terms to be used if J is an anion.

I^* is defined by Eq. (1.24).

The sum of the Debye–Hückel coefficients in the potential function E_{Df} is

$$\Phi_1\,(x) = x(-h\lambda_H - z_B{}^2 b\lambda_B - \Delta c_A \lambda_A + l\, z_L{}^2\, \lambda_L) + C(\lambda_Y - \lambda_A) \qquad (4.110b)$$

4.3.1 Emf Studies Where Strong Complexes Are Formed

4.3.1.1 Studies on the Formation of Metal Ion Complexes According to Section 4.2.1.1

The Total Emf for Cell B

The total emf for Cell B is given by Eq. (4.41), where V = h, b, l , Δc_A. Δc_A is defined by Eq. (4.108d), and the Q(B, V) functions by Eqs. (4.44), (4.45) and (4.46). Moreover,

$$Q(B, \Delta c_A) = -g\, \lambda_A/[2.303\, C\, (\lambda_A + \lambda_Y)] + g\, t_Y \varepsilon''(A, Y) \qquad (4.111)$$

The Total Emf for Cell H

The total emf for Cell H is given by Eq. (4.57), where V = b, h, l, Δc_A, again. Δc_A is defined by Eq. (4.110), and the functions Q(H, V) by Eqs. (4.51), (4.52) and (4.53). Moreover,

$$Q(H, \Delta c_A) \equiv Q(B, \Delta c_A),\ \text{cf. Eq.(4.111.)}$$

The value of this function was found to be, for $NaClO_4$ ionic medium:

$$Q(H, \Delta c_A) = -2.67\ \text{mV}\ M^{-1}\ (\Delta c_A)$$

This is much smaller than the effect of the composition changes of the ionic medium at the experimental condition $[Na^+] = 3$ M, constant.

The Effect of the Composition Changes of the Ionic Medium on the Total Potential Anomalies and on the Equilibrium Constants for Cell H

The effect of the composition change of 3 M $NaClO_4$, defined as $Q(H,\Delta c_A)\ \Delta c_A$, on the equilibrium constants, $\Delta \log_{10} \beta_{pqr}{}^{(2)} = q\,(1/g)\, Q(H,\Delta c_A)\, \Delta c_A$, for two sets of *usual emf titrations* where $B_T \leq 0.1$ M, is given in Table 4.7.

Table 4.7 The effect of the composition changes of 3 M $NaClO_4$ on the equilibrium constants, when strong complexes are formed in Cell H, for two sets of usual emf titrations, at t = 25°C and $[ClO_4^-]$= C M, is kept constant

				$\Delta\log_{10}\beta_{pqr}^{(2)} = q(1/g)\,Q(H, \Delta c_A)\,\Delta c_A$		
B_T M	L_T M	$\sim\Delta c_A$ M	$Q(H, \Delta c_A)\Delta c_A$ mV	q=1	q=2	q=3
For $z_B = 2$						
0.010	0.050	0.03	−0.08	−0.001	−0.003	−0.004
0.030	0.100	0.04	−0.11	−0.002	−0.004	−0.006
0.050	0.150	0.05	−0.13	−0.002	−0.004	−0.006
0.100	0.300	0.100	−0.27	−0.004	−0.009	−0.012
For $z_B = 3$						
0.010	0.050	0.02	−0.05	0	0	0
0.030	0.100	0.01	−0.03	0	0	0
0.050	0.150	0	0	0	0	0
0.100	0.300	0	0	0	0	0

As is seen from this table, the systematic errors in E_H are small for $z_B = 2$ and change within the range (− 0.08) – (− 0.27) mV, and the corresponding systematic errors in the equilibrium constants are also small. For $z_B = 3$, these errors are nearly zero. **This cell and the experimental conditions used are the best for studying metal ion complex formation.**

In order to reach $\Delta E_H = 0.01$ mV for the total potential anomalies, a small correction is necessary for the composition change of the ionic medium, $Q(H,\Delta c_A)\,\Delta c_A$, and the potential contributions of the $B^{z(B)+}$ and L^{y-} ions to ΔE_H, namely, Q(H, b) b and Q(H, l) l , must also be taken into account. The term Q(H, h) h is probably negligible. The terms mentioned can be estimated through the difference functions

(a) Q(H, l) – SL(H, l), and knowing $SL(H, l)_{exp}$ [cf. Eqs. (4.53), (4.129), (4.130) and (4.131)],

(b) Q(H, b) - $SL(H, c_B)_1$, and knowing $SL(H, c_B)_{1exp}$.

Hence,

$$Q(H, b) - SL(H, c_B)_1 = \text{Eq. (4.52)} - g\ \text{Eq. (2.28)} = -g\, z_B\lambda_A/[2.303\, C\, (\lambda_A + \lambda_Y)] + g\, t_Y\varepsilon''(A, Y)\, z_B = \text{difference function} \tag{4.112}$$

From here,

$$Q(H, b) = SL(H, c_B)_{1\,exp} + \text{the difference function} \tag{4.113}$$

where

$SL(H, c_B)_{1\,exp}$ is the slope of the plot $E_H' = E_H - g\log_{10} c_H + g\,[D(I) - D(C)]$ versus c_B, at constant c_H, determined in Mixture 1.

$SL(H, c_B)_1 = g\,d_3$, where $d_3 = d_1$ given by Eq. (2.28).

4.3.1.2 Survey of the Potential Functions for the Protolysis of the Weak Acid HL, According to Section 4.2.1.2

The following protolysis equilibrium is studied

$$HL \rightleftharpoons H^+ + L^-, \quad K_1 = [H^+]\,[L^-]/[HL] \tag{4.114}$$

This can be done in two ways:

(a) by titration with dilute NaOH solution, when the concentration of the weak acid is kept constant during the titration,
(b) by titration with a buffer solution HL – AL.

Titration by Adding Dilute NaOH Solution

First, the experimental constant E_{0H} should be determined through an acid – base titration, in the presence of HL of a constant level (cf. Section 4.2.1.2.). The titration should be evaluated with a Gran plot [26]. Then we can decrease the volume of the test solution (to v_0^x) by sucking out a portion of solution with a calibrated pipette. After that, two solutions should be added, in equal volumes, with the composition:

$$S_1 : HY_1 = [H^+],\ \text{is present in trace amounts}$$
$$2c_{HL} = [HL]$$
$$c_{AY1} = C - HY_1,\ \text{the concentration of the ionic medium}$$
$$S_2 : c_{AOH2} = [AOH]$$
$$c_{AY2} = C\ M$$

For the composition of the ionic medium in the test solution, we have now

$$c_Y = [Y^-] = C\ M,\ \text{is kept constant} = [AY] + HY_T \tag{4.115a}$$
$$c_A = [A^+] = C - HY_T + AOH_T\ M = C + \Delta c_A \tag{4.115b}$$

where

$$\Delta c_A = c_A - C = AOH_T - HY_T \tag{4.115c}$$

The necessary equations for the deduction of the value ΔE_H, valid in this system, can be obtained from the potential functions derived for metal ion complex formation, presented in Ref. [35]. Here, we give only the final results for some important functions. We have the species

$$H^+, L^-, HL, \ A^+ \text{and } Y^- \text{in the test solution.}$$

$$I = C + (1/2)\,(h + \Delta c_A + l\,y^2)$$

$$w = h\lambda_H + \Delta c_A\lambda_A + y\,l\,\lambda_L$$

$$\log_{10} f_{HTS2} = -[D(I) - D(C)] \ + \varepsilon''(H, L)\,l$$

$$\Phi_1\,(x) = x\,(-h\lambda_H - \Delta c_A\lambda_A + l\,\lambda_L y^2) + C\,(\lambda_Y - \lambda_A)$$

$$a = C(\lambda_A + \lambda_Y)$$

For small values of w/a we obtained:

$$E_H = E_{0H} + g\ \log_{10} h - g\,[D(I) - D(C)] + g\,\varepsilon''(H, L)\,l - g\,F_0[h\lambda_H + \Delta c_A\lambda_A - l\lambda_L] - g\,t_A\varepsilon''(A, L)l + g\,t_Y[\varepsilon''(H, Y)\,h + \varepsilon''(A, Y)\Delta c_A] + \text{corr} \tag{4.116}$$

This equation can even be written as

$$E_H = E_{0H} + g\ \log_{10} h + \Delta E_H \tag{4.117a}$$

where

$$\Delta E_H \equiv g\ \log_{10} f_{HTS2} + E_D + E_{Df} = \ -g\,[D(I) - D(C)] + Q(H, l)\,l + Q\,(H, \Delta c_A)\Delta c_A + SL(H, \text{acid})\,[HL] + \text{corr} \tag{4.117b}$$

From Eqs. (4.117a) and (4.117b), h can be calculated by successive approximations knowing E_{0H} and the functions which are included. The function Q(H, l) can be calculated by Eq. (4.53), from the ionic molar conductivities involved and measured in the equilibrium solution studied, as well as some interaction coefficients. Another possibility is to estimate an approximate Q(H, l) function through the slope function SL(H, l) [cf. Eq. (4.129)] to be determined below. The function $Q(H,\Delta c_A)$ can be calculated from Eq. (4.111), as $Q(H,\Delta c_A\ ) \equiv Q(B,\Delta c_A)$, as it was found in Ref. [35]. The slope function SL(H, acid) can be obtained as the slope of the plot E_H – g $\log_{10}$ h versus $[H_yL]_T$, at constant c_H, in a solution where, e.g. [HY] = 0.050 M, constant, and $[Y^-]$ = C M, is kept constant.

Knowing h, the equilibrium constant, $\log_{10} K_1$, can be obtained by either graphical methods or a curve-fitting computer program.

Titration by Adding a Buffer Solution

After the determination of E_{0H}, in the absence of HL, we can continue the titration by adding a buffer solution of the composition: e.g. 0.1 M HL, 1.8 M AL, C M AY.

For the composition of the ionic medium in the test solution, we have

$$\begin{gathered} \mathrm{c_Y = [Y^-] = C\ M,\ is\ kept\ constant, = [AY] + HY_T} \\ \mathrm{c_A = [A^+] = [AY] + AOH_T + y\ L_T = C - HY_T + AOH_T + y\ L_T} \\ \mathrm{\Delta c_A = c_A - C = y\ L_T + AOH_T - HY_T} \end{gathered} \tag{4.118}$$

where $\mathrm{AOH_T - HY_T \cong 0}$ at the end of the $\mathrm{E_0}$ – titration. As $\mathrm{[AL] \equiv L_T >> [HL]}$, the approximations valid in a buffer system can be used (cf. Section 1.1) and

$$\mathrm{\log_{10}[H^+] = \log_{10} K_1 - \log_{10}(c_{salt}/c_{acid})} \tag{4.119}$$

The deduction of $\mathrm{E_H}$ was done in Ref. [35]. Here, we give only the final results for some important functions.

$$\mathrm{I = C + (1/2)(h + y\ L_T + AOH_T - HY_T + y^2\ L_T} \tag{4.120}$$

$$\mathrm{w = h\lambda_H + [y\ L_T + AOH_T - HY_T]\lambda_A + y\ L_T\lambda_L} \tag{4.121}$$

$$\mathrm{\log_{10} f_{HTS2} = -[D(I) - D(C)] + \varepsilon''(H, L)\ L_T} \tag{4.122}$$

$$\mathrm{\Phi_1\ (x) = x\ [-h\ \lambda_H - \lambda_A(y\ L_T + AOH_T - HY_T) + y^2\ L_T\ \lambda_L] + C\ (\lambda_Y - \lambda_A)} \tag{4.123}$$

For small values of w/a, we obtain

$$\begin{aligned} \mathrm{E_H} \cong{} & \mathrm{E_{0H} + g\ \log_{10} h - g\ [D(I) - D(C)] + g\varepsilon''(H, L)\ L_T - g\ F_0[h\ \lambda_H} \\ & \mathrm{+ \lambda_A(y\ L_T + AOH_T - HY_T) - L_T\lambda_L] - g\ t_A\varepsilon''(A, L)L_T + g\ t_Y[\varepsilon''(HY)h} \\ & \mathrm{+ \varepsilon''(A, Y)(y\ L_T + AOH_T - HY_T)] + corr} \end{aligned} \tag{4.124}$$

According to an earlier treatment of the problem, we have, considering $\mathrm{h \cong 0}$,

$$\mathrm{E_H \cong E_{0H} + g\ \log_{10} h + SL(H, acid)\ [HL] - g\ [D(I) - D(C)] + SL(H, l)\ l + corr} \tag{4.125}$$

where

$$\begin{aligned} \mathrm{\Delta E_H = g\ \log_{10} f_{HTS2} + E_D + E_{Df}} ={} & \mathrm{-g\ [D(I) - D(C)] + SL(H, l)\ l} \\ & + SL(H, acid)\ \mathrm{c_{acid} + corr} \end{aligned} \tag{4.126}$$

Inserting g $\log_{10}$ h from Eq. (4.119) into Eq. (4.125), we have

$$\begin{aligned} \mathrm{E_H''} \equiv{} & \mathrm{E_H + g\ \log_{10}(c_{salt}/c_{acid}) + g\ [D(I) - D(C)] - SL(H, acid)c_{acid}} \\ & \mathrm{- corr = E_{0H} + g\ \log_{10} K_1 + SL(H, l)\ L_T} \end{aligned} \tag{4.127}$$

where

$$\mathrm{the\ intercept = constant = E_{0H} + g\ \log_{10} K_1} \tag{4.128}$$

Plotting E_H'' versus $l = L_T$, the slope is SL(H, l). From the intercept, the protolysis constant, $\log_{10} K_1$, can be calculated.

The theoretical slope function can be obtained as

$$SL(H, l) \equiv d\, E_H''/d\, l = g\varepsilon''(H, L) - g\, F_0(y\lambda_A - \lambda_L) - g\, t_A\varepsilon''(A, L) + g\, t_Y\varepsilon''(A, Y)\, y \tag{4.129}$$

cf. Eqs. (4.124) and (4.127). If we want to recalculate SL(H, l) into an approximate function of Q(H, l), we should calculate the difference function as given below.

$$Q(H, l) - SL(H, l) = \text{Eq. (4.53)} - \text{Eq. (4.129)} = g\, F_0\lambda_A\, y - g\, t_Y\varepsilon''(A, Y)\, y \tag{4.130}$$

Then we have

$$Q(H, l) = SL(H, l)_{exp} + g\, F_0\lambda_A\, y - g\, y\, t_Y\varepsilon''(A, Y) \tag{4.131}$$

where exp denotes experimental.

For the calculation of the slope function Sl(H, l), we need the ionic molar conductivities determined in the present mixture. It can be done in a similar way as discussed in “Estimation Through Conductivity Measurements” of Section 4.2.1.1.2. and in Ref. [21].

The experimental value for SL(H, l) can be obtained through the graphical treatment discussed above. In order to improve the constancy of the ionic molar conductivities involved in the slope function SL(H, l), the linearity of the experimental slope must be checked.

The interaction coefficient $\varepsilon''(H, L)$ and $\varepsilon''(A, L)$ can be determined by emf titrations as suggested by the author in Ref. [31].

In order to be able to calculate accurate functions of Q(H, V), we need to carry out conductivity measurements.

4.3.1.3 Experimental Studies

The Determination of $\log_{10} K_1$ for the Acetic Acid and the Slope Function SL(H, Acetate$^-$) in a HAc–NaAc Buffer

Constant Level of HAc is Used

First, E_{0H} should be determined through an acid–base titration, at a constant level of HAc, e.g. 0.1 M. For this titration, the following function is valid.

$$\begin{aligned} E_H = E_{0H} + g\ \log_{10} h - g\,[D(I) - D(C)] + SL(H, \text{acid})\,[CH_3COOH]_T \\ + g\, c_H(d_4 \equiv d_2) + \text{corr} \end{aligned} \tag{4.132}$$

where the function d_4 is given by Eq. (2.29). Plotting $\{E_H - g \log_{10} h + g\,[D(I) - D(C)] - SL(H, \text{acid})\,[CH_3COOH]_T - \text{corr}\}$ versus c_H, we shall obtain E_{0H} as the intercept at $c_H = 0$. This value is as accurate as possible, and it is not a conditional constant.

Then we can add a solution from the burette with the composition, e.g. 0.100 M CH_3COOH, 1.8 M CH_3COONa and 3 M $NaClO_4$. We plot the data according to Eq. (4.127) as E_H'' versus $l = L_T$. The slope of this plot is SL(H, CH_3COO^-) according to Eqs. (4.127), (4.128) and (4.129). The protolysis constant $\log_{10} K_1$ can be obtained from the intercept.

Constant Ratio of c_{acid}/c_{salt} is Used

This case has been investigated by the author.

We determine the experimental constant, E_{0H}, in the absence of the weak acid, CH_3COOH. Then we add a solution from the burette with the composition: 0.300 M CH_3COOH, 1.5 M CH_3COONa and 3 M $NaClO_4$. The concentration of the salt was varied in the test solution in the range: 0 - 0.7 M. We plot the data according to Eq. (4.127). The slope of the plot E_H'' versus L_T is SL(H, CH_3COO^-), the intercept = $E_{0H} + g \log_{10} K_1$. This plot is given in Fig. 4.5.

We obtain:

$$\mathrm{SL(H,\ CH_3COO^-)} = -10.5\ \mathrm{mV\ M^{-1}(CH_3COO^-)}$$

$$\log_{10} K_1 = -5.017 \pm 0.014$$

$$\mathrm{Q(H,\ CH_3COO^-)} = -7.8\ \mathrm{mV\ M^{-1}\ (CH_3COO^-),\ cf.\ Tables\ 2.10,\ 2.11.}$$

These results agree well with those values obtained at the experimental condition $[Na^+] = 3$ M, which is kept constant (cf. Section "Study at Constant Ratio of c_{acid}/c_{salt}").

For the foreword titration there, we obtained

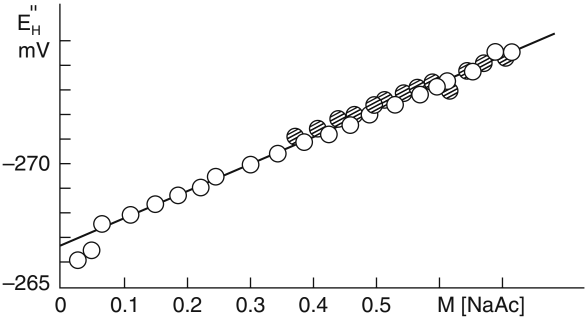

Fig. 4.5 Determination of the slope function SL(H, CH_3COO^-) and the dissociation constant of the acetic acid, $\log_{10} K_1$, according to Eq. (4.127) in the concentration range $0 \leq [CH_3COONa] \leq 0.7$ M. Filled symbols refer to back titration. CH_3COO^- is denoted by Ac^-. Reproduced with kind permission of Springer Science and Business Media from Néher-Neumann E (2006) The liquid junction potential in potentiometric titrations. IX. J Solution Chem 35: 1109–1136 DOI: 10.1007/s10953-006-9052-y (Fig. 1)

$$0 \leq [CH_3COONa]_F \leq 0.58\ M,$$
$$SL(H,\ CH_3COO^-) = -9.3\ mV.\ M^{-1}\ (CH_3COO^-)$$
$$\log_{10} K_1 = -5.024;$$
$$0.58 \leq [CH_3COONa]_F \leq 1.3\ M$$
$$SL(H,\ CH_3COO^-) = -7.8\ mV.M^{-1}\ (CH_3COO^-),$$
$$\log_{10} K_1 = -5.039.$$

For the back titration we obtained:

$$SL(H,\ CH_3COO^-) = -8.0\ mV.M^{-1}\ (CH_3COO^-)$$
$$\log_{10} K_1 = -5.035.$$

There we obtained the average value

$$\log_{10} K_1 = -5.033 \pm 0.006$$

at the experimental condition $[Na^+] = 3$ M, constant.

As is seen, the same $\log_{10}$ K_1 values were obtained at the two different experimental conditions by the graphical treatments. On the other hand, the slope function SL(H, CH_3COO^-) is slightly different. This is probably due to the different [CH_3COOH] concentrations used at these two experimental conditions. These molecules may have an isolation effect.

The slope function SL(H, acid) was also checked by titration of solution S_0: 0.050 M $HClO_4$, constant, 2.950 M $NaClO_4$, at $[ClO_4^-] = 3$ M, constant, with solution T_1: 0.050 M $HClO_4$, 2.950 M $NaClO_4$ and 1.00 M CH_3COOH. The concentration of acetic acid in the test solution was varied within the range 0–0.5 M. In the plot E_H versus $[CH_3COOH]_F$, we obtained:

$$SL(H,\ CH_3COOH) = 0\ mV\ M^{-1}\ (CH_3COOH).$$

As can be seen, the suggestion of the formation of dimer or trimer species was unnecessary, in spite of the broad concentration range of [CH_3COONa] studied.

On the other hand, if we neglect the potential contributions SL(H, CH_3COO^-) x c_{salt} to the total cell emf, the protolysis constant, $\log_{10}$ K_1, will be a function of $[CH_3COONa]_F$ and it will increase in one direction. Consequently, it will appear as the formation of dimer, trimer. etc. species. This is seen from Table 4.8.

The correct value of $\log_{10}$ K_1 is at $[CH_3COONa]_F = 0$ M:

$$\log_{10} K_1 = -5.017 \pm 0.014.$$

Table 4.8 Estimation of the systematic error in the dissociation constant of the acetic acid ($\log_{10}K_1$) caused by neglecting the potential contribution of the acetate ions to E_H: SL(H, CH_3COO)$[CH_3COO^-]_F$ in mV and $\log_{10} K_1$ units, using the $NaClO_4$ ionic medium at $[ClO_4^-]$= 3 M, constant, and the cell:-RE //3 M $NaClO_4$//Test soln/Ge^+, where RE denotes the reference half-cell

$[CH_3COONa]_F$	Neglected effect (mV)	$\log_{10}K_1+\Delta\log_{10}K_1$
Forward titration		
0.023047	−0.24	−5.021
0.045842	−0.48	−5.025
0.063838	−0.67	−5.028
0.110178	−1.15	−5.037
0.150950	−1.51	−5.043
0.188477	−1.98	−5.050
0.223964	−2.35	−5.057
0.256918	−2.70	−5.063
0.304021	−3.19	−5.071
0.348512	−3.66	−5.079
0.388751	−4.08	−5.086
0.426137	−4.47	−5.093
0.461989	−4.85	−5.099
0.495086	−5.20	−5.105
0.536047	−5.63	−5.112
0.574235	−6.03	−5.119
0.608741	−6.39	−5.125
0.624718	−6.56	−5.128
0.663354	−6.96	−5.135
0.698703	−7.33	−5.141
0.731165	−7.68	−5.147
Back titration		
0.711523	−7.47	−5.143
0.683962	−7.18	−5.139
0.658457	−6.91	−5.134
0.627269	−6.59	−5.129
0.598564	−6.28	−5.124
0.57299	−6.02	−5.119
0.554864	−5.83	−5.116
0.527356	−5.54	−5.111
0.502351	−5.27	−5.107
0.470996	−4.94	−5.101
0.447029	−4.69	−5.097
0.412240	−4.33	−5.090
0.375641	−3.94	−5.084

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In the table, $\Delta \log_{10} K_1 \equiv q \log_{10} h = q\ (1/g)$ SL(H, L) $[AL]_F$. The slope SL(H, Ac^-) = -10.5 mV M^{-1} was used.

If we had used a curve-fitting computer program instead, for the data treatment at both experimental conditions, we should have obtained the same $\log_{10} K_1$ values and the formation of dimer, trimer species, with two different sets of equilibrium constants for these minor species, because the composition changes of the ionic medium are different at these two different experimental conditions.

For $[Na^+] = 3$ M, constant:

$$Q(H,\ \Delta c_Y) = 14.77\ \text{mV}\ M^{-1}\Delta c_Y,\ \text{cf. Eq. (4.54)}$$

For $[ClO_4^-] = 3$ M, constant

$Q(H, \Delta c_A) = -2.67$ mV M^{-1} Δc_A, cf. Eq. (4.111)

These minor species, dimer, trimer, etc. are artefacts.

4.3.1.4 Survey of the Potential Functions for the Protolysis of the Weak Acid H_2L

We assume, first, that the protolysis constants $\log_{10} K_1$ and $\log_{10} K_2$ are well separated, namely at least by 5 pK units. In this case, the two steps of the protolysis of H_2L can be treated in two separate steps. This can be seen from the titration curve obtained with dilute NaOH. The shape of the plot E_H versus v ml NaOH added shows how many steps of the protolysis we have. The jumps in the plot indicate the position of the equivalence points. Such an exploratory titration should always be carried out.

The First Step of the Protolysis Equilibrium of the Weak Acid H_2L

The first step can be written as:

$$H_2L \rightleftharpoons H^+ + HL^-,\ K_1 = [H^+]\,[HL^-]/[H_2L] \qquad (4.133)$$

We can study this system after the determination of the experimental constant E_{0H} (in the absence of H_2L), by titrating the test solution with the buffer solution, e.g. 0.1 M H_2L, 1.8 M AHL $= L_T$ and C M AY. This system was treated in Section 4.3.1.2. in “Titration by Adding a Buffer Solution”. We can use the same treatment again, by substituting L^- by HL^- and HL by H_2L. The plot of E_H'' versus $l = [HL^-]_F$ on the basis of Eq. (4.127) gives the slope function SL(H, l) [cf. Eq. (4.129)]. From the intercept, $\log_{10} K_1$ can be calculated as

intercept $= E_{0H} + g \log_{10} K_1$

The Second Step of the Protolysis Equilibrium of the Weak Acid H_2L

The second step can be described as:

$$HL^- \rightleftharpoons H^+ + L^{2-},\ K_2 = [H^+]\,[L^{2-}]/[HL^-] \qquad (4.134)$$

in the ionic medium AY under the experimental condition that $[Y^-] = C$ M, constant. We shall study this system by first determining the constant E_{0H} through an acid–base titration, in the absence of the ligand. During the main titration, we can add a solution with the composition, e.g. 0.2 M AHL, 1 M A_2L, C M AY. In the equilibrium solution, the following ions are present: $[H^+]$, $[HL^-] = c_{acid} = HL_T$, $l = [L^{2-}] = c_{salt} = L_T$, Y^- and A^+. The $\log_{10}$ $[H^+]$ of the test solution can be calculated as:

$$\log_{10}[H^+] = \log_{10} K_2 - \log_{10}(c_{salt}/c_{acid}) \tag{4.135}$$

because the usual buffer approximations are valid (cf. Section 1.1). The composition of the test solution is also described previously (cf. Section 4.1). The concentrations of the ions of the ionic medium are:

$$c_Y = C\ M = AY_T + HY_T \tag{4.136}$$

$$c_A = AY_T + AOH_T + y\ L_T + HL_T = C - HY_T + AOH_T + y\ L_T + HL_T \tag{4.137}$$

$$c_A = C + \Delta c_A \tag{4.138}$$

where

$$\Delta c_A = c_A - C = yL_T + HL_T + AOH_T - HY_T \tag{4.139}$$

The test solution is a mixture of the strong electrolytes AHL, A_2L and AY. The total cell emf can be described as

$$\begin{aligned} E_H &= E_{0H} + g\ \log_{10} h - g[D(I) - D(C)] + SL(H, l \\ &= [HL^-])HL_T + SL(H, l = [L^{2-}])L_T + corr \end{aligned} \tag{4.140}$$

assuming $h \cong 0$.

Deduction for $pK_2 - pK_1 \geq 5$

Inserting $\log_{10}$ h from Eq. (4.135) into Eq. (4.140), we can form the function E_H'' and neglect corr.

$$\begin{aligned} E_H'' &\equiv E_H + g\log_{10}(c_{salt}/c_{acid}) + g[D(I) - D(C)] - SL\{H, l = [HL^-] =\}HL_T \\ &= E_{0H} + g\ \log_{10} K_2 + Sl\{H, l = [L^{2-}]\}L_T \end{aligned} \tag{4.141}$$

The slope function SL $\{H, l = [HL^-]\}$ is given by Eq. (4.129). Plotting the function E_H'' versus L_T, $\log_{10} K_2$ can be calculated from the intercept:

$$\log_{10} K_2 = (\text{intercept} - E_{0H})/g. \tag{4.142}$$

The slope of this plot is $SL\{H, l = [L^{2-}]\}$.

When dilute NaOH and a H_yL containing solution, or A_yL are used at the study of the protolysis of H_2L, the slope function $SL\{H, l = [L^{2-}]\}$ should be recalculated into Q (H, L^{2-}). For this purpose, we must know *the theoretical slope function*. This was derived by the author in Ref. [35]. The following result was obtained:

$$SL\{H, l = [L^{2-}]\} = g\,\varepsilon''(H, L) + g\,F_0(\lambda_L - y\lambda_A) - g\,t_A\varepsilon''(A, L) + g\,y\,t_Y\varepsilon''(A, Y) \tag{4.143}$$

Then we form the difference function

$$\begin{aligned} Q\{H, l = [L^{2-}]\} - SL\{H, l = [L^{2-}]\} &= \text{Eq.}(4.53) - \text{Eq.}(4.143) \\ &= g\,y\,F_0\lambda_A - g\,y\,t_Y\varepsilon''(A, Y) \end{aligned} \tag{4.144}$$

And knowing the experimental slope function, we have

$$Q\{H, l = [L^{2-}]\} = SL\{H, l = [L^{2-}]\}_{exp} + \text{the difference function.}(4.144) \tag{4.145}$$

Deduction for pK_2–$pK_1 < 5$

If the values of pK_2 and pK_1 are not well separated, only *the brutto equilibrium constant*, $\beta_{q,\,r}$, can be determined. This can be defined as

$$\beta_{q,r} = K_1.K_2 = [H^+]^2[L^{2-}]/[H_2L] \tag{4.146}$$

Taking the logarithm of this equation and after rearranging, we obtain

$$\log_{10}[H^+] = (1/2)(\log_{10} K_1 + \log_{10} K_2) - (1/2)\log_{10}\{[L^{2-}]/[H_2L]\} \tag{4.147}$$

As is seen, this case can be studied by titrating with the buffer solution $H_2L - A_2L$. We can use a composition for the titrating solution, e.g.

$$[H_2L] \cong c_{acid} = 0.100\text{M},$$

$$[L^{2-}] \cong c_{salt} = L_T = 1.5 \text{ M } A_2L,$$

$$\text{C M AY}$$

This high concentration for the salt insures that the important species are: H_2L, L^{2-}, H^+, A^+ and Y^- . Hence, we have

$$\log_{10} h = (1/2)\log_{10}\beta_{qr} + (1/2)\log_{10}(c_{acid}/c_{salt}) \tag{4.148}$$

Inserting this equation into Eq. (4.140), we can form the function $E_H{}^x$

$$\begin{aligned} E_H{}^x &\equiv E_H + (g/2)\log_{10}(c_{salt}/c_{acid}) + g[D(I) - D(C)] - SL(H, \text{acid})c_{acid} \\ &= \text{constant} + SL\{H, l = [L^{2-}]\}L_T \end{aligned} \tag{4.149a}$$

where

$$\text{constant} = E_{0H} + (g/2)\log_{10}\beta_{qr}. \tag{4.149b}$$

Plotting $E_H{}^x$ versus L_T, $\log_{10}\beta_{qr}$ can be calculated from the intercept = constant, and the slope is $SL\{H, l = [L^{2-}]\}$.

The data can also be treated with a curve-fitting computer program.

4.3.2 Emf Studies on Weak Complex Formation at [Y⁻] = C M, Constant

At weak complex formation, only 1–2 % of the total concentration of the central metal ion, B_T, is bound in metal ion complexes. In order to measure such small effect accurately, high metal ion concentrations should be used. Hietanen and Sillén developed [34] the use of very high and constant total concentration of the central metal ion to be studied. For example $B_T = 0.1, 0.3, 0.5, 0.7, 1.0$ M, which acts as a constant ionic medium and is called the self-medium method. Therefore, a very low total concentration is used for the ligand, e.g. $L_T < 0.025$ M, in order not to change the composition of the ionic medium much. This method favours the formation of complexes with high ratio of p/q. At these high metal ion concentrations, the approximation $b = [B^{z(B)+}] \cong [BY_{z(B)}] = B_T$ is valid. The formation of protolysis products, such as $H_{y\text{-}1}L^{-y+1}$, $H_{y\text{-}2}L^{-y+2}$, etc. is neglected too. This means that only the species H^+, $B^{z(B)+}$, L^{y-}, A^+ and Y^- are taken into account. This is the same condition what was used at the deduction of the potential functions for the preliminary data treatment and for the formation of strong complexes, discussed above. Those potential functions are valid, here, as well.

Moreover, it should be pointed out that in the self-medium method conditional constants are used: E_{0H1}. These cause an enormous systematic errors in the equilibrium constants.

In Ref. [35], a number of titrations were investigated by the author, where weak complexes are formed, using Cells B and H, respectively. These titrations are carried out in different ways and are realizing different approximations. Potential functions are suggested, based upon the results of strong complex formation. Conditional constant for E_{0H} is supposed to be determined, which is wrong. *The statement that the potential contribution of the B* $^{z(B)+}$ *ions to* E_H, *namely* gd_3 c_B and $Q(H, b = B_T)\, B_T$, *can be incorporated into* E_{0H}, *is the result of a misunderstanding. This causes the suggestion of polynuclear complexes, which are* artefacts.

4.3.2.1 Critical Analysis of the So-Called Self-Medium Method for Cell H

The high metal ion concentrations mentioned above cause an enormous change of the composition of the inert ionic medium. This and the use of the conditional constant E_{0H1} results in very large systematic errors in the equilibrium constants, what nobody has investigated before.

Table 4.9 Checking the validity of the approximation $\ln[(w/a)+1] = w/a$ appearing in the potential terms derived, using B_T M Cd $(ClO_4)_2$ as self-medium in $NaClO_4$ inert ionic medium at $[ClO_4{}^-]=$ 3 M, constant, when weak complexes are formed, at t = 25 °C. B = Cd^{2+}

B_T M	$\sim\Delta c_A$ M	$\lambda_A\Delta c_A$	w	w/a	ln[(w/a) + 1]
0.1	−0.2	−4.696	−2.074	−0.0127	−0.0127
0.2	−0.4	−9.392	−4.148	−0.0253	−0.0256
0.3	−0.6	−14.088	−6.222	−0.0380	−0.0387
0.5	−1.0	−23.480	−10.370	−0.0633	−0.0654
0.7	−1.4	−32.872	−14.518	−0.0886	−0.0928
0.9	−1.8	−42.264	−18.666	−0.1139	−0.1210

As a first step, it is to be checked if the equations derived earlier can be used, in principle, in the self-medium method. The equations are valid for the cases when the values of w/a are small and the approximation $\ln[(w/a) + 1] \cong w/a$ can be used. This validity has been checked in Table 4.9. The conditions given below were used in the calculations.

$$c_H \text{ is negligible, } b = [B^{z(B)+}] \cong [BY_{z(B)}] = B_T = Cd(ClO_4)_2$$

$$L = [L^{y-}] \text{ M, is negligible, } L_T \prec 23x10^{-3} \text{ M, is negligible,}$$

$$c_Y = C\,M = AY_T + HY_T + z_B\,B_T$$

$$c_A = AY_T + yL_T + AOH_T = C - z_B\,B_T - HY_T + AOH_T + yL_T = C + \Delta c_A \quad (4.150)$$

$$\Delta c_A = c_A - C \cong -z_B\,B_T$$

$$w = h\,\lambda_H + b\,z_B\,\lambda_B + \Delta c_A\lambda_A + y\,l\lambda_L \cong B_T\,z_B\lambda_B + \Delta c_A\,\lambda_A$$

$$\Lambda(3M\ NaClO_4) = 54.60 \text{ (cf. Table 2.11)}$$

$$a = C(\lambda_A + \lambda_Y) = 3 \text{ x } 54.60 = 163.8$$

$$t_{Cd} \approx t_{Zn}(1.5\text{ M } Zn(ClO_4)_2) = 0.319 \text{ [36a]}$$

$$\lambda_B = 41.1x0.319 = 13.11, \text{ approximated value (Table 3.2 and Ref.[36a])}$$

$$\Lambda[0.05\text{ M } Cd(ClO_4)_2] = 90.39, \text{ cf. Ref.[10]}$$

$$\Lambda[0.7 - 1.5\text{ M } Cd(ClO_4)_2] = 41.1 \text{(cf. Table 3.2)}$$

$$\lambda_{ClO4} = 54.60 \text{ x } 0.57 = 31.12 \text{ (cf.Tables 2.10, 2.11)}$$

$$\lambda_{Na} = 54.60 \text{ x } 0.43 = 23.48$$

As is seen from Table 4.9, the approximation and the derived equations are valid up to and inclusive $B_T = 0.7$ M.

As a second step, it was investigated how large systematic errors occur in $\log_{10}\beta_{pqr}$ due to the use of the conditional constant E_{0H1}. The results are given in Table 4.10. Here, the following conditions were used beside those given above.

For these calculations

$$E_{0H1} = E_{0H} + g\, d_3\, c_B$$

$$\varepsilon''(\text{Cd}, \text{ClO}_4) = 0.40 \text{ liter. mol}^{-1}[31]$$

$$\varepsilon''(\text{Na}, \text{ ClO}_4) = 0.03 \text{ liter. mol}^{-1}[31]$$

$$\Delta \log_{10}\beta^{(1)}_{pqr} = -q\Delta \log_{10} h = q\,(gd_3\, B_T)/g \qquad (4.151)$$

according to

$$\log_{10} h = (E_H - E_{0H} - g\, d_3\, B_T)/g + [D(I) - D(C)] - (1/g)\Sigma_V\, Q\,(H, V)\, V \quad (4.152)$$

where $V = b, h, l, \Delta c_A$

and due to Eq. (IV) in Section 4.1,

$$\log_{10}\beta_{pqr} = \log_{10}[\text{complex}] - p \log_{10} b - q\ \log_{10} h - r\ \log_{10} l \qquad (4.153)$$

As is seen from this table, the systematic errors are changing between 1.4 – 11.7 mV and can reach 0.6 $\log_{10}\beta$ units at $B_T = 0.7$ M and q = 3. These errors are large

Table 4.10 The effect of the use of the conditional constant E_{0HI} on the equilibrium constants, when weak complexes are formed in Cell H and B_T M $Cd(ClO_4)_2$ has been used as self-medium together with $NaClO_4$ inert ionic medium, at$[ClO_4^-]$= 3 M, constant, and at 25°C. B = Cd^{2+}

					$\Delta\log_{10}\beta_{pqr}{}^{(1)}$		
B_T M	$\sim\Lambda[B_T \text{ M } Cd(ClO_4)_2]$	$\sim\lambda_B$	$\sim d_3$	gd_3B_T mV	q = 1	q = 2	q = 3
0.1	90.4	28.8	0.242	1.43	0.024	0.048	0.072
0.3	41.1	13.1	0.284	5.04	0.085	0.170	0.255
0.5	41.1	13.1	0.284	8.40	0.142	0.284	0.426
0.7	41.1	13.1	0.284	11.76	0.199	0.397	0.597

Here, the following conditions were used: $d_3 = d_1$, given by Eq. (2.28): $E_{0HI} = E_{0H} + gd_3c_B$, $c_B = b \cong B_T$, $t_{Cd} \cong t_{Zn}[1.5 \text{ M } Zn(ClO_4)_2]$= 0.319 [36a], $\Lambda[0.05 \text{ M } Cd(ClO_4)_2]$= 90.39 (cf. Ref. [21]), $\Lambda[(0.7-1.5) \text{ M } Cd\ (ClO_4)_2] = 41.1$ (cf. Table 3.2), $\Delta\log_{10}\beta_{pqr}{}^{(1)} = -q\Delta\log_{10}h = q(gd_3B_T)/g$

Table 4.11 The effect of the composition change of the ionic medium on the equilibrium constants, at the formation of weak complexes, when B_T M $Cd(ClO_4)_2$ has been used as self-medium together with $NaClO_4$ inert ionic medium, at $[ClO_4^-] = 3$ M, constant, and 25°C. Cell H is considered and $B = Cd^{2+}$. For the ligand $[L^-]= 0.050$ M, is kept constant

			$\Delta\log_{10}\beta_{pqr}^{(2)}$		
B_T M	$\sim\Delta c_A$M	$Q(H, \Delta c_A)\,\Delta c_A$ mV	q=1	q=2	q=3
0.1	−0.15	0.40	0.007	0.014	0.021
0.3	−0.55	1.44	0.024	0.048	0.072
0.5	−0.95	2.54	0.043	0.086	0.129
0.7	−1.35	3.60	0.061	0.122	0.183

Here, the following conditions were used. $\Delta c_A \cong -z_B B_T + y L_T$, cf. Eq. (4.110), Complexing agent : AL. $Q(H,\Delta c_A) = -2.67$ mV M^{-1}, cf. Eq. (4.111a). $\Delta\log_{10}\beta_{pqr}^{(2)} = -\,q\Delta\log_{10}h = q(1/g)\,Q(H,\Delta c_A)\Delta c_A$.

and are a function of B_T. These errors will result in the suggestion of polynuclear complexes.

The systematic errors in $\log_{10}\beta_{pqr}^{(2)}$, due to composition changes of the ionic medium, are presented in Table 4.11. These are defined as

$$\Delta\log_{10}\beta_{pqr}^{(2)} = -q\Delta\log_{10}h = q(1/g)Q(H, \Delta c_A)\Delta c_A \tag{4.154}$$

where

$$Q\,(H, \Delta c_A) = -2.67\ \text{mV}.\ M^{-1}(\Delta c_A)\text{for } NaClO_4 \text{ ionic medium.}$$

As is seen from this table, the errors are of medium magnitude and change with B_T between 0.40 – 3.60 mV for q = 1. They are a function of q as well. Again, it will cause the suggestion of polynuclear species which are artefacts.

The total systematic errors in $\log_{10}\beta_{pqr}$ and Cell H, when weak complexes are formed and the self-medium method is used, in $NaClO_4$ inert ionic medium and

Table 4.12 Survey of the total systematic error in $\log_{10}\beta_{pqr}$ in Cell H, when weak complexes are formed and the self-medium method is used, in $NaClO_4$ inert ionic medium and at 25°C. For $B_T = 0.50$ M $[Cd^{2+}]$, $L_T = 0.050$ M NaAcetate, $[H^+] = h = 1\times10^{-3}$ M and $[ClO_4^-] = 3$ M, is kept constant, we have

q=1	q=3
$0.043 \le \Delta\log_{10}\beta_{pqr}^{(2)}$	≤ 0.129
$0.142 \le \Delta\log_{10}\beta_{pqr}^{(1)}$	≤ 0.426
$q(1/g)\,Q(H, Cd)B_T$	
$0.114 \le q(1/g)\,13.74\,B_T$	≤ 0.342
$q(1/g)\,Q(H, h)h$	
$0 \le q(1/g)\,(-24.5)h$	≤ 0.001
$q(1/g)\,Q(H, Acetate^-)L_T$	
$-0.006 \le q(1/g)\,(-7.8)L_T$	≤ -0.018

The total systematic errors are $0.293 \le \log_{10}\beta_{pqr}^{T} \le 0.880$

at $[\mathrm{ClO_4^-}] = 3$ M, constant, and 25.00° C, are presented in Table 4.12. The level $B_T = 0.50$ M Cd^{2+} was assumed and the use of acetate⁻ ligand.

As is seen from this table, almost every error is of positive sign and they strengthen the effects of each other. This will result in such a high value as $0.293 < \Delta\log_{10}\beta_{pqr}{}^{T} < 0.880$. This means that complexes and stability constants determined earlier by this method are completely erroneous.

4.3.3 Experimental Examples Taken from the Literature

4.3.3.1 The Hydrolysis of the Lanthanum Ion, La^{3+}

In Ref. [33], the hydrolysis equilibria of the La(III) ion have been studied at 25° C by hydrogen ion concentration measurements, using a glass electrode. The total [La(III)] was varied between 0.1 and 1.0 M, whilst the concentration of the $\mathrm{ClO_4^-}$ ion was held constant at 3 M by the addition of $\mathrm{LiClO_4}$. The data indicated a slight hydrolysis in the $\log_{10}$ h range −6.5 to −8.1, which corresponds to $0.001 \leq Z = (h\text{-}H)/B_T \leq 0.018$. Z denotes the average number of hydrogen ions set free per Lanthanum atom [33].

The hydrogen ion concentration of solution S was measured by means of the cell

$$- \text{GE /solution S}||\text{SE} + \qquad \text{(A)}$$

where GE denotes a glass electrode and SE is the reference half-cell

$$||3.000\ \mathrm{M\ LiClO_4}\ ||\ 2.990\ \mathrm{M\ LiClO_4},\ 0.010\ \mathrm{M\ AgClO_4}\ |\ \mathrm{AgCl},\ \mathrm{Ag}.$$

The emf of cell (A) at 25° C was written

$$E_H = E_{0H} - 59.16\ \log_{10} h - 59.16\, f(H^+) + E_j(h, B) \qquad \text{(i)}$$

where E_{0H} is an experimental constant and h is the hydrogen ion concentration at equilibrium. $f(H^+)$ denotes the activity factor of H^+. The reference state is defined so that $f(H^+)$, as well as the activity factors of the other reacting species, tend to unity when the composition of the solution approaches 3 M $\mathrm{LiClO_4}$. For each series of measurements, when B_T was kept constant, they assumed that $f(H^+) =$ constant, consequently they wrote

$$E = E_{0H}' - 59.16\ \log_{10} h + E_j(h, B) \qquad \text{(ii)}$$

where E_{0H}' is a function of B_T.

This assumption is not true, and the liquid junction term (E_j) is very simplified. As it was found by the author, all ions present in the test solution S contributes to the total potential anomalies. $E_j(h, B)$ was determined with the help of two separate cells (B and C) and it was found to be: $E_j(h,0) = -15.8$ h mV (from cell B) and E_j(h, 0.967) = −20.0 h mV (from cell C). Thus, up to h = 0.01 M $E_j(h,0)$ was used in the entire B range 0.1 – 1.0 M. The cells hade the compositions

$$-\mathrm{GE\ and\ H_2(Pt)\ |\ h\ M\ H^+,\ (3.000 - h)\ M\ Li^+,\ 3.000\ M\ ClO_4^-\ |\ SE+} \qquad \text{(B)}$$

$$-\mathrm{GE\ |\ 0.967M\ La^{3+},\ h\ M\ H^+,\ (0.100 - h)Li^+,\ 3.000M\ ClO_4\ |\ SE+} \qquad \text{(C)}$$

in the h range 0.01 – 0.1 M.

The solutions had the general composition B M La(III), H_S M H^+ , (3.000 – 3B – H_S + H_0) M Li^+, (3.000 + H_0) M ClO_4 = solution S, where H_S, the analytical excess of hydrogen ions, is equal to

$$H_S = [v_0H_0 + v_T(H_T + H_0)]/(v_0 + v_T) = H_0 + (v_TH_T)/(v_0 + v_T) \qquad \text{(iii)}$$

The measurements were performed by starting with v_0 ml solution (S_0) containing an initially unknown deficit of hydrogen ions (- H_0) and adding to it successively increasing volumes (v_T ml) of solution (T) containing about 0.02 to 0.10 M $HClO_4$ (= $H_T > -H_0$).

Each of the potentiometric titrations was divided in two parts. The measurements in the low acidity range ($\log_{10}$ h > −5, part I) were made to determine h in hydrolysed solutions, whereas the E_H data at higher acidities (part II) served to calculate H_0 and E_{0H}. The value of H_0 was obtained by means of a Gran plot (cf. Section 4.2.1.2.), which was constructed on the basis of the E_H values obtained in part II. E_{0H}' proved to be constant at least within ± 0.2 mV. The E_{0H}' values used were not published. Finally, the values of H_0 and E_{0H}' thus obtained were used for the calculation of $\log_{10}$ h and Z corresponding to the experimental points of part I.

But besides that the activity factors are not constant and that all ions present in the test solutions contribute to E_H, we should, moreover, think about that

(a) the liquid junction potential, E_j, consist of two parts: E_D + E_{Df}, namely, the diffusion potential and the activity factor contributions of all ions present, to E_D,
(b) the conditional experimental constants, E_{0H}', include large potential terms which depend on B_T. Biedermann and Ciavatta did not think about what consequences this results in Z and the equilibrium constants β_{pq}.
(c) The function E_H in the emf cells used for the determination of E_{0H} is not the same as that one valid in cells with complex formation. The authors used exactly the same function for E_H in entirely different emf cells. This was also wrong.

Checking the Validity of the Approximation ln[(*w/a*) +*1*] ≅ *w/a*

First, it should be investigated if the derived equations, with the approximation ln [(w/a) +1] ≅ w/a, is valid in the self-medium method. In the calculations, the following data are needed.

$$\Lambda(3\mathrm{M\ LiClO_4}) = 52.53$$

$$a = C(\lambda_A + \lambda_Y) = 3 \times 52.53 = 157.59$$

$$c_A = [AY] + yL_T = C - z_B\,B_T - HY_T + yL_T = C + \Delta c_A$$

$$c_Y = [Y^-] = C\,M = [AY] + HY_T + z_B\,B_T$$

$$\Delta c_A = c_A - C \cong -z_B\,B_T$$

$$w = h\lambda_H + B_T\,z_B\lambda_B + \Delta c_A\lambda_A + yl\lambda_L \cong B_T\,z_B\lambda_B + \Delta c_A\lambda_A$$

$$t_A(3\ \mathrm{M\ LiClO_4}) = 0.35$$

$$t_{La} \cong t[B_T\ \mathrm{M\ Zn(ClO_4)_2}] \text{ from Ref. [36b]}$$

$$\Lambda\ \text{molar}[B_T\mathrm{M\ La(ClO_4)_3}] = \Lambda_{\text{equiv.}}(B_T\ \mathrm{M})\mathrm{x}3 \cong \Lambda[B_T\ \mathrm{M\ LaCl_3}] \text{ from Ref. [36a]}$$

For the hydrolysis of La^{3+} solutions $NaHCO_3$ was used.

The results of the calculation of the approximations are presented in Table 4.13. As is seen from this table, the approximation in question is valid at $B_T \le 0.3$ M.

The Effect of the Use of the Conditional Constant E_{0H}' *on* $log_{10}\beta_{pq}^{(1)}$

This constant is defined as

$$E_{0H1} = E_{0H} + gd_3(c_B = B_T)$$

where

$$d_3 \equiv d_1 = \{-(\lambda_B - z_B\lambda_A)/[2.303\ C(\lambda_A + \lambda_Y)]\} + t_Y[\varepsilon''(B,Y) - \varepsilon''(AY)z_B]$$

cf. Eq. (2.28).

Table 4.13 The hydrolysis of the Lanthanum ion, La^{3+}. Checking of the validity of the approximation $\ln[(w/a)+1] \cong w/a$, using B_T M $La(ClO_4)_3$ as self-medium, together with $LiClO_4$ inert ionic medium at $[ClO_4^-] = 3$ M, constant, at 25°C

B_T M	Δc_{Li} M	w	w/a	ln[(w/a)+1]	λ_{La}
0.9667	−2.9001	95.7453	0.6075	0.4747	51.40
0.4865	−1.4595	78.5569	0.4985	0.4045	72.21
0.3000	−0.9000	62.7521	0.3982	0.3352	88.11
0.1946	−0.5838	45.5332	0.2889	0.2538	96.38
0.0973	−0.2919	26.1118	0.1657	0.1533	107.84

The caused systematic error in the equilibrium constant is

$$\Delta \log_{10} \beta_{pq}^{(1)} = -q\Delta \log_{10} h = q(g\, d_3\, B_T)/g$$

According to Eq. (4.57), by using E_{0H1}

$$\log_{10} h = (E_H - E_{0H} - g\, d_3\, B_T)/g + [D(I) - D(C)] - (1/g)\Sigma_V\, Q(H, V)V$$

where

$$V = h,\ b,\ l,\ \Delta c_A$$

and

$$\log_{10} \beta_{pq} = \log_{10}[\text{complex}] - p\ \log_{10} b - q \log_{10} h$$

$$\varepsilon''(\text{Li},\ \text{ClO}_4) \cong \varepsilon(\text{Li},\ \text{ClO}_4) = 0.15, \varepsilon''(\text{La},\ \text{ClO}_4) \cong \varepsilon(\text{La},\ \text{ClO}_4) = 0.47$$

The results of the calculations are given in Table 4.14.

As is seen from this table, the systematic errors in E_{0H1} are changing between –1.38 mV ($B_T = 0.3$ M) and -0.76 mV ($B_T = 0.0973$ M). Moreover, $B_T = 1$ M was the highest level of La(III) used in this study. It means that these systematic errors were much higher in this investigation. These are not negligible. The systematic errors in $\Delta \log_{10} \beta_{pq}^{(1)}$ are a function of B_T, and will be interpreted as a formation of polynuclear complexes.

The Effect of the Composition Change of the Ionic Medium on the Equilibrium Constants

This effect is defined as

$$\Delta \log_{10} \beta_{pq}^{(2)} = -q\Delta \log_{10} h = q(1/g)Q(H, \Delta c_A)\Delta c_A$$

Here, Q $(H,\Delta c_{Li}) = 2.8$ mV M^{-1} (Li). The effects are shown in Table 4.15.

Table 4.14 The hydrolysis of the Lanthanum ion, La^{3+}. The systematic errors in E_{0H} and the equilibrium constants, caused by the use of the conditional constant E_{0H1}. $E_{0H1} = E_{0H} + gd_3\, c_B$ mV, $\Delta\log_{10} \beta_{pq}^{(1)} = -q\ \Delta\log_{10} h = q(gd_3B_T)/g$

			$\Delta\log_{10} \beta_{pq}^{(1)}$		
B_T M	~d_3 M^{-1}	~gd_3B_T mV	q = 1	q = 2	q = 3
0.300	−0.0778	−1.38	−0.023	−0.047	−0.070
0.1946	−0.1006	−1.16	−0.019	−0.039	−0.059
0.0973	−0.1322	−0.76	−0.013	−0.026	−0.038

B_T M $La(ClO_4)_3$ self-medium was used together with $LiClO_4$ inert ionic medium at $[ClO_4^-] = 3$ M, constant and 25°C.

Table 4.15 The hydrolysis of the Lanthanum ion, La^{3+}. The systematic errors in the equilibrium constants caused by the composition change of the ionic medium. B_T M $La(ClO_4)_3$ self-medium was used together with $LiClO_4$ inert ionic medium at $[ClO_4^-] = 3$ M, constant, and 25°C. $\Delta\log_{10} \beta_{pqr}^{(2)} = -q\Delta\log_{10} h = q(1/g)\, Q(H,\Delta c_{Li})\Delta c_{Li}$, $\Delta c_{Li} \cong -z_B B_T$, $Q(H,\Delta c_{Li}) = 2.8$ mV M^{-1}

			$\Delta\log_{10} \beta_{pq}^{(2)}$		
B_T M	Δc_{Li} M	$Q(H,\Delta c_{Li})\Delta c_{Li}$ mV	q=1	q=2	q=3
0.3000	−0.900	−2.52	−0.042	−0.084	−0.126
0.1946	−0.5838	−1.63	−0.027	−0.054	−0.081
0.0973	−0.2919	−0.82	−0.014	−0.028	−0.042

As is seen from this table, the systematic errors in the equilibrium constants are a function of B_T. This looks like the formation of polynuclear complexes.

The Potential Contribution of the La^{3+} Ion to the Total Potential Anomalies

This effect is defined as

$$\Delta \log_{10} \beta_{pq}^{(3)} = -q\, \Delta \log_{10} h = q\,(1/g)\, Q\,(H, b)\, B_T$$

where

$$Q(H, b) = -g\, \lambda_B^{tr}/[2.303\, C\, (\lambda_A + \lambda_Y)] + g\, t_Y \varepsilon''(B, Y), \text{ (cf. Eq. (4.52))}.$$

The results are presented in Table 4.16.

As is seen, this systematic error is also the function of B_T.

The total systematic errors in the equilibrium constants are:

$$\Delta \log_{10} \beta_{pq}^{T} = \Delta \log_{10} \beta_{pq}^{(1)} + \Delta \log_{10} \beta_{pq}^{(2)} + \Delta \log_{10} \beta_{pq}^{(3)} \qquad (4.155)$$

We can conclude that all these systematic errors are the function of the total concentration of the central metal ion (B_T) and will be interpreted as the formation of polynuclear complexes. These effects must be taken into account when calculating $\log_{10}$ h. Only after that can we look for the real formation of polynuclear complexes,

Table 4.16 The hydrolysis of the Lanthanum ion, La^{3+}. The potential contribution of the La^{3+} ion to the total potential anomalies. This effect is defined as $\Delta\log_{10} \beta_{pq}^{(3)} = -q\, \Delta\log_{10} h = q\,(1/g)\, Q(H, b)\, B_T$. The function Q(H, b) is given by Eq. (4.52)

		$\Delta\log_{10} \beta_{pq}^{(3)}$		
B_T M	$Q(H, b)B_T$ mV	q=1	q=2	q=3
0.3000	1.11	0.019	0.037	0.057
0.1946	0.46	0.008	0.015	0.024
0.0973	0.05	0.001	0.002	0.0024

e.g. through the comparison with normalized functions [33, 34, 37]. Moreover, it should be pointed out that for B_T(III) metal ions, the highest B_T(III) level should be ≤ 0.300 M. Otherwise, we cannot make corrections for the effect of the total potential anomalies.

Biedermann and Ciavatta found the complexes $La\,OH^{2+}$, La_2OH^{5+}, $La_5(OH)_9{}^{6+}$ or $La_6(OH)_{10}{}^{8+}$. As significant systematic errors were neglected at the calculation of $\log_{10}$ h, it is probable that several of these complexes do not exist.

It should be noted that in the paper investigated the cells had opposite poles than those used in the deduction of the formulas. Therefore, the final results presented in the tables should be taken with the opposite sign.

4.3.3.2 Carbonate Complex Formation of the La^{3+} Ion [37]

In Ref. [37], the following complex formation reactions were studied by Ciavatta and others.

$$p\,La^{3+} + q\,H_2\,O + r\,CO_2 \rightleftharpoons La_p\,(OH)_q\,(CO_2)_r^{3p-q} + q\,H^+ \tag{4.156}$$

$$\text{where } (OH)\,CO_2^- \equiv HCO_3^- \text{ and } (OH)_2CO_2{}^{2-} \equiv CO_3{}^{2-}.$$

The equilibrium concentration of the H^+ ions, h, was measured with a glass electrode using the emf cell

$$-\ \text{GE} \mid \text{Test solution} \parallel 3\text{M NaClO}_4 \parallel \text{Reference half-cell} +$$

The equilibrium constants were defined as

$$\beta_{pqr} = [\text{complex}]\,[H^+]^q\,[La^{3+}]^{-p}\,a^{-r} \times f\,(pqr) f\,(H^+)^q \times f\,(La^{3+})^{-p}\,a\,(H_2O)^{-q} \tag{4.157}$$

where

f = the activity factor of the ions present in the test solution,
a = partial pressure of CO_2 and
$a(H_2O)$ = activity of water

The acidity of the test solutions was changed by coulometric generation of H^+ or OH^- ions. The B_T levels of 0.1, 0.3, 0.5 and 1 M were investigated, while the partial pressure of CO_2 was varied between 0.1 – 0.98 atm. The $[ClO_4{}^-] = 3$ M, kept constant, was ensured in all test solutions, by adding $NaClO_4$.

In Ref. [37], the following potential functions should have been taken into account.

(1) For the total cell emf with a glass measuring electrode:

$$E_H = E_{0H} - g\,\log_{10} c_H - g\,\log_{10} f_{HTS2} - E_D - E_{Df} \tag{4.158a}$$

The total potential anomalies are

$$\Delta E_H = g\,[D(I) - D(C)] - g\log_{10} f_{HTS2} - E_D - E_{Df} \tag{4.158b}$$

which were not taken into account.

(2) During the determination of the experimental constant E_{0H}, we have

$$E_H = E_{0H} - g\ \log_{10} c_H + g\,[D(I) - D(C)] - g\,d_3\,c_B - g\,d_4\,c_H \tag{4.159}$$

Conditional constants were determined at constant B_T.

$$E_{0H1} = E_{0H} - g\,d_3\,B_T \tag{4.160}$$

The term $g\,d_3\,B_T$ was not taken into account, which is a large potential contribution and depends on B_T.

Only the function

$$E_H = E_{0H1} - g\ \log_{10} c_H + 17c_H \tag{4.161}$$

was considered, where

$$E_{0H1} = E_{0H} - g\ \log_{10} f(H^+) - g\,d_3\,B_T \tag{4.162}$$

(3) During the complex formation study, the following function is valid

$$E_H = E_{0H} - g\ \log_{10} h + g\,[D(I) - D(C)] - \Sigma_V\, Q(H, V)\, V - \text{corr} \tag{4.163}$$

where

$$V = h,\ b,\ l,\ \Delta c_A$$

$$\Delta c_A = c_A - C = AOH_T - HY_T - z_B\,B_T \tag{4.164}$$

Δc_A is the correct expression for the composition change of the ionic medium. None of those terms of Q(H, V) was considered, in spite of that these potential contributions are not negligible, except Q (H, h)h.

The emf data were interpreted on the basis of the functions given below.

$$(h - H)/a = \Sigma_q\, qK_q\, h^{-q} \tag{4.165}$$

which denotes the moles of OH^- bound per unit partial pressure of CO_2.

$$H = \text{analytical excess of } H^+ = [ClO_4^-] - [Na^+] - 3B_T$$

K_q is equal to the formation constant for all species containing q OH groups on the molar scale.

$$K_q = \Sigma\beta_{pq1}\ f(pq)^{-1} f(La^{3+})^p\ f(H^+)^{-q}\ B_T^p \tag{4.166}$$

The interpretation of the data was done according to the self-medium method [33, 34, 37], using normalized functions.

The systematic errors in the conditional constants and in the equilibrium constants have been investigated as it was done in the previous Section (4.3.3.1). For the molar conductivity of $La(ClO_4)_3$ that of $LaCl_3$ was used as an approximation. The results of the calculation are given in Table 4.17.

As is seen from this table, the systematic errors in E_{0H1} change between 3.02 mV (in $B_T = 0.300$ M) and 0.7 mV (in $B_T = 0.1$ M). At higher B_T levels, these errors will be higher. As $B_{Tmax} = 1$ M was used, the systematic errors in E_{0H1} was higher than 10 mV. In the first part of the calculations, $b = B_T$ was used. In order to get an idea of the error introduced by this approximation, the calculations were repeated with the correction $b = B_T - (h - H)$. The constants found with the two approximations were very similar.

The effect of the use of E_{0H1} at the calculation of $\beta_{pqr}^{(1)}$ and of the composition change of the ionic medium on $\beta_{pqr}^{(2)}$ are presented in Table 4.18.

The systematic errors, $\Delta \log_{10} \beta_{pqr}^{(3)}$, caused by the potential contributions of the La^{3+} ions to the total potential anomalies, are given in Table 4.19.

As is seen from these tables, the real errors in the equilibrium constants are much higher than those given in this paper.

Moreover, all these systematic errors are function of B_T. This results in the assumption of the formation of polynuclear complexes. The authors of this paper

Table 4.17 The carbonate complex formation of the Lanthanum ion, La^{3+}. Survey of the systematic errors in E_{0H}, caused by the use of the conditional constant E_{0H1}. B_T M $La(ClO_4)_3$ was used as self-medium, together with $NaClO_4$ as inert ionic medium, at $[ClO_4^-] = 3$ M, constant, and t = 25°C. Weak complexes were formed

$t_{La(III)} \sim t_{Zn(II)}$	$[LaCl_3]B_T$, M	$\Lambda(B_T\ M)\ LaCl_3$	λ_{La}	$\sim d_3$	$\sim gd_3\ B_T$ mV
0.380	0.3000	231.87	88.11	0.17014	3.02
0.409	0.1000	263.67	107.84	0.11784	0.70

Table 4.18 The carbonate complex formation of the Lanthanum ion, La^{3+}. The effect of the conditional constant, E_{0H1}, on $\Delta \log_{10} \beta_{pq}^{(1)}$ and the composition change of the ionic medium on $\Delta \log_{10} \beta_{pq}^{(2)}$ when the self-medium method was used for study at $[ClO_4^-] = 3$ M, constant, and t = 25°C. Weak complexes were formed

	$\Delta \log_{10} \beta_{pqr}^{(1)}$			$q(1/g)\ Q(H,\Delta c_A)\Delta c_A$		
$[LaCl_3]\ B_T$, M	q=1	q=2	q=3	q=1	q=2	q=3
0.3000	0.051	0.102	0.153	0.041	0.081	0.123
0.1000	0.012	0.024	0.036	0.013	0.027	0.039

$Q(H,\Delta c_A) = -2.67$ mV. M^{-1} (Δc_A).
$\Delta c_A \cong - z_B B_T$

Table 4.19 The carbonate complex formation of the Lanthanum ion, La^{3+}. The potential contribution of the La^{3+} ion to the total potential anomalies. This effect is defined as $\Delta\log_{10} \beta_{pqr}{}^{(3)} = -q\, \Delta \log_{10} h = q(1/g)Q(H, b)\, B_T$. The function Q(H, b) is given by Eq. (4.52),

		q(1/g) Q(H, b)B_T		
[$LaCl_3$] B_T, M	Q(H, b)	q=1	q=2	q=3
0.3000	2.03	0.010	0.020	0.030
0.1000	−1.06	−0.002	−0.003	−0.005

The effect of the total systematic errors on the equilibrium constans:
$\Delta\log_{10} \beta_{pqr}{}^{T} = \Delta\log_{10} \beta_{pqr}{}^{(1)} + \Delta\log_{10} \beta_{pqr}{}^{(2)} + \Delta\log_{10} \beta_{pqr}{}^{(3)}$

	$\Delta\log_{10} \beta_{pqr}{}^{T}$		
[$LaCl_3$] B_T, M	q=1	q=2	q=3
0.300	0.102	0.203	0.306
0.100	0.023	0.048	0.070

have also found polynuclear species, but they did not accept it, as they thought that the composition change of the inert ionic medium ($NaClO_4$) was too large. They draw the final conclusion that the species $LaCO_3{}^+$ and $La(CO_3)_2{}^-$ are the dominating species, while $LaHCO_3{}^{2+}$ and $La_2CO_3{}^{4+}$ are negligible in a typical granitic ground water.

4.4 Emf Cells Where I = C M, Is Kept Constant [38]

4.4.1 Introduction

The deduction of the potential functions, E_D, E_{Df}, ΔE_B and ΔE_H in a general form [1] and for the experimental condition [A^+] = C M, constant, [23] is presented in these references for emf cells containing equilibrium systems. Here, we shall follow this general treatment. In the present work, the content of some special functions will be given for emf cells with complex formation at the experimental condition I = C M, constant, which are included in the general equations presented in Ref. [1, 23].

The complex formation reactions studied are presented in Section 4.3. These titrations can be carried out in different ways, e.g. as it is given in the Appendix A for [A^+] = C M, is kept constant [23]. The potential functions, here, will be deduced for the case when the titration is carried out according to Section 1 of Appendix A. Here, A_yL is used as complexing agent at various concentrations (L_T).

First, the constants E_{0B} or E_{0H} should be determined.

4.4.1.1 The Determination of the Constant E_{0B}

This should be done at constant level of HY by titrating v_0 ml solution S_0 with v_1 ml solution T_1 of the compositions given here.

Solution S_0 : 5×10^{-3} M $BY_{z(B)}$

$HY_0 = 25\times10^{-3}$ M, is kept constant
AY_0 M AY

Solution T_1 : $c_B = 2B_T$ M $BY_{z(B)}$

$HY_1 = 25\times10^{-3}$ M HY, is kept constant
AY_1 M AY

c_B should be varied within the range $5\times10^{-3} \le c_B \le B_T$ M

For the ionic strength we have:

$$I = (1/2)(c_H + c_B\, z_B{}^2 + c_A + c_Y) = C\ M,\ \text{constant} \tag{4.167}$$

For solution S_0 we have:

$$c_A = AY_0$$

$$c_Y = AY_0 + HY_0 + z_B\, c_B \tag{4.168a}$$

Inserting c_A and c_Y into Eq. (4.167), we obtain:

$$I = HY_0 + AY_0 + [(z_B{}^2 + z_B)/2]c_B = C\ M \tag{4.168b}$$

From here,

$$AY_0 = C - HY_0 - [(z_B{}^2 + z_B)/2]c_B,\ \text{the concentration to be used for } AY_0 \text{ in } S_0. \tag{4.168c}$$

For solution T_1 we have:

$$I = (1/2)(c_H + 2\,B_T\, z_B{}^2 + c_A + c_Y) = C\ M,\ \text{constant} \tag{4.169a}$$

$$c_A = AY_1 M$$

$$c_Y = AY_1 + HY_1 + z_B\, 2\, B_T \tag{4.169b}$$

Inserting c_A and c_Y into Eq. (4.169a), we obtain:

$$I = HY_1 + AY_1 + (z_B{}^2 + z_B)B_T = C\ M,\ \text{constant.} \tag{4.169c}$$

From here, we can express

$$AY_1 = C - HY_1 - (z_B{}^2 + z_B)B_T \qquad (4.169d)$$

the concentration to be used for AY in solution T_1.

The total cell emf is defined by Eq. (2.48). The intercept of the plot $E_B' = E_B$ - $(g/z_B)\log_{10} c_B$ versus c_B, at constant c_H, gives a conditional constant:

$$E_{0B1} = E_{0B} + g\, d_2\, c_H \qquad (4.169e)$$

where the function d_2 is defined by Eq. (2.50). Knowing the ionic molar conductivities involved in Mixture 1, E_{0B} can be calculated from E_{0B1}.

4.4.1.2 The Determination of the Constant E_{0H}

This should be done at constant level of $BY_{z(B)}$, by titrating v_0 ml solution S_0 with v_1 ml solution $T_1 = v_2$ ml solution T_2 with the compositions given here.

Solution S_0: $c_B = B_T$ M $B^{z(B)+}$, is kept constant

$c_H = HY_0 = 25 \times 10^{-3}$ M HY

AY_0 M AY

Solution T_2: AOH2 = 0.10 M

AY_2 M AY

c_H should be varied within the range $1\times10^{-3} < c_H < 25\times10^{-3}$.

For solution S_0 we have:

$$I = (1/2)(c_H + B_T\, z_B{}^2 + c_A + c_Y) = C\ \text{M},\ \text{constant} \qquad (4.170a)$$

where

$$c_A = AY_0$$

$$c_Y = AY_0 + HY_0 + z_B\, B_T \qquad (4.170b)$$

Inserting c_A and c_Y into Eq. (4.170a), we obtain:

$$I = HY_0 + AY_0 + [(z_B{}^2 + z_B)/2]B_T = C\ \text{M},\ \text{constant} \qquad (4.170c)$$

From here, we can express

$$AY_0 = C - HY_0 - [(z_B{}^2 + z_B)/2]B_T\ \text{M} \qquad (4.170d)$$

the concentration to be used for AY in solution S_0.

For solution T_2 we have:

$$I = (1/2)(AOH2 + c_A + c_Y) = C\ M, \text{ constant} \qquad (4.171a)$$

where

$$c_A = AY_2 + AOH2\ M \qquad (4.171b)$$

$$c_Y = AY_2$$

Inserting c_A and c_Y into Eq. (4.171a), we obtain

$$AY_2 = C - AOH2 \qquad (4.171c)$$

In the test solution,

what is the mixture of solutions S_0 and T_1, T_2, we have

$$c_B = B_T, \text{ is kept constant}$$

$$I = (1/2)(c_H + c_B\, z_B{}^2 + c_A + c_Y) = C\ M, \text{ constant} \qquad (4.172a)$$

$$c_A = AY_T + AOH_T \qquad (4.172b)$$

$$c_Y = AY_T + HY_T + z_B\, B_T \qquad (4.172c)$$

Inserting c_A and c_Y into Eq. (4.172a), we obtain

$$I = HY_T + AY_T + [(z_B{}^2 + z_B)/2]B_T + (1/2)AOH_T = C\ M, \text{ constant} \qquad (4.172d)$$

From Eq. (4.172d), we obtain

$$AY_T = C - HY_T - [(z_B{}^2 + z_B)/2]B_T - (1/2)\ AOH_T \qquad (4.172e)$$

The total cell emf is defined by Eq. (2.54). Plotting the function $E_H' = E_H - g \log_{10} c_H$ versus c_H, at constant c_B, it results in a conditional constant

$$E_{0H1} = E_{0H} + g\ d_3\ c_B \qquad (4.173)$$

where the function d_3 is given by Eq. (2.55).

Knowing the ionic molar conductivities in Mixture 2, the constant E_{0H} can be calculated from Eq. (4.173). If we do not have conductivity data, E_{0H} should be determined in the absence of the metal ions, $B^{z(B)+}$.

After the E_{0H} determination is finished, we can reduce the volume of the test solution to v^x ml, by sucking out a known volume of the test solution with a calibrated pipette, if it is necessary.

4.4.2 Emf Studies Where Strong Complexes Are Formed At $I = C$ M, Constant

4.4.2.1 The Main Titration

After the determination of the constant E_{0B} or E_{0H}, we can continue the titration with the study of the formation of metal ion complexes. We keep B_T constant and vary A_yL. Till v^x ml test solution S, we add v_1 ml solution $T_1{}^x$ of the composition given below.

$$\text{Solution S: } B_T = [BY_{z(B)}] \text{ M}$$

$$HY_S = [HY] \text{ M}$$

$$AY_S = C - [(z_B{}^2 + z_B)/2]B_T - HY_S - (1/2)AOH_T \text{ M}$$

$$\text{Solution } T_1^x : B_T = [BY_{z(B)}] \text{ M}$$

$$HY_1 = [HY] \text{ M}$$

$$L_T = [A_yL] \text{ M}$$

$$AY_1 = C - [(z_B{}^2 + z_B)/2]\, B_T - [y^2 + y)/2]\, L_T - HY_1 - (1/2)\, AOH_T \text{ M} \quad (4.174)$$

Both solutions S and $T_1{}^x$ have a composition which insures the constancy of the ionic strength at C M, if no complex formation takes place between the components.

In this publication, approximate potential functions will be suggested for the preliminary treatment of the emf data, taking into account, first, only the potential contribution of the H^+, $B^{z(B)+}$, L^{y-}, A^+ and Y^- ions to ΔE_J. Here, J denotes an ion, and y is the absolute value of z_L. We can measure the free concentration of the $B^{z(B)+}$ or H^+ ions in equilibrium, b or h, respectively, with the help of the emf cell given in Chapter 1. The composition of the test solution TS2 is given in Néher-Neumann [1]. c_Y is given by Eq. (4.172c).

$$c_A = AY_T + yL_T + AOH_T \quad (4.175)$$

The concentration of AY_T can be obtained from the expression of the ionic strength:

$$I = (1/2)(c_H + z_B{}^2\, B_T + c_Y + y^2\, L_T + c_A) = C \text{ M} \quad (4.176)$$

Inserting Eqs. (4.172c) and (4.175) into Eq. (4.176), we obtain

$$AY_T = C - HY_T - (1/2)\, AOH_T - [(z_B{}^2 + z_B)/2]\, B_T - [(y^2 + y)/2]\, L_T \quad (4.177)$$

Therefore, we have

$$c_Y = [Y^-] = C + z_B\, B_T - (1/2)\, AOH_T - [(z_B{}^2 + z_B)/2]\, B_T - [(y^2 + y)/2]\, L_T \quad (4.178)$$

$$c_A = [A^+] = C - HY_T + (1/2)AOH_T - [(z_B{}^2 + z_B)/2]B_T - [(y^2 + y)/2]L_T + y\,L_T \quad (4.179)$$

For the composition change of the ionic medium, we have

$$\Delta c_Y = c_Y - C = z_B B_T - (1/2)\,AOH_T - [(z_B{}^2 + z_B)/2]\,B_T - [(y^2 + y)/2]\,L_T \quad (4.180)$$

$$\Delta c_A = c_A - C = -HY_T - [(z_B{}^2 + z_B)/2]\,B_T + (1/2)\,AOH_T - [(y^2 + y)/2]\,L_T + y\,L_T \quad (4.181)$$

The general deduction of the potential functions E_B, E_H, E_D, E_{Df}, ΔE_B, and ΔE_H was done in Ref. [38]. Here, we give only the final results and some important functions.

4.4.2.2 Studies on the Formation of Metal Ion Complexes

$$w = c_H\,\lambda_H + c_B\,\lambda_B\,z_B + \lambda_A \Delta c_A + \lambda_Y\,\Delta c_Y + y\,l\,\lambda_L \quad (4.182)$$

$$a = C(\lambda_A + \lambda_Y) \quad (4.183)$$

$$\log_{10} f_{HTS2} = \varepsilon''(H, L)\,l + \varepsilon''(H, Y)\Delta c_Y \quad (4.\,184)$$

$$\log_{10} f_{BTS2} = \varepsilon''(B, L)l + \varepsilon''(B, Y)\Delta c_Y \quad (4.185)$$

The Total Emf of Cell B

The following function was obtained for E_B.

$$E_B = E_{0B} + (g/z_B)\log_{10} b + \Sigma_V\,Q(B, V)\,V \quad (4.186)$$

where, V denotes the ion concentrations h, b, l, Δc_Y and Δc_A, in equilibrium.

The functions Q(B, V) have the following values:

$$Q(B, l) = (g/z_B)\,\varepsilon''(B, L) + g\,F_0\lambda_L - g\,t_A\varepsilon''(A, L) \quad (4.187)$$

$$F_0 = 1/[2.303C(\lambda_A + \lambda_Y)] \quad (4.188)$$

$$Q(B, b) = -g\,F_0\lambda_B + g\,t_Y\varepsilon''(B, Y) \quad (4.189)$$

$$Q(B, h) = -g\ F_0\lambda_H + g\ t_Y\varepsilon''(H, Y) \tag{4.190}$$

$$Q(B, \Delta c_Y) = (g/z_B)\varepsilon''(B, Y) + g\ F_0\ \lambda_Y - g\ t_A\varepsilon''(A, Y) \tag{4.191}$$

$$Q(B, \Delta c_A) = -g\ F_0\ \lambda_A + g\ t_Y\varepsilon''(A, Y) \tag{4.192}$$

The functions Q(B, V) can be estimated in a similar way as discussed in “The Estimation of the Functions Q(H, b) Respective Q(B, b)” and “The Estimation of $\lambda_L{}^{tr}$, λ_A and λ_Y in Mixtures of Strong Electrolytes” of section 4.2.1.1. As is seen, b can be calculated from Eq. (4.186) by successive approximation, knowing E_{0B} and the functions Q(B, V).

If it is recognized in a separate experiment that the undissociated molecules, H_yL, influence the total cell emf, E_B, the potential term SL(B, acid)$[H_yL]_F$ should be added to Eq. (4.186). SL(B, acid) is the slope of the plot E_B – $(g/z_B)\ \log_{10} c_B$ versus $[H_yL]_F$, if E_B was measured at constant c_H, e.g. 0.050 M, and constant c_B, e.g. 0.050 M and I = C M, constant.

The Total Emf of Cell H

The following function was obtained for Cell H.

$$E_H = E_{0H} + g\ \log_{10} h + \Sigma_V\ Q(H, V)\ V \tag{4.193}$$

where V has the same meaning as above.

The functions Q(H, V) have the following values. Q(H, b), Q(H, h) and Q(H, Δc_A) are identical with the corresponding Q(B, V) functions.

$$Q(H, \Delta c_Y) = g\ \varepsilon''(H, Y) + g\ F_0\lambda_Y - g\ t_A\varepsilon''(A, Y) \tag{4.194}$$

$$Q(H, l) = g\ \varepsilon''(H, L) + g\ F_0\lambda_L - g\ t_A\varepsilon''(A, L) \tag{4.195}$$

The function Q(H, b) can be estimated by calculating the difference function Q(H, b) – SL(H, c_B). The slope function SL(H, c_B) is given by Eqs. (2.58), (2.55). Considering the function d_3, given in Eq. (2.55), we obtain

$$\begin{aligned} SL(H, c_B) = {} & [g\,\varepsilon''(H, Y)(z_B - z_B^2)/2] - g\ F_0[\lambda_B - z_B\lambda_Y + (\lambda_Y - \lambda_A)(z_B{}^2 + z_B)/2] \\ & - g\ t_A\varepsilon''(A, Y)(z_B - z_B{}^2)/2 + g\ t_Y[\varepsilon''(B, Y) - \varepsilon''(A, Y)(z_B{}^2 + z_B)/2] \end{aligned} \tag{4.196}$$

Hence, we have

$$Q(H, b) = SL(H, c_B)_{exp} + \text{Eq. (4.189)} - \text{Eq. (4.196)} \tag{4.197a}$$

where exp = experimental.

The difference function is

$$\text{Eq. (4.189)} - \text{Eq. (4.196)} = [-g\,\varepsilon''(\mathrm{H, Y})(z_B - z_B^2)/2] + g\,F_0[-z_B\,\lambda_Y + (\lambda_Y - \lambda_A)\,x\,(z_B^2 + z_B)/2] + g\,t_A\varepsilon''(\mathrm{A, Y})(z_B - z_B^2)/2 + g\,t_Y\varepsilon''(\mathrm{A, Y})(z_B^2 + z_B)/2 \tag{4.197b}$$

Similarly, Q(H, l) can be estimated using the difference function Q(H, l) – SL(H, l), as it will be discussed later.

If it is recognized in a separate experiment that the undissociated molecules, H_yL, influence the total cell emf, E_H, the potential term SL(H, acid) $[H_yL]_F$ should be added to Eq. (4.193). SL(H, acid) is the slope of the plot $E_H - g \log_{10} c_H$ versus $[H_yL]_F$, if E_H was measured at constant c_H, e.g. 0.050 M, and constant c_B and I = C M, constant. The use of formal concentration is motivated if the c_H level is high enough and the dissociation of H_yL is pressed back at the determination of this slope.

According to the treatment presented above, Eq. (4.193) is the correct function for the calculation of the free, equilibrium concentration of the H^+ ions, h, for small values of w/a. This can be done by successive approximations, knowing E_{0H} and the functions Q(H, V).

For the total potential anomalies, we have

$$\Delta E_H = \Sigma_V Q(\mathrm{H, V})\,V \tag{4.198}$$

The Effect of the Composition Changes of the Ionic Medium on the Total Potential Anomalies and on the Equilibrium Constants, for Cell H

At the experimental condition that I = C M, is kept constant, both the concentration of the cation of the ionic medium and that of the anion of the ionic medium, Δc_A and Δc_Y, respectively, deviate from C M AY. These are defined by Eqs. (4.180) and (4.181). Here, the approximate versions given below were used.

$$\Delta c_Y \cong z_B\,B_T - [(z_B^2 + z_B)/2]\,B_T - [y^2 + y)/2]\,L_T \tag{4.199}$$

$$\Delta c_A \cong -[(z_B^2 + z_B)/2]\,B_T - [(y^2 + y)/2]\,L_T + yL_T \tag{4.200}$$

The corresponding potential contributions to the total potential anomalies are

$Q(\mathrm{H}, \Delta c_A)\Delta c_A$ and $Q(\mathrm{H}, \Delta c_Y)\Delta c_Y$. These two functions are very different:

$$Q(\mathrm{H}, \Delta c_Y) = 14.77\ \mathrm{mV\ M^{-1}}(\Delta c_Y),\ [\text{cf. Eq. (4.194)}]$$

$$Q(H, \Delta c_A) = -2.67\ \mathrm{mV\ M^{-1}}(\Delta c_A),\ [\text{cf. Eq. (192)}]$$

for $NaClO_4$ ionic medium.

The neglect of these effects causes systematic errors in ΔE_H, in mV, which can be significant. The caused systematic errors in the equilibrium constants are:

$$\Delta \log_{10} \beta^{(2)}_{pqr} = q\ (1/g)\ Q(H, \Delta c_Y)\Delta c_Y$$

$$\Delta \log_{10} \beta^{(3)}_{pqr} = q\ (1/g)\ Q(H, \Delta c_A)\Delta c_A$$

which can be high as well.

These systematic errors have been estimated in Cell H for two sets of usual emf titrations, where $B_T \le 0.1$ M and strong complexes are formed with the ligand AL, in $NaClO_4$ ionic medium, in Tables 4.20 A. and 4.20 B.

As is seen from Table 4.20 A, the effects of composition changes of the ionic medium on the total potential anomalies are:

$$0.08 - 0.80\ \text{mV for}\ z_B = 2\ \text{and}\ Q(H, \Delta c_A)\ \Delta c_A$$

$$0.16 - 1.60\ \text{mV for}\ z_B = 3\ \text{and}\ Q(H, \Delta c_A)\Delta c_A$$

$$(-0.88) - (-5.91)\ \text{mV for}\ z_B = 2\ \text{and}\ Q(H, \Delta c_Y)\ \Delta c_Y$$

Table 4.20A Survey of the systematic errors in E_H, in mV, due to the composition changes of 3 M $NaClO_4$ when strong complexes are formed in Cell H, for two sets of usual emf titrations, at 25°C and I = 3 M, is kept constant

B_T M	L_T M	Δc_A M	$Q(H, \Delta c_A)\Delta c_A$ mV	Δc_Y M	$Q(H, \Delta c_Y)\Delta c_Y$ mV
For $z_B = 2$					
0.010	0.050	−0.03	0.08	−0.06	−0.89
0.030	0.100	−0.09	0.24	−0.13	−1.92
0.050	0.150	−0.15	0.40	−0.20	−2.95
0.100	0.300	−0.30	0.80	−0.40	−5.91
For $z_B = 3$					
0.010	0.050	−0.06	0.16	−0.08	−1.18
0.030	0.100	−0.18	0.48	−0.19	−2.81
0.050	0.150	−0.30	0.80	−0.30	−4.43
0.100	0.300	−0.60	1.60	−0.60	−8.86

$Q(H, \Delta c_Y) = 14.77\ \mathrm{mV\ M^{-1}}\ (\Delta c_Y)$, $Q(H, \Delta c_A) = -2.67\ \mathrm{mV\ M^{-1}}$ (Δc_A): Δc_Y is defined by Eq. (4.180), Δc_A is defined by Eq. (4.181)

Table 4.20B The effect of the composition changes of 3 M $NaClO_4$, on the equilibrium constants, when strong complexes are formed in Cell H, for two sets of usual emf titrations at 25°C and I = C M, is kept constant. The definition of the change of the equilibrium constants are: $\Delta\log_{10}\beta_{pqr}{}^{(2)} = q(1/g)Q(H,\Delta c_Y)\Delta c_Y$, $\Delta\log_{10}\beta_{pqr}{}^{(3)} = q(1/g)Q(H,\Delta c_A)\Delta c_A$

B_T	$\Delta\log_{10}\beta_{pqr}{}^{(2)}$			$\Delta\log_{10}\beta_{pqr}{}^{(3)}$		
M	q = 1	q = 2	q = 3	q = 1	q = 2	q = 3
For $z_B = 2$						
0.010	−0.015	−0.030	−0.045	0.001	0.002	0.003
0.030	−0.032	−0.065	−0.096	0.004	0.008	0.012
0.050	−0.050	−0.100	−0.150	0.007	0.014	0.021
0.100	−0.100	−0.200	−0.300	0.013	0.026	0.039
For $z_B = 3$						
0.010	−0.020	−0.040	−0.060	0.003	0.006	0.009
0.030	−0.047	−0.095	−0.141	0.008	0.016	0.024
0.050	−0.075	−0.150	−0.225	0.013	0.026	0.039
0.100	−0.150	−0.300	−0.450	0.027	0.054	0.081

$Q(H, \Delta c_Y) = 14.77$ mV M^{-1} (Δc_Y), $Q(H, \Delta c_A) = -2.67$ mV M^{-1} (Δc_A). Δc_Y is defined by Eq (4.180), Δc_A is defined by Eq (4.181)

$$(-1.18) - (-8.86) \text{ mV for } z_B = 3 \text{ and } Q(H, \Delta c_Y)\Delta c_Y$$

The uncertainty level in E_H is not 0.01 mV. These errors are the function of the total concentration of the central metal ion, B_T. Consequently, they will be interpreted as the formation of polynuclear complexes when using a curve-fitting computer program for the explanation of emf data.

The corresponding systematic errors in the equilibrium constants are presented in Table 4.20 B, calculated for different z_B and q values when the complexes $B_pH_qL_r$ are formed. The errors $\Delta\log_{10}\beta_{pqr}{}^{(2)}$ are dominating and can reach – 0.300 $\log_{10}\beta$ units for $z_B = 2$ and – 0.450 $\log_{10}\beta$ units at $z_B = 3$. The errors $\Delta\log_{10}\beta_{pqr}{}^{(3)}$ are much smaller, and have the opposite sign.

4.4.2.3 The Calculation of the Total Potential Anomalies in Emf Cells Where Protolysis of the Weak Acids HL and H₂L Takes Place, Respectively

The Protolysis of HL

We shall study the protolysis

$$HL \rightleftharpoons H^+ + L^-, \quad K_1 = [H^+][L^-]/[HL] \text{ equilibrium constant.}$$

First, the constant of the Nernst equation, E_{0H}, should be determined through an acid–base titration, in the absence of HL. v_0 ml solution S_0 with the composition

$$HY_0 = 0.025 \text{ M HY} + (C - HY_0) \text{ M } AY_T$$

should be titrated with v_1 ml of solution

$$S_{1:}\ AOH_1 = [AOH]\ M, (C - AOH_1)\ M\ AY$$

until we reach pH = 3. The acidity level HY_0 should be checked by a Gran plot [35] (cf. Section 4.2.1.2.). Then we can decrease the volume of the test solution to $v_0{}^x$ ml, if necessary, by sucking out a known volume of the solution with a calibrated pipette. Then v_2 ml of buffer solution S_2 should be added with the composition, e.g. 0.1 M HL, 1.8 M AL = L_T and C – $[(y^2 + y)/2]\ L_T$ M AY. In this buffer system, the approximations discussed in Section (1.1) are valid.

The total cell emf is given by Eqs. (4.192), (4.193), (4.194) and (4.195). For the change of the composition of the ionic medium, we have

$$\Delta c_Y = -(1/2)\ AOH_T - L_T\ \text{[cf. Eq. (4.180)]}$$

$$\Delta c_A = -HY_T + (1/2)\ AOH_T\ \text{[cf. Eq. (4.181)]}$$

The total cell emf can also be written as

$$E_H = E_{0H} + g\ \log_{10} h + SL(H, acid)[acid]_F + SL(H, l)\ L_T + corr \tag{4.201}$$

The acidity of the test solution can be calculated as

$$\log_{10}[H^+] = \log_{10} K_l - \log_{10}(c_{salt}/c_{acid}) \tag{4.202}$$

Inserting Eq. (4.202) into Eq. (4.201), we can form the function E_H''

$$E_H'' = E_H - SL(H, acid)[acid]_F + g \log_{10}(c_{salt/}c_{acid}) = constant + SL(H, l)\ L_T, \tag{4.203a}$$

where

$$constant = E_{0H} + g\ \log_{10} K_l \tag{4.203b}$$

As is seen, the slope of the plot E_H'' versus L_T gives SL(H, l) and from the intercept = constant, the protolysis constant $\log_{10} K_l$ can be obtained with high accuracy in a broad concentration range.

Considering E_H, defined by Eq. (45) in Ref. [38] and Δc_Y and Δc_A, we obtain for the calculated slope

$$\begin{aligned} SL\{H, l = [L^-]\} = dE_H''/d(l = L_T) = g[\varepsilon''(H, L^-) - \varepsilon''(H, Y)] - gF_0(\lambda_Y - \lambda_L) \\ - gt_A[\varepsilon''(A, L^-) - \varepsilon''(A, Y)] \end{aligned} \tag{4.204}$$

This slope function is valid if the buffer system HL – AL is used as the titrating solution.

The Protolysis of H_2L

The first protolysis equilibrium of the acid H_2L can be written as

$$H_2L \rightleftharpoons H^+ + HL^-, \quad K_1 = [H^+][HL^-]/[H_2L] \tag{4.205}$$

We can study this system after the determination of the constant E_{0H} (in the absence of H_2L) by titrating the test solution with the buffer solution, e.g. 0.1 M H_2L, 1.8 M AHL = L_T and $\{C - [(y^2 + y)/2]\ L_T\}$ M AY. In this buffer system, the following approximations are valid:

$$[H_2L] \cong c_{acid}$$

$$[HL^-] = l \cong c_{salt} = HL_T$$

The slope function SL $\{H, l = [HL^-]\}$ is given by Eq. (4.204) (where the species L^- should be replaced by HL^-), obtained by plotting E_H'' [cf. Eq. (4.203a)] versus HL_T.

The slope of this plot is SL$\{(H, l = [HL^-]\ \}$ and the intercept is given by Eq. (4.203b), from which $\log_{10} K_1$ can be calculated.

*For the second protolysis equilibrium of the acid H_2*L, we shall study the reaction

$$HL^- \rightleftharpoons H^+ + L^{2-}, \quad K_2 = [H^+][L^{2-}]/[HL^-] \tag{4.206}$$

in the ionic medium AY under the experimental condition that I = C M, is kept constant. The values $\log_{10} K_1$ and $\log_{10} K_2$ should be well separated.

Deduction for $pK_2 - pK_1 \geq 5$

First, we determine the constant E_{0H} through an acid–base titration, in the absence of the ligand. During the main titration, we can add a solution with the composition, e.g. 0.2 M AHL + 1 M A_2L + $\{C - HY_T - (1/2)\ AOH_T - [(y^2 + y)/2]\ L_T - HL_T\}$ M AY. In the equilibrium solution, the following ions are present: H^+, $[HL^-] \cong c_{acid} = HL_T$, $[L^{2-}] = l \cong c_{salt} = L_T$, Y^- and A^+. The $\log_{10} [H^+]$ of the test solution can be calculated as:

$$\log_{10}[H^+] = \log_{10} K_2 - \log_{10}(c_{salt}/c_{acid}) \tag{4.207}$$

The composition of the test solution is also described in Section 4.1. The concentrations of the ions of the ionic medium are:

$$c_Y = AY_T + HY_T \tag{4.208a}$$

$$c_A = AY_T + AOH_T + yL_T + HL_T \tag{4.208b}$$

For constant ionic strength, we can write

$$I = (1/2)(h + c_A + c_Y + y^2\ L_T + HL_T) = C\ M \tag{4.209}$$

Inserting the values of c_Y and c_A into Eq. (4.209), we have

$$I = HY_T + AY_T + (1/2)\ AOH_T + [(y^2 + y)/2]\ L_T + HL_T = C\ M \tag{4.210}$$

From here, we can express AY_T, the total concentration of the ionic medium, as

$$AY_T = C - HY_T - (1/2)AOH_T - [(y^2 + y)/2]\ L_T - HL_T \tag{4.211}$$

Hence, we have

$$c_A = C - HY_T + (1/2)\ AOH_T - [y^2 + y)/2]\ L_T + y\ L_T \tag{4.212}$$

$$\Delta c_A = c_A - C = -HY_T + (1/2)\ AOH_T - [(y^2 + y)/2]\ L_T + y\ L_T \tag{4.213}$$

$$c_Y = C - (1/2)AOH_T - [(y^2 + y)/2]\ L_T - HL_T \tag{4.214}$$

$$\Delta c_Y = c_Y - C = -(1/2)AOH_T - [(y^2 + y)/2]\ L_T - HL_T \tag{4.215}$$

The test solution is a mixture of the strong electrolytes AHL, A_2 L and AY. The total cell emf is:

$$E_H = E_{0H} + g\ \log_{10} h + SL(H, HL^-)\ HL_T + SL(H, L^{2-})\ L_T + corr \tag{4.216}$$

Assuming h $\approx$ 0 and inserting $\log_{10}$ h from Eq. (4.207) into Eq. (4.216), we can form E_H'' and neglect corr.

$$\begin{aligned} E_H'' &= E_H + g\ \log_{10}(c_{salt}/c_{acid}) - SL(H, HL^-)\ HL_T \\ &= E_{0H} + g\ \log_{10} K_2 + SL(H, L^{2-})\ L_T \end{aligned} \tag{4.217}$$

The theoretical slope function SL(H, HL^-) is given by Eq. (4.204), where the species L^- should be replaced by HL^-. Plotting E_H'' versus L_T, the experimental slope is SL(H, L^{2-}) and for the intercept, we obtain: E_{0H} + g $\log_{10}$ K_2, from which $\log_{10}$ K_2 can be calculated.

For the theoretical slope function SL(H, L^{2-}), the following equation was deduced [38]:

$$\begin{aligned}\mathrm{SL\{H, l = [L^{2-}]\}} &\equiv \mathrm{d\,E_H''/d\,L_T = g\varepsilon''(H, L) - g\varepsilon''(H, Y)[(y^2 + y)/2]}\\ &- \mathrm{g\,F_0\{\lambda_A[(y - (y^2 + y)/2] + \lambda_Y[(y^2 + y)/2] - \lambda_L\} - g\,t_A[\varepsilon''(A, L)}\\ &- \mathrm{\varepsilon''(A, Y)(y^2 + y)/2] + g\,t_Y\varepsilon''(A, Y)[y - (y^2 + y)/2]}\end{aligned} \tag{4.218}$$

Using the difference and experimental slope functions, we obtain:

$$\mathrm{Q\{H, l = [L^{2-}]\} = SL\{H, l = [L^{2-}]\}_{exp} + Eq.\ (4.195) - Eq.\ (4.218)} \tag{4.219}$$

If the complexes formed in the test solution, TS2, are present at dominant concentrations, the complete functions for E_D and E_{Df} should be used and integrated graphically, without approximations, as presented in Section 4.1.

It should be mentioned that $I \neq C$ M, constant, when complex formation takes place in the cell. It means that $D(I) \neq D(C)$ in the expressions for the activity coefficients.

Deduction for $pK_2 - pK_1 < 5$

If both the first and second step of the protolysis equilibrium takes place simultaneously, only a brutto protolysis constant can be determined according to

$$\beta_{0qr} = \mathrm{K_1.K_2 = [H^+]^2[L^{2-}]/[H_2L]} \tag{4.220}$$

These processes can be studied by titrating with the buffer solution H_2L-A_2L, after the determination of E_{0H} (in the absence of H_2L). The composition of the titrating solution can be:

$$\mathrm{[H_2L] \cong c_{acid} = 0.1\ M}$$

$$\mathrm{[L^{2-}] \cong c_{salt} = L_T = 1.5\ M\ A_2L}$$

$$\mathrm{AY_T = \{C - HY_T - (1/2)\ AOH_T - [(y^2 + y)/2]L_T\}M\ AY}$$

The brutto protolysis constant, β_{0qr}, can be obtained from the emf data graphically or by using a curve-fitting computer program, as discussed in “Deduction for $pK_2-pK_1 < 5$” in section 4.3.1.4.

4.4.3 Emf Studies on Weak Complex Formation At I = C M, Kept Constant

When formation of weak complexes is studied in the $HY - BY_{z(B)} - AY - A_yL$ system, only the presence of the species H^+, $B^{z(B)+}$, L^{y-}, A^+ and Y^- is considered. This means that the formation of metal ion complexes and the protolysis products are neglected in B_T and L_T. These are the same conditions as those used at the deduction of the potential functions for formation of strong complexes used for the preliminary treatment of emf data (cf. Section 4.4.2.). It is advisable to use higher B_T levels: 0.1−0.2 M. But the effect of the composition change of the inert ionic medium cannot be neglected. As only 1−2 % of the total concentration of the central metal ion is bound in weak metal ion complexes, the approximation $b = [B^{z(B)+}] \cong [BY_{z(B)}] = B_T$ can be used, first. The total concentrations of the ligand should be low: $L_T < 0.025$ M.

The titrations can be carried out as described in Sections 4.4.1 and 4.4.2 E_{0B} should be determined at constant level of HY_1. Conductivity data are necessary for the calculation of E_{0B} from the conditional constant obtained:

$$E_{0B1} = E_{0B} + gd_2c_H$$

where E_{0B1} is the intercept of the plot $E_B' = E_B - (g/z_B) \log_{10} c_B$ versus c_B, at constant c_H. The function d_2 is defined by Eq. (2.50).

If we use a glass indicator electrode, the constant E_{0H} should be determined in the absence of the metal ions, $B^{z(B)+}$, if we do not have conductivity data on the system studied. On the other hand, it is advisable to have a constant level of $[H_yL]$, because the effect of these undissociated molecules on E_H is changing with the experimental conditions. In this way, a conditional constant is obtained, from which the term SL(H, acid) $[H_yL]_F$ should be subtracted.

It is important that *we do not use conditional constants, E_{0B1} or E_{0H1}*. Until now, E_{0H1} has been determined in the presence of high concentration of $BY_{z(B)}$. No correction was made for the term $g\ d_3\ c_B$.

In Ref. [38], a number of titrations have been investigated by the author, where weak complexes are formed, using Cells B and H, respectively. These titrations are carried out in different ways and are realizing different approximations, which are based upon the results of strong complex formation. The conditional constant E_{0H1} is supposed to be determined, which is wrong. *The statement that the potential contributions of the $B^{z(B)+}$ ions to E_H, during the determination of E_{0H},* $g\ d_3\ c_B$, and *the term $Q(H, c_B)B_T$, can be incorporated in E_{0H}, is the result of a misunderstanding. The reported formation of polynuclear complexes is erroneous.*

The Main Titration

After the determination of the constant E_{0B} or E_{0H}, we can study the complex formation reactions. We add v_1 ml solution $T_1 = v_2$ ml solution T_2 with the composition given below, to the test solution.

$$\text{Solution } T_1\text{: } B_T \text{ M } BY_{z(B)}$$

$$HY_1 \text{ M strong acid}$$

$$AY_1 = \{C - HY_1 - [(z_B{}^2 + z_B)/2]\, B_T\} \text{ M AY}$$

$$\text{Solution } T_2\text{: } (H_yL_T - HY_1/y)\ 2\ M\ H_yL \text{ weak acid} = \text{constant}$$

$$(A_yL_T - HY_1/y)\ M\ A_yL$$

$$AY_2 = \{C - HY_1 - [(y^2 + y)/2]\ L_T\}\ M\ AY$$

In this case, B_T is varied during the main titration. If we want to keep a constant B_T level, we should adjust it at the end of the determination of E_{0H}. Then $2B_T = c_B$ M should be used in solution T_1.

For the total cell emf, we obtain at I = C M, constant.

$$E_B = E_{0B} + (g/z_B)\ \log_{10} b + \Sigma_V\ Q(B, V)\ V + SL(B, \text{acid})[H_yL]_F \tag{4.221}$$

$$E_H = E_{0H} + g\ \log_{10} h + \Sigma_V\ Q(H, V)\ V + SL(H, \text{acid})[H_yL]_F \tag{4.222}$$

where $V = b, h, l, \Delta c_Y, \Delta c_A$. The terms Q(B, h) h and Q(H, h) h are probably negligible, as $h < 1\times10^{-3}$ M.

4.4.4 *On the Ionic Medium Dependence of the Equilibrium Constants*

Potential functions were derived for the calculation of the total potential anomalies for small values of w/a, in the systems, $HY - BY_{z(B)} - H_yL - AY$ when strong or weak complexes are formed, respectively, and for the systems, HL – AL – AY and $AHL - A_2L - AY$ at the experimental conditions

(a) $[A^+] = C$ M, constant,
(b) $[Y^-] = C$ M, constant,
(c) I = C M, constant,

respectively.

The potential contributions obtained, $\Sigma_V\ Q(H, V)\ V$ with $V = b, h, l, \Delta c_Y$ or/and Δc_A, e.g. for Cell H in the total cell emf, are the systematic errors in $\log_{10}$ h, which influence the value of the equilibrium constants. These effects will be investigated in two steps:

(a) The value of the functions Q(H, V) in mV M^{-1} for $V = [H^+], [Cd^{2+}], \Delta c(ClO_4^-), \Delta c_{Na}$, [acetate⁻] and [Hascorbate⁻] will be estimated in a *given ionic medium, e.g.* $NaClO_4$.
(b) The value of the functions $Q(H, \Delta c_Y)$ or/and $Q(H, \Delta c_A)$, which describe the potential contributions caused by the composition change of the ionic medium, will be estimated in various ionic medium: $NaClO_4$, $LiClO_4$ and NaCl, at the experimental conditions defined above.

The functions Q(H, V) can be estimated in two ways:

(i) through conductivity data, measured in the equilibrium system studied,
(ii) using known slope functions, determined in mixtures of strong electrolytes. This method results in approximate values for the Q(H, V) functions.

As conductivity data are not available for the equilibrium system studied, the known slope functions were used for the estimations. Most of these treatments were already described in several chapters, here. The necessary functions are summarized in Appendix 2 for the reader's convenience, in order to get a better survey.

4.4.4.1 Comparison of the Values of the Mentioned Potential Functions Q(H, V) at Different Experimental Conditions

These potential functions are presented in Table 4.21. The slope functions they were calculated from, are also included in the table. It is seen from this table that the function Q{H, $[Cd^{2+}]$} has almost the same value at $[Na^+] = 3$ M and $[ClO_4^-] = 3$ M experimental condition. But it should be pointed out that the difference is not the result of experimental errors. Every value was obtained by a forward and back titration on the slope function SL(H, c_B). These values are accurate at a given experimental condition, although they are the result of the approximation that the ionic molar conductivities have the same values in both functions. The differences are due to the different values of $\lambda_B{}^{tr}$ which are valid at different experimental conditions. These were calculated from the definition:

$$Q(H, b) = -g\, F_0 \lambda_B^{tr} + g\, t_Y \varepsilon''(B, Y) \tag{4.189}$$

and are given in Table 4.21. The value ε'' (Cd, ClO_4) = 0.40 liter solution (mol solute)$^{-1}$ [31] was used in the calculations.

As is seen from this table, the function Q{H, $[Cd^{2+}]$} defines very different values for $\lambda_{Cd}{}^{tr}$ at the different experimental conditions. They cannot be interchanged. Moreover, it is obvious that the functions Q(H, V), valid in equilibrium systems, are quite different than the corresponding slope functions, valid in mixtures of strong electrolytes.

The same conclusions can be drawn from the analysis of the function Q{H, $[H^+]$}. Here, the values of $\lambda_H{}^{tr}$ were calculated from the definition:

$$Q(H, h) = -g\, F_0 \lambda_H^{tr} + g\, t_Y \varepsilon''(H, Y) \tag{4.190}$$

The values $\varepsilon''(H, ClO_4) = 0.18$ and $\varepsilon''(Na, ClO_4) = 0.03$ [31], both in liter solution (mol solute)$^{-1}$ were used in the calculations, moreover, t_Y data from Table 2.10.

The value of Q(H, Acetate$^-$) is very different at $[Na^+] = 3$ M, constant, and at $[ClO_4] = 3$ M, constant. This is due to the fact that in the previous case, there is a

Table 4.21 Comparisons of the values of the potential functions Q(H, V) for V = $[H^+]$, $[Cd^{2+}]$, $[CH_3COO^- = Ac^-]$, $[HAscorbate^- = HAsc^-]$, Δc_Y and Δc_A at different experimental conditions in the system $HClO_4 - Cd(ClO_4)_2 - NaClO_4 - Na_YL$

Experimental condition	$[Na^+] = 3$ M (constant)	$[ClO_4{}^-] = 3$ M (constant)	I = 3 M (constant)
mV M^{-1} ()			
Q(H, Δc_Y)	14.8		14.8
Q(H, Δc_A)		−2.7	−2.7
SL(H, c_B) (Cd^{2+})	42.4 ± 0.5	19.06	1.6
Q{H, $[Cd^{2+}]$} (Cd^{2+})	13.0	13.74	8.35
$\lambda_{Cd}{}^{tr}$ S cm^2. $(g\ mol)^{-1}$	3.12	−1.59	32.78
SL(H, c_H) (H^+)	−4.2 ± 1	−21.8	−17.7
Q{H, $[H^+]$} (H^+)	−17.3	−24.5	−20.4
$\lambda_H{}^{tr}$ S cm^2 $(g\ mol)^{-1}$	71.62	117.54	91.20
SL(H, $HAsc^-$) ($HAsc^-$)	−9.6		
Q{H, $[HAsc^-]$} ($HAsc^-$)	5.47		
SL(H, Ac^-) (Ac^-),		$0 \leq [NaAc] \leq 0.58$ M	
		−9.3	−10.5
		$0.58 \leq [NaAc] \leq 1.3$ M	
		−7.8	
Q{H, $[Ac^-]$} (Ac^-)		$0 \leq [NaAc] \leq 0.58$ M	
		5.6	−7.8
		$0.58 \leq [NaAc] \leq 1.3$ M	
		7.1	

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large positive term, $g\varepsilon''(H, ClO_4) = 10.45$ mV M^{-1}, in the difference function [cf. Eq. (4.93 a, b)]. This will result in that different species/equilibrium constants will be found at these two experimental conditions, if we do not take them into account. The definition of this potential function is:

$$Q(H, l) = g\ \varepsilon''(H, L) + g\ F_0\lambda_L{}^{tr} - g\ t_A\varepsilon''(A, L) \qquad (4.53)$$

The value of $\lambda_L{}^{tr}$ could have been calculated from it, but only ε'' (H, Ac^-) was measured [31] and not ε'' (Na, Ac^-). The opposite case is valid for the H_2Asc − NaHAsc system.

Moreover, it can be seen from Table 4.21 that the magnitude of the potential functions, due to changes in the composition of the ionic medium, Q(H, Δc_Y) or/and Q(H, Δc_A), are very much different at the various experimental conditions. This will result in the change of the equilibrium constants with the experimental conditions within a given ionic medium, if we do not take into account these effects.

Table 4.22 Presentation of the values of the potential functions Q (H, Δc_Y) and Q(H, Δc_A) in the ionic media $LiClO_4$ and NaCl. Here, Y = ClO_4^- or Cl^- and the temperature: t = 25°C

Ionic medium: $LiClO_4$ Experimental condition mV M^{-1} ()	$[Li^+]$ = 3 M constant[18]	$[ClO_4^-]$ = 3 M constant[19]	I = 3 M constant
Q(H, Δc_Y) (Δc_Y)	13.1		13.1
Q(H, Δc_{Li}) (Δc_{Li})		2.8	2.8
Ionic medium: NaCl, Experimental condition mV M^{-1}	$[Na^+]$ = 3 M constant[18]	$[Cl^-]$ = 3 M constant[19]	I = 3 M constant
Q(H, Δc_{Cl})(Δc_{Cl})	10.45		10.45
Q(H, Δc_{Na})(Δc_{Na})		0.7	0.7

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4.4.4.2 The Dependence of the Equilibrium Constants ($\log_{10} \beta_{pqr}$) on the Ionic Medium

The composition changes in the ionic media $LiClO_4$ and NaCl have also been estimated. These are given in Table 4.22. In these calculations, we have used: ε'' (H, Cl) $\cong \varepsilon$(H, Cl) = 0.12 [13]; ε'' ($LiClO_4$) $\cong \varepsilon$ ($LiClO_4$) = 0.15 [17]; ε'' (Na, Cl) = 0.10 [31]; ε'' (H, ClO_4) = 0.18 (cf. Table 2.3). The ε'' values are given in units of (liter solution) mol^{-1} and the ε values in (kg solution) mol^{-1}. The molar conductivities and transport numbers of the ionic media are given in Tables 2.10 and 2.11.

The formation of complex species is described by Eqs. (I)–(III) given in Section 4.3 for emf cells containing the reacting compounds, $BY_{z(B)} + HY + A_yL$, and the ionic medium (A^+,Y^-). For example, for reaction (II) we have, considering the formation of strong complexes

$$\begin{aligned} pB + qH + rL^{y-} &\rightleftharpoons B_pH_qL_r \equiv cpx \\ \log_{10} \beta_{pqr} &= \log_{10} [cpx] - p \log_{10} b - q \log_{10} h - r \log_{10} l \end{aligned} \tag{4.223}$$

where for $[A^+]$ = C M and $[Y^-]$ = C M, constant, with a H^+-sensitive indicator electrode, we have

$$\begin{aligned} -q \log_{10} h = (-q/g)\{&-E_H + E_{0H} - g[D(I) - D(C)] + Q(H, h)h + Q(H, b)b \\ &+ Q(H, l)l + Q(H, \Delta c_A)\Delta c_A \text{ or/and } Q(H, \Delta c_Y)\Delta c_Y\} \end{aligned} \tag{4.224}$$

The change in $\log_{10} \beta_{pqr}$ with the composition of the ionic medium is

(i) (q/g) Q(H, Δc_Y) Δc_Y, for $[A^+]$ = C M, constant,
(ii) (q/g) Q(H, Δc_A) Δc_A, for $[Y^-]$ = C M, constant,
(iii) (q/ g) {Q(H, Δc_A) Δc_A + Q(H, Δc_Y) Δc_Y}, for I = C M, constant.

As can be seen from Tables 4.21 and 4.22, the magnitude of the potential functions, due to changes in the composition of the ionic medium, are different in the different ionic media. This will contribute to changes of the equilibrium constants in the different ionic media, if we do not take into account the composition changes of the ionic medium.

The magnitude of the Q functions due to the composition change of the ionic media in Cell H is at C = 3 M: smallest in NaCl at $[Cl^-] = 3$ M < as in $NaClO_4$, at $[ClO_4^-] = 3$ M < as in $LiClO_4$ at $[ClO_4^-] = 3$ M < as in NaCl at $[Na^+] = 3$ M < as in NaCl at I = 3 M < as in $NaClO_4$ at I = 3 M < as in $LiClO_4$ at I = 3 M.

The composition change Δc_Y for I = C M, constant, is given by Eq. (4.180) and is a function of B_T, L_T and AOH_T. Δc_A is given by Eq. (4.181) and is also a function of the same total concentrations and HY_T. If we do not take into account the potential contributions Q(H, Δc_A) Δc_A and Q(H, Δc_Y) Δc_Y, the calculated equilibrium constants will be a function of B_T, L_T, and AOH_T/HY_T. Consequently, this effect will be interpreted as the formation of polynuclear complexes which are artefacts. The potential contribution Q(H, b) b will also have the same effect.

Moreover, it can be added that the transport numbers, t_A and t_Y, the molar conductivities, Λ_{AY}, the ionic molar conductivities, $\lambda_A = \Lambda_{AY}\, t_A$, $\lambda_Y = \Lambda_{AY}\, t_Y$ (cf. Tables 2.10 and 2.11) and the interaction coefficients, ε''(A, Y), ε''(H, Y) and ε''(B, Y), are different in the various ionic media. Therefore, the term, F_0, and the potential functions, Σ_V Q(H, V) V and Σ_V Q(B, V) V with V = h, b, l, Δc_A and/or Δc_Y, will also be different. Consequently, for cell H for example, in the different ionic media the potential terms, Σ_V Q(H, V) V, will result in a medium dependence of the equilibrium constants.

In a given ionic medium, the equilibrium constants also change with the experimental conditions used, $[A^+] = C$ M, $[Y^-] = C$ M, I = C M. This is due to the change in composition of the ionic medium and the change of the ionic molar conductivities λ_H, λ_B and λ_L with the experimental conditions. Compare the different slope functions at the different experimental conditions, for cell H:

$$\mathrm{SL(H,\ c_H),\ SL(H, c_B), SL(H,\ l = [L^-]), SL(H,\ l = [HL^-])\ and\ SL(H,\ l = [L^{2-}]).}$$

Consequently, the functions Q(H, h), Q(H, b) and Q(H, l) will also change. Such slope functions have been measured systematically only in aqueous $NaClO_4$ medium.

As a summary, we can write that the ionic medium dependence of the equilibrium constants is caused by the total potential anomalies, modified by the Debye–Hückel term of the $\log_{10} f_{JTS2}$ value of the measuring electrode. We assume that the species, H^+, $B^{z(B)+}$, L^{y-}, A^+ and Y^- are present in the test solution. Then we have the following potential functions which cause the ionic medium dependence of the equilibrium constants.

For $[A^+] = C$ M (constant) with V = h, b, l and Δc_Y:
Cell H

$$\begin{aligned}\Delta E_H + g[D(I) - D(C)] - \mathrm{corr} &= g[\varepsilon''(H,\ L)l + \varepsilon''(H,\ Y)\Delta c_Y] \\ &\quad + E_D + E_{Df} = \Sigma_V Q(H,\ V)V \text{ mV}\end{aligned} \tag{4.225a}$$

and

$$\Delta \log_{10} \beta_{pqr} = -q\Delta \log_{10} h = q(1/g)\Sigma_V\, Q(H,\ V)V \tag{4.225b}$$

Cell B

$$\Delta E_B + gz(B)[D(I) - D(C)] - corr = (g/z_B)[\varepsilon''(B,\ L)l + \varepsilon''(B,\ Y)\Delta c_Y] + E_D + E_{Df} = \Sigma_V\, Q(B,\ V)V\ mV \tag{4.226a}$$

and

$$\Delta \log_{10} \beta_{pqr} = -p\Delta \log_{10}\ b = p(z_B/g)\Sigma_V\, Q(B,\ V)V \tag{4.226b}$$

For $[Y^-] = C$ M (constant) with V = h, b, l and Δc_A:

Cell H

$$\Delta E_H + g[D(I) - D(C)] - corr = g\,\varepsilon''(H,\ L)l + E_D + E_{Df} = \Sigma_V\, Q(H,\ V)V\ mV \tag{4.227}$$

Cell B

$$\Delta E_B + gz_B[D(I) - D(C)] - corr = (g/z_B)\varepsilon''(B,\ L)l + E_D + E_{Df} = \Sigma_V Q(B,\ V)V\ mV \tag{4.228}$$

For I = C M (constant) with V = h, b, l, Δc_A and Δc_Y:

Cell H

$$\Delta E_H = g[\varepsilon''(H,\ L)l + \varepsilon''(H,\ Y)\Delta c_Y] + E_D + E_{Df} = \Sigma_V Q(H,\ V)V\ mV \tag{4.229}$$

Cell B

$$\Delta E_B = (g/z_B)[\varepsilon''(B,\ L)l + \varepsilon''(B,\ Y)\Delta c_Y] + E_D + E_{Df} = \Sigma_V\, Q(B,\ V)V\ mV \tag{4.230}$$

The term “corr”, defined by Eqs. (1.23), (1.24), is negligible.

Considering complex formation at the experimental condition $[Y^-] = C$ M, constant, and cell H, the total cell emf is,

$$E_H = E_{0H} + g\ \log_{10} h - g[D(I) - D(C)] + \Sigma_V\, Q(H,\ V)V + corr \tag{4.231}$$

From here

$$\log_{10} h = \{E_H - E_{0H} + g[D(I) - D(C)] - \Sigma_V\, Q(H,\ V)V\}/g \tag{4.232}$$

neglecting corr.

This means that the contribution to the medium dependence of $\log_{10} \beta_{pqr}$ is

$$(q/g)\Sigma_V Q(H,\ V)V,\ \text{for } V = h,\ b,\ l \text{ and } \Delta c_A.$$

If we use cell B, at the same experimental condition, we have:

$$E_B = E_{0B} + (g/z_B)\log_{10} b - g\, z_B[D(I) - D(C)] + \Sigma_V\, Q(B,\ V)V \qquad (4.233)$$

$$\log_{10} b = (z_B/g)\{E_B - E_{0B} + g\, z_B[D(I) - D(C)] - \Sigma_V\, Q(B,\ V)V\} \qquad (4.234a)$$

As can be seen, the contribution to the medium dependence of $\log_{10}\beta_{pqr}$ is (p z_B/g) Σ_V Q(B, V)V, different from that in cell H and is probably greater at the same experimental condition. Consequently, we obtain different $\log_{10}\beta_{pqr}$ values in the different cells, if we do not correct for these potential contributions.

The estimated functions Q in Tables 4.21 and 4.22 are approximate and are based on the assumption that the ionic molar conductivities λ_B, λ_H, λ_L, λ_A and λ_Y are the same in the slope and Q functions at a given experimental condition. Moreover, λ_A and λ_Y are identical with those valid in C M ionic medium AY. This must be proven by conductivity measurements (cf. Section 2.1 on p. 561 in Part 6A [23] and Chapter 3). In order to be able to calculate accurate Q functions, we must do conductivity measurements, because the ionic molar conductivities involved in them are functions of the composition of the test solutions.

4.5 Conclusion on Cells with Complex Formation

From the emf studies of the total potential anomalies in the equilibrium systems HY − $BY_{z(B)}$ − A_yL − AY which appear in Cell B and Cell H at the experimental conditions generally used in potentiometric titrations, the following conclusions could be drawn. We have treated emf cells where either strong or weak complexes are formed, respectively.

4.5.1 Strong Complexes Are Formed

1.1. The main species are most probably correct which have been found by curve-fitting computer programs, if for the total potential anomalies the following criterion is fulfilled: $\Delta E_B = 0.01$ mV and $\Delta E_H = 0.01$ mV. This is valid for usual concentration conditions, when the total concentration of the central metal ion, B_T, is equal or smaller than 0.1 M. The following titration set was investigated at the experimental condition that $[ClO_4^-] = 3$ M, constant, and for $z_B = 2$ and 3.

B_T/M	A_yL_T/M
0.010	0.050
0.030	0.100
0.050	0.150
0.100	0.300

The total concentration of the ligand ≤ 0.3 M.

1.2. Among all possible experimental conditions with Cell H, the case $[Y^-] = C$ M, is kept constant, was the best (cf. Table 4.7).

It is seen from this table that the systematic errors in E_H, due to composition changes of the ionic medium, are

(a) for $z_B = 2$:
change between (−0.08) − (−0.27) mV, which corresponds to (−0.001) − (0.012) $\log_{10} \beta$ units in the equilibrium constants, depending upon B_T and q, if the species $B_p\, H_q\, L_r$ are formed.

(b) for $z_B = 3$:
The systematic errors in E_H are practically zero, and in the equilibrium constants too.

1.3. For Cell H with the experimental condition $[Na^+] = C$ M, constant, the results of Table 4.1 are valid. The systematic errors in E_H, due to composition change of the ionic medium, vary

(a) for $z_B = 2$:
between (−0.44) and (−1.48) mV, which corresponds to (−0.007) − (−0.075) $\log_{10} \beta$ units in the equilibrium constants, depending upon B_T and q. These systematic errors cannot be neglected, and the uncertainty level 0.01 mV cannot be used for the fit.

(c) for $z_B = 3$:
The systematic errors in E_H vary between (−0.29) − (0) mV with relatively small errors in $\log_{10} \beta_{pqr}$.

1.4. For Cell H with the experimental condition $I = C$ M, constant, the results of Tables 4.20 A and 4.20 B are valid. The systematic errors in E_H, due to composition changes of the ionic medium, are

(a) for $z_B = 2$:

$$Q(H, \Delta c_A)\Delta c_A \text{ varies between (0.08) and (0.80) mV with } \Delta \log_{10} \beta_{pqr}^{(3)} :$$

$$(0.001) - (0.039) \log_{10} \beta \text{ units}$$

$$Q(H, \Delta c_Y)\Delta c_Y \text{varies between (–0.89) and (–5.91) mV with } \Delta \log_{10} \beta_{pqr}^{(2)} :$$

$$(-0.015) - (-0.300) \log_{10} \beta \text{ units, depending upon } B_T \text{ and q.}$$

(b) for $z_B = 3$:

$$Q(H, \Delta c_Y)\Delta c_Y \text{ varies between (–1.18) and (–8.86) mV, with } \Delta \log_{10} \beta_{pqr}^{(2)} :$$

$$(-0.020) - (-0.450)\log_{10}\beta \text{ units.}$$

$$Q(\mathrm{H},\,\Delta c_{\mathrm{A}})\Delta c_{\mathrm{A}} \text{ varies between (0.16) and (1.60) mV, with } \Delta\log_{10}\beta_{\mathrm{pqr}}{}^{(3)}:$$

$$(-0.003) - (-0.081)\log_{10}\beta \text{ units, depending upon } \mathrm{B_T} \text{ and q.}$$

These are large systematic errors, which cannot be neglected.

1.5. The functions Q(H, V)V, with V = $[\mathrm{B}^{z(\mathrm{B})+}]$, $[\mathrm{H}^+]$, $[\mathrm{L}^{y-}]$, contribute also to the total potential anomalies. These were estimated for the Cd^{2+}, acetate$^-$ and Hascorbate$^-$ ions. Moreover, for the ions of the ionic medium, the potential functions Q(H, Δc_{Y}) and Q(H, Δc_{A}) are also included (cf. Table 4.21). Except for Q(H, h)h with $h < 1\times10^{-3}$ M, these potential contributions must also be taken into account.

1.6. The use of the conditional constants $E_{0\mathrm{H}1}$ and $E_{0\mathrm{B}1}$ causes also systematic errors in $\log_{10}\beta_{\mathrm{pqr}}{}^{(1)}$, which is a function of $\mathrm{B_T}$, q and p. These cases have already been discussed for cells with mixtures of strong electrolytes (cf. Tables 2.1, 2.8 and 2.15).

1.7. In order to be able to estimate ΔE_{H} and ΔE_{B}, either accurate conductivity measurements must be carried out in the test solutions studied (cf. Chapter 3 and Section 4.2.1.4.), or the slope functions SL(B, c_{B})$_1$ and SL(B, c_{H})$_1$ for Cell B, moreover, SL(H, c_{H})$_1$ and SL(H, c_{B})$_1$ for Cell H should be determined.

1.8. The total potential anomalies, ΔE_{B} and ΔE_{H}, must be estimated in advance, when planning the experiments, having the necessary conductivity data, in order to know that which uncertainty level should be used in the fit, when curve-fitting computer program is used for the explanation of emf data.

1.9. The activity factors definitely are not constant at the use of the constant ionic medium method. But this method is useful, because

(a) the ionic activity factors can be estimated with enough accuracy,
(b) the ionic molar conductivities are constant in liquid junctions of constant ionic medium type. This can be seen from the plots of the different slope functions. Otherwise, it would be impossible to calculate or determine experimentally the total potential anomalies.

1.10. If $\Delta E_{\mathrm{B}} > 0.01$ mV and $\Delta E_{\mathrm{H}} > 0.01$ mV, formation of polynuclear complexes or dimer and trimer species will be suggested, which do not exist, namely, they are artefacts.

1.11. The experimental constant $E_{0\mathrm{H}}$ should be determined in the absence of the central metal ions $\mathrm{B}^{z(\mathrm{B})+}$, if we do not have conductivity data on the test solutions. In the studies of metal ion complex formation, the undissociated weak acid, $\mathrm{H_yL}$ (ligand), should be present at a constant concentration level even during the $E_{0\mathrm{H}}$ titration. In the main titration, a buffer solution should be used as a titrating solution with a constant level of $[\mathrm{H_yL}]$.

1.12. In order to keep the interaction coefficients constant, at planning the potentiometric titrations, we should choose the total concentrations B_T and L_T so that the change of the ionic strength is on a minimum level:

$$\Delta I_A = I_A - C,\ \Delta I_Y = I_Y - C,\ I - C$$

Cf. Chapter 6.

4.5.2 Weak Complexes Are Formed

For the study of weak complex formation with Cell H, usually the self-medium method is used at the experimental condition $[Y^-] = C$ M, constant. In this case, high and constant concentrations are used for the total concentrations of the central metal ion, e.g. $B_T = 0.1, 0.3, 0.5, 0.7$ M. These cells have been analysed in detail, before.

The use of conditional constants, E_{0H1}, moreover, the composition change of the ionic medium, $Q(H, \Delta c_A)\ \Delta c_A$ or/and $Q(H,\Delta c_Y)\ \Delta c_Y$, and the potential contributions $Q(H, V)V$ with $V = h, b, l$ result in huge systematic errors in E_{0H1}, E_H and the equilibrium constants. The systematic errors in ΔE_H and in the equilibrium constants are a function of B_T. This looks like the formation of polynuclear complexes. This conclusion is valid for both graphical methods and curve-fitting computer treatments. The systematic errors can reach 1 $\log_{10} \beta_{pqr}$ units. This method is not suitable for emf studies, if we do not correct the effects of the conditional constant E_{0H1} and the total potential anomalies.

According to Table 4.12, the effect of the use of the conditional constant E_{0H1} on the equilibrium constants gives the highest systematic errors ($-\ q\ \Delta\log_{10} h$), followed by the contribution of the central metal ion and the composition change of the ionic medium:

$$\Delta \log_{10} \beta_{pqr}{}^{(1)} = q(gd_3\ c_B)/g \succ \Delta \log_{10} \beta_{pqr}{}^{(3)} = q(1/g)Q(H, Cd)Cd_T \succ$$

$$\Delta \log_{10} \beta^{(2)}_{pqr} = q(1/g)Q(H, \Delta c_A)\Delta c_A$$

$$\text{at}[ClO_4^-] = 3\ \text{M},\ \text{constant}.$$

In Refs. [18, 35, 38], the statement that the potential contributions $g\ d_3\ c_B$ and $Q(H, b = B_T)\ B_T$ can be incorporated into E_{0H} is a misunderstanding.

These studies of the author are based upon

(a) theoretical equations derived by the author [Ref. 1, 7, 10, 18, 20–23, 25, 35, 38] for the calculation of the total potential anomalies ΔE_B and ΔE_H, using only assumptions which have been proved to be true,
(b) accurate emf measurements of the author, where the total emf values, E_B and E_H, were red with ±0.01 mV uncertainties,
(c) accurate conductivity measurements of the author, where the uncertainty of the resistance measurements was 0.02% [20–22],
(d) accurate conductivity data of Georg Biedermann and Gerard Douhéret [39, 40].

Appendix 1

Some proposals for the preparation of the test solution in emf cells with complex formation.

The potentiometric titration for the $HY-BY_{Z(B)}-H_yL$ system can be carried out in different ways, as it is discussed below.

(1) First, the constants E_{0B} and E_{0H} should be determined by titrating v_0 ml solution S_0 with v_0 ml solution T_0 with the compositions given here.

$$\begin{aligned}
S_0 &= 2B_T \text{ M } B^{z(B)+} \\
&\quad 25 \times 10^{-3} \text{ M HY} \\
&\quad AYS_0 = C \text{ M AY} \\
T_0 &= 20 \times 10^{-3} \text{M AOH} \\
&\quad AYT_0 = (C - 20 \times 10^{-3} \text{ M } AOH_T) \text{ M AY}
\end{aligned}$$

At the end of the E_0 − titration, we have the composition of solution S:

$$S = B_T,\ HYS = 2.5 \times 10^{-3} \text{ M HY},\ AOH_T,\ AYS = C - AOH_T \text{ M AY}.$$

The cell solution, TS_2, can be prepared during the main titration by adding v_1 ml T_1 and $v_2 = v_1$ ml solution T_2 to v_S ml solution S.

$$\begin{aligned}
&\text{Solution } T_1 : 2B_T,\ HY_1,\ AY_1 = C \text{ M}. \\
&\text{Solution } T_2 : L_{T2},\ AY_2, = C - yL_{T2}.
\end{aligned}$$

This titration can be carried out if the total concentrations $[A^+]$ and $[BY_{z(B)}]$ should be kept constant during the main titration at the levels C and B_T M, respectively. The constants E_{0B} and E_{0H} can be determined as shown in Chapter 2.

(2) If the total concentrations c_{AT}, $[BY_{z(B)}]$ and $[H_yL_T]$ should be kept constant during the main titration at the levels C, B_T, c_{H_yL}, respectively, we have for the composition of the solutions

$$\begin{aligned}
S_0 &: 2B_T \text{ M } B^{z(B)+} \\
&\quad 25 \times 10^{-3} \text{M HY} \\
&\quad AYS_0 = C \text{ M AY} \\
&\quad 2c_{H_yL} \text{ M } H_y \text{ L}
\end{aligned}$$

T_0 has the same composition as before. Moreover,

$$\mathrm{S} : \mathrm{B_T},\ \mathrm{HYS},\ c_{\mathrm{H_yL}},\ \mathrm{AYS} = \mathrm{C} - \mathrm{AOH_T}\ \mathrm{M\ AY}$$
$$\mathrm{T_1} : 2\mathrm{B_T},\ \mathrm{HY_1},\ 2c_{\mathrm{H_yL}},\ \mathrm{AY_1} = \mathrm{C\ M}$$
$$\mathrm{T_2} : \mathrm{AOH_2},\ \mathrm{AY_2} = \mathrm{C} - \mathrm{AOH_2 M\ A_y}$$

(3) If the total concentrations $[A^+]$, $[BY_{z(B)}]$ and $[A_yL]$ should be kept constant during the main titration at the values C, B_T and L_T M, respectively, we have for the composition of the solutions

$$\mathrm{S_0} = 2\ \mathrm{B_T}\ \mathrm{M}\ \mathrm{B}^{z(B)+}$$
$$\mathrm{HY} = 25 \times 10^{-3} + \mathrm{y}2\mathrm{L_T}\ \mathrm{M}$$
$$\mathrm{AYS_0} = \mathrm{C} - \mathrm{y}2\mathrm{L_T}\ \mathrm{M\ AY}$$
$$2\mathrm{L_T}\ \mathrm{M\ A_yL}$$

T_0 has the same composition as before.

$$\mathrm{S} : \mathrm{B_T},\ \mathrm{L_T},\ \mathrm{HYS} = 1 \times 10^{-3} + \mathrm{yL_T}\ \mathrm{M},\ \mathrm{AYS} = \mathrm{C} - \mathrm{AOH_T} - \mathrm{yL_T}\ \mathrm{M\ AY}$$
$$\mathrm{T_1} : \mathrm{B_T},\ \mathrm{L_T},\ \mathrm{HY_1} = \mathrm{x}\ 10^{-3}\ \mathrm{M},\ \mathrm{AY_1} = \mathrm{C} - \mathrm{yL_T}\ \mathrm{M}$$

(4) The main titration can be carried out by the addition of a buffer solution containing $[\mathrm{acid}]_F = [\mathrm{HL}^{-y+1}]_F$ M, $[\mathrm{salt}]_F = [\mathrm{L}^{y-}]_F = L_T$ and C $-$y $[\mathrm{salt}]_F$ M AY to solution S.
The composition of the solutions S_0, T_0, S and T_1 has the same values as given under point (1). Here, F denotes formal concentration.

$$\mathrm{T_2} : c_{\mathrm{HL}},\ L_{\mathrm{T2}},\ \mathrm{AY_2C} - \mathrm{yL_{T2}}$$

This titration can be carried out in different ways.

(4a) We can either keep the formal concentration of the acid constant, when the ratio $[\mathrm{acid}]_F$ / $[\mathrm{salt}]_F$ is changing,

(4b) or we can keep the ratio $[\mathrm{acid}]_F$ / $[\mathrm{salt}]_F$ constant, and titrations are made at different ratios.

Notation
Appendix 2

Survey of the Estimated Q(H, V) Functions with $V = h, b, l = [L^-]$, $l = [L^{2-}]$, Δc_A and/or Δc_Y at $[A^+] = C$ M, Is Kept Constant

(1) The difference function is

$$\mathrm{Q(H, h)} - \mathrm{SL(H,}\ c_{\mathrm{H}})_1 = \mathrm{Eq.\ (4.51)} - \mathrm{Eq.\ (2.14b)\ g}$$

and

$$Q(H,\ h) = SL(H,\ c_H)_{1\,exp} - g\varepsilon''(H,\ Y) - gF_0\lambda_Y + g\ t_A\varepsilon''(A,\ Y) \quad (4.235)$$

where

$$F_0 = 1\ /\ [2.303\ C\ (\lambda_A + \lambda_Y)] \quad (2.5)$$

$$t_Y = \lambda_Y/(\lambda_A + \lambda_Y) \text{ and } t_A = \lambda_A/(\lambda_A + \lambda_Y) \quad (2.6)$$

$$\text{exp} = \text{experimental.}$$

(2) The difference function is

$$Q(H,\ b) - SL(H,\ c_B)_1 = \text{Eq. (4.52)} - \text{Eq. (2.14a) g}$$

and

$$Q(H,\ b) = SL(H,\ c_B)_{1\,exp} - g\ z_B\varepsilon''(H,\ Y) - g\ z_B\ F_0\lambda_Y + g\ z_Bt_A\varepsilon''(A,\ Y) \quad (4.60bc)$$

(3) The difference function is

$$Q(H,\ L^-) - SL(H,\ L^-) = \text{Eq. (4.53)} - \text{Eq. (4.89)}$$

and

$$Q(H,\ L^-) = SL(H,\ L^-)_{exp} + g\varepsilon''(H,\ Y) + gF_0\lambda_Y - g\ t_A\varepsilon''(A,\ Y) \quad (4.93ab)$$

(4) The difference function is

$$Q(H,\ L^{2-}) - SL(H,\ L^{2-}) = \text{Eq. (4.53)} - \text{Eq. (4.105)}$$

and

$$Q(H,\ L^{2-}) = SL(H,\ L^{2-})_{exp} + g\ y\varepsilon''(H,\ Y) + g\ y\ F_0\lambda_Y - g\ y\ t_A\varepsilon''(A,\ Y) \quad (4.106)$$

$SL(H, L^{2-})_{exp}$ can be obtained on the basis of Eq. (4.101).

(5) The composition change of the ionic medium is

$$Q(H, \Delta c_Y) = g\varepsilon''(H,\ Y) + g\ F_0\lambda_Y - g\ t_A\varepsilon''(A,\ Y) \quad (4.54)$$

and

$$\Delta c_Y = HY_T + z_B\ B_T - AOH_T - yL_T \quad (4.56)$$

At $[Y^-] = C$ M, Is Kept Constant

(1) The difference function is

$$Q(H,\ h) - SL(H,\ c_H)_1 = Eq.\ (4.51) - Eq.\ (2.29)\ g$$

and

$$Q(H,\ h) = SL(H,\ c_H)_{1\,exp} - g\ F_0\lambda_A + g\ t_Y\varepsilon''(A,\ Y) \tag{4.236}$$

(2) The difference function is

$$Q(H,\ b) - SL(H,\ c_B)_1 = Eq.\ (4.52) - Eq.\ (2.28)\ g$$

and

$$Q(H,\ b) = SL(H,\ c_B)_{1\,exp}\ {}_{-}gF_0 z_B\lambda_A\ g\ F_0\ z_{B\lambda A} + g\ t_Y\ z_B\varepsilon''(A,\ Y) \tag{4.237}$$

(3) The difference function is

$$Q(H,\ L^-) - SL(H,\ L^-) = Eq.\ (4.53) - Eq.\ (4.129)$$

and

$$Q(H,\ L^-) = SL(H,\ L^-)_{exp} + g\ F_0\ y\lambda_A - g\ y\ t_Y\varepsilon''(A,\ Y) \tag{4.131}$$

(4) The difference function is

$$Q(H,\ L^{2-}) - SL(H,\ L^{2-}) = Eq.\ (4.53) - Eq.\ (4.143)$$

and

$$Q(H,\ L^{2-}) = SL(H,\ L^{2-})_{exp} + g\ y\ F_0\lambda_A - g\ y\ t_Y\varepsilon''(A,\ Y) \tag{4.144}$$

(5) The composition change of the ionic medium is

$$Q(H, \Delta c_A) \equiv Q(B, \Delta c_A) = -g\ y\ F_0\lambda_A + g\ t_Y\varepsilon''(A,\ Y) \tag{4.111}$$

and

$$\Delta c_A = c_A - C = AOH_T - HY_T - z_B\ B_T + y\ L_T \tag{4.110}$$

At $I = C$ M, Is Kept Constant

(1) The difference function is

$$Q(H,\ h) - SL(H,\ c_H) = Eq.\ (4.51) - Eq.\ (2.50)\ g$$

and

$$Q(H,\ h) = SL(H,\ c_H)_{exp} - g\ F_0\lambda_A + g\ t_Y\varepsilon''(A,\ Y) \tag{4.238}$$

(2) The difference function is

$$Q(H,\ b) - SL(H,\ c_B) = \text{Eq. (4.189)} - \text{Eq. (4.196)}$$

and

$$Q(H,\ b) = SL(H,\ c_B)_{exp} + \text{Eq. (4.197b)}$$

(3) The difference function is

$$Q(H,\ L^-) - SL(H,\ L^-) = \text{Eq. (4.195)} - \text{Eq. (4.204)}$$

and

$$Q(H,\ L^-) = SL(H,\ L^-)_{exp} + g\ \varepsilon''(H,\ Y) + g\ F_0\lambda_Y - g\ t_A\varepsilon''(A,\ Y) \tag{4.239}$$

(4) The difference function is

$$Q(H,\ L^{2-}) - SL(H,\ L^{2-}) = \text{Eq. (4.195)} - \text{Eq. (4.218)}$$

and

$$Q(H,\ L^{2-}) = SL(H,\ L^{2-})_{exp} + \text{difference function} \tag{4.219}$$

(5) The composition change of the ionic medium is

$$Q(H, \Delta c_A) = -g\ F_0\lambda_A + g\ t_Y\varepsilon''(A,\ Y) \tag{4.192}$$

and

$$\begin{aligned}\Delta c_A = c_A - C = -HY_T - [(z_B{}^2 + z_B)/2]B_T + (1/2)AOH_T \\ -\ [(y^2 + y)/2]\ L_T + y\ L_T\end{aligned} \tag{4.181}$$

$$Q(H, \Delta c_Y) = g\varepsilon''(H,\ Y) + g\ F_0\lambda_Y - g\ t_A\varepsilon''(A,\ Y) \tag{4.194}$$

and

$$\Delta c_Y = c_Y - C = z_B\ B_T - (1/2)\ AOH_T - [(z_B{}^2 + z_B)/2]\ B_T - [(y^2 + y)/2]\ L_T \tag{4.180}$$

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Chapter 5

Estimation of the Total Potential Anomalies and the Determination of the Equilibrium Constants in Emf Cells Where Every Kind of Complex Can Be Present

In the previous chapters, equations have been derived for the estimation of the total potential anomalies and the preliminary data treatment for the equilibrium systems $HY - BY_{z(B)} - A_yL - AY$. In these calculations, the species $B^{z(B)+}$, L^{y-}, A^+, Y^- and H^+ were assumed to be present. The potential functions Q(H, V)V with $V = [B^{z(B)+}]$, $[H^+]$, $[L^{y-}]$, Δc_Y or / and Δc_A have been estimated, partly by conductivity measurements and partly by the use of known slope functions. Having these functions, $\log_{10}$ h can be calculated by successive approximations. Then preliminary chemical models and equilibrium constants can be established with the help of a curve-fitting computer program. From these results, one can see if the presence of the metal ion complexes is negligible or not. If they are not negligible, new treatment of emf data must be planned. This can take place through several steps.

First, we make an emf titration for the system studied, and carry out a preliminary treatment of the data:

estimation of the total potential anomalies,

calculation of the preliminary $\log_{10}$ h values,

establishment a preliminary chemical model,

calculation of the preliminary equilibrium constants,

calculation of the preliminary equilibrium concentrations.

As a second step, an identical titration should be carried out where the conductivity of the test solution is measured. The ionic molar conductivities of the species formed are determined with the help of a curve-fitting computer program, using the equilibrium concentrations obtained above.

With the help of the conductivity data, new $\log_{10} h_{exp}$ values should be calculated, taking into account the formation of the complexes found during the preliminary data treatment: P_i, N_j, L_k. For Cell H, we have for the total cell emf:

$$E_H = E_{0H} + g \log_{10} h_{exp} - g[D(I) - D(C)] + \Sigma_v Q(H, V)V + E_D{}^x + E_{Df}{}^x \quad (5.1)$$

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where

$V = h, b, l, \Delta c_Y$ or/and Δc_A for the Q(H, V)V functions defined before,

$E_D{}^x$ and $E_{Df}{}^x$ defined on the basis of Eqs. (4.28) and (4.34b), respectively, including only the metal ion complexes and the protolysis products of the weak acid (ligand). In these equations, N is defined by Eq. (4.29a). Then we have

$$E_D{}^x = -(g/2.303)\int_{x=0}^{x=1}(1/N)[\Sigma_i\lambda_{P_i}u_ip_ix^{ui-1} - \Sigma_{k>1}\lambda_{L_k}l_ku_kx^{uk-1} - \Sigma_j\lambda_{Nj}n_j^{uj}x^{uj-1}]dx \tag{5.2}$$

$$\begin{aligned}E_{Df}{}^x = -g\int_{x=0}^{x=1}(1/N)[\Sigma_i\lambda_{Pi}p_ix^{ui}\,d\log_{10}f^*_{P_i} - \Sigma_{k>1}\lambda_{L_k}l_kx^{uk}d\log_{10}f^*_{L_k}\\ -\Sigma_j\lambda_{Nj}n_jx^{uj}d\log_{10}f_{Nj}{}^*]dx\end{aligned} \tag{5.3}$$

For $[A^+] = C$ M, constant, we have

$$\begin{aligned}w &= \lambda_Hh + \lambda_Bbz_B + \lambda_Ly1 + \lambda_Y\Delta c_Y\\ a &= C(\lambda_A + \lambda_Y)\end{aligned} \tag{5.4}$$

At the other experimental conditions, the first three terms of Eq. (5.4) are the same. The last term appears due to the composition change of the ionic medium.

For $[Y^-] = C$ M, constant, the term concerning the composition change is $\Delta c_A\ \lambda_A$. For $I = C$ M, constant, it will be: $\Delta c_Y\ \lambda_Y + \Delta c_A\ \lambda_A$.

The term $E_D{}^x$ can be estimated by graphical integration for every titration point, as the equilibrium concentrations and the corresponding λ_J values are known.

The term $E_{Df}{}^x$ should also be integrated graphically, using approximate values for the interaction coefficient of P_i, $L_{k>1}$ and N_j ions, taken from ε''(ions) of the same charges.

Now, new $\log_{10} h_{\,exp}$ values (cf. Eq. (5.1)) should be calculated and minimizing the least–squares sum U.

The function $\log_{10} h$ should be combined with the expression for the equilibrium constants. Considering the equilibrium

$$pB + qH + rL \rightleftharpoons B_pH_qL_r \equiv \text{complex, cpx} \tag{I}$$

the concentration equilibrium constant is defined as

$$\log_{10}\beta_{pqr} = \log_{10}[\text{complex}] - p\log_{10}b - q\log_{10}h - r\log_{10}l \tag{5.5}$$

The theoretical value for $\log_{10} h$ can be obtained as

$$\log_{10} h_{calc} = -(1/q)\log_{10}\beta_{pqr} + (1/q)\log_{10}[\text{complex}] - (p/q)\log_{10}b - (r/q)\log_{10}l \tag{5.6}$$

or

$$h_{calc} = H_T - \Sigma_{pqr}\ q\beta_{pqr}\ b^p\ h^q\ l^r \tag{5.7a}$$

where calc = calculated and β_{pqr}, (p,q,r) pairs belonging together, are parameters.

Now, one can minimize residual-squares sum with a curve-fitting computer program, e.g.:

$$U = \Sigma_i w_i (h_{exp} - h_{calc})_i^2 = \Sigma_i w_i r^2 \tag{1.53}$$

until we reach a minimum value of U. This is the "best" fit for the parameters involved. This means an uncertainty of 0.01 mV on ΔE_H respective ΔE_B.

The total potential anomalies are, for Cell H:

$$\Delta E_H = -g[D(I) - D(C)] + \Sigma_V Q(H, V)V + E_D{}^x + E_{Df}{}^x \tag{5.7b}$$

with V = h, b, l, Δc_Y or/and Δc_A.

For Cell B, we have

$$\Delta E_B = -g z_B[D(I) - D(C)] + \Sigma_V Q(B, V)V + E_D{}^x + E_{Df}{}^x \tag{5.8}$$

If we want to calculate thermodynamical equilibrium constants, on the activity scale, we should calculate the ionic activity factors of the ions involved.

The definition of the activity coefficients

We define $\log_{10} f_J$ in general, according to the specific interaction theory (SIT) [1-8] cf. Eqs. (12) and (13) in the Definitions. The reference state is chosen in such a way that the trace activity coefficients $f_J{}^{tr} \to 1$ as $c_J \to 0$ in C M AY as solvent. Hence, we can write for some intermediate plane in the transition layer

$$\begin{aligned}\log_{10} f_J{}^* = -z_J^2[D(I^*) - D(C)] &+ [\Sigma_k \varepsilon''(J, L_k) l_k{}^* \\ &+ \Sigma_j \varepsilon''(J, N_j) n_j{}^* + \varepsilon''(J, Y)(c_Y{}^* - C)]_{ca} \\ &+ [\varepsilon''(J, H)h^* + \varepsilon''(J, B)b^* + \Sigma_i \varepsilon''(J, P_i) p_i{}^*]_{an}\end{aligned} \tag{5.9}$$

$$\begin{aligned}&\text{Here, } [\ldots]_{ca} = \text{the terms to be used if J is a cation,}\\ &[\ldots]_{an} = \text{the terms to be used if J is an anion.}\\ &(I^*) = \text{the ionic strength in the transition layer}\\ &= xI(TS2) + (1 - x)I(TS1)\end{aligned} \tag{5.10}$$

With x =1, we obtain $\log_{10} f_J$ values in the test solution (TS2).

Different $\log_{10} \beta_{pqr}$ values can be calculated.

The definition of the equilibrium constants

We consider the complex formation reaction denoted (I).

The thermodynamical equilibrium constant is defined as

$$\beta_{pqr}^{TD} = [cpx]b^{-p}h^{-q}l^{-r}.f(cpx)f(B)^{-p}f(H)^{-q}f(L)^{-r} \equiv \beta_{pqr} f(cpx)f(B)^{-p}f(H)^{-q}f(L)^{-r} \tag{5.11}$$

It denotes the formation constant of reaction (I), expressed on the activity scale. The magnitude of $\beta_{pqr}{}^{TD}$ depends on the choice of the reference or standard state for the activity coefficients.

β_{pqr} is the so-called *concentration constant* valid in the test solution studied, expressed on the concentration scale at the ionic strength I = C M, defined by Eq. (5.12). The ratio of the activity coefficients involved in Eq. (5.12) is generally considered to be constant

$$= [cpx]b^{-p}h^{-q}l^{-r} = \beta^{TD}_{pqr} f(B)^{p} f(H)^{q} f(L)^{r} f(cpx)^{-1} \tag{5.12}$$

$\beta_{pqr}{}^{C}$ is valid at trace levels of the species J (c_J) in C M AY as reference state. It can be determined on the basis of Eq. (5.12), which now takes the form of Eq. (5.13). Here, $\log_{10} f_J$ values defined by Eq. (5.9) should be inserted.

$$\log_{10} \beta_{pqr} = \log_{10} \beta^{C}_{pqr} + p\log_{10} f(B) + q\log_{10} f(H) + r\log_{10} f(L) - \log_{10} f(cpx), \tag{5.13}$$

$\beta_{pqr}{}^{0}$ = is *the equilibrium constant in pure water as standard state* for the activity coefficients. This can be determined through extrapolation of a suitable function to I = 0, using $\beta_{pqr}{}^{C}$ values belonging to different C levels. This procedure is based upon Eq. (5.12), which now takes the form of (5.14). The $\log_{10} f(J)$ values defined by Eq. (5.15) should be inserted.

$$\log_{10} \beta^{C}_{pqr} = \log_{10} \beta^{0}_{pqr} + p\log_{10} f(B) + q\log_{10} f(H) + r\log_{10} f(L) - \log_{10} f(cpx) \tag{5.14}$$

$$\begin{aligned} \log_{10} f(J) = {} & -z_J^2 D(I) + \{\varepsilon''(J, Na)[Na^+] + \varepsilon''(J, B)[B^{z(B)+}] \\ & + \Sigma_i \varepsilon''(J, P_i) p_i + \varepsilon''(J, H) h\}_{an} + \{\varepsilon''(J, ClO_4)[ClO_4^-] \\ & + \Sigma_k \varepsilon''(J, L_k) l_k + \Sigma_j \varepsilon''(J, N_j) n_j\}_{ca}, \end{aligned} \tag{5.15}$$

Equilibrium constants can be determined by standard methods [9–11], mostly graphical ones (normalized curves) [9, 11–14]. These give the main species present and the average composition of the system studied. For the refinement of the constants and finding the minor species, curve-fitting computer programs [12, 15] are used, which should be revised according to the theory presented here.

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Chapter 6
On Emf Titrations Proposed for the Determination of Some Interaction Coefficients [1]

Certain galvanic cells without liquid junctions, used together with a titration technique, are proposed to determine interaction coefficients for the various ion pairs present in the solutions. The experimental values of the interaction coefficients are needed in calculations of the total emf of cells with liquid junctions considered in other chapters of this book.

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6.1 Introduction

The emf cells studied in this book are used in potentiometric titrations and comprise the following:

(i) Mixtures of strong electrolytes (cf. Chapter 2) with liquid junctions of constant ionic medium type: $AY \mid AY + HY + BY_{z(B)}$;
(ii) Equilibrium systems where formation of strong [2–5] or weak (cf Chapter 4) complexes takes place with liquid junctions of the type:

$$AY \mid AY + HY + BY_{z(B)} + A_yL$$

The total cell emf (E_B or E_H) and the total potential anomalies ΔE_J have been calculated. For these calculations, we must know interaction coefficients for ion pairs $\varepsilon''(H^+, Y^-)$, $\varepsilon''(B^{z(B)+}, Y^-)$, $\varepsilon''(A^+, Y^-)$, $\varepsilon''(A^+, Cl^-)$, $\varepsilon''(H^+, Cl^-)$, $\varepsilon''(A^+, L^{z(L)-})$, $\varepsilon''(H^+, L^{z(L)-})$. A few of the coefficients can be found in the literature (cf. Refs. [6–9]) or in Tables 2.3 and 4.2. But in the present emf studies, we need many new interaction coefficients. Long ago Guggenheim and Turgeon [6] suggested using cells without liquid junctions for the determination of interaction coefficients for some dilute 1:1 electrolytes. In this study, suitable cells will be proposed for the determination of the interaction coefficients listed above.

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In order to obtain the highest possible accuracy, the concentration of the ion, which is the independent variable, has to be increased in the cell, as much as possible, by titration. As the interaction coefficients depend on the ionic strength I, this should be varied within a broad range: $0.5 \leq I \leq 3$ M.

The study of the liquid junctions is important, as the neglect of their effects results in systematic errors; these might be interpreted erroneously as indicating that polynuclear complexes have formed [3]. In the following, ionic charges in superscript and in the symbols used for the interaction coefficients will be omitted for simplicity. For the estimation of the activity coefficients, the standard state is defined in such a way that activity coefficients $f_J \rightarrow 1$ as $I \rightarrow 0$.

6.2 Survey of Some Emf Cells for Determination of Interaction Coefficients

6.2.1 Determination of the Interaction Coefficient ε″(B,Y)

The interaction coefficient $\varepsilon''(B, Y)$ between an amalgam-forming cation B and the anion Y of the medium can be determined by emf measurements, as we have done for the determination of ε'' (Cd, ClO_4). The symbol Y can denote ClO_4^-. Cell 1 is used:

$$- \text{Hg, Cd } (0.01\%) \mid \text{Cell solution} \mid \text{GE} + \qquad \text{Cell 1}$$

where GE denotes a glass electrode.

The cell solution has the composition:

$0.020M\ Cd(ClO_4)_2$

$0.020\ M\ HClO_4$

$0.459\ M\ NaClO_4$

The cell solution was titrated with a solution of the composition: 0.020 M $Cd(ClO_4)_2$, 0.020 M $HClO_4$, and X M $NaClO_4$. $[ClO_4^-]$ in the cell solution was varied over the range $0.5 \leq [ClO_4^-] \leq 4.1$ M. The emf of the cell (in mV) at 25°C can be written as

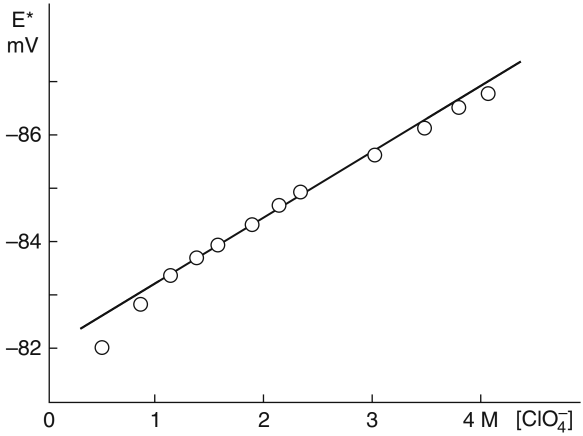
$$E = E_0 + 29.58 \log_{10}\{h^2\, f_H^2\, [Cd^{2+}]^{-1}\, f_{cd}^{-1}\} \tag{6.1}$$

where E_0 is an experimental constant.

The activity coefficients involved can be expressed using the Specific Interaction Theory [6–12] (SIT): cf. Eqs. (12, 13).

$$\log_{10} f_H = -D(I) + \varepsilon''(H, ClO_4)\, [ClO_4^-] \tag{6.2}$$

Fig. 6.1 Determination of the interaction coefficient $\varepsilon''(Cd^{2+}, ClO_4^-)$. Plot of E* vs. $[ClO_4^-]$. Reproduced with kind permission of Springer Science and Business Media from Néher-Neumann E (2003) The liquid junction potential in potentiometric titrations. VII. On emf titrations proposed for the determination of some interaction coefficients. J Solution Chem 32: 645–662 (Fig. 1)



$$\log_{10} f_{Cd} = -z_{Cd}^2 D(I) + \varepsilon''(Cd, ClO_4)\,[ClO_4^-] \tag{6.3}$$

where D(I) is the Debye–Hückel term for the cell solution, given by Eq. (2), in the Definitions.

By plotting the function E*, as defined by:

$$\begin{aligned} E^* &\equiv E - 29.58 \log_{10}\{h^2\,[Cd^{2+}]^{-1}\} - 59.16\,D(I) \\ &= E_0 + 29.58\,[2\varepsilon''(H, ClO_4) - \varepsilon''(Cd, ClO_4)]\,[ClO_4^-] \end{aligned} \tag{6.4}$$

against $[ClO_4^-]$, the unknown ε'' (Cd, ClO_4) could be calculated from the slope of the straight line obtained, using ε'' (H, ClO_4) = 0.18 liter solution/mol solute, taken from Table 2.3. This plot is shown in Fig. 6.1.

The results are as follows:

$$\varepsilon''(Cd, ClO_4) = 0.40 \text{ liter solution/mol solute}$$

$$\varepsilon(Cd, ClO_4) = 0.32 \text{ kg solvent/mol solute}$$

The ε value obtained here is in good agreement with the value suggested in Ref. [9] and with the predicted value [7] ε (Cd, ClO_4) = 0.27 – 0.34 based on the interaction coefficients of [(Ca, Mg, Co, Cu, Zn, Hg, with z = +2) ClO_4^-].

6.2.2 Determination of ε (A^+ = Na, L)

For the determination of the interaction coefficient between a ligand anion $L^{z(L)-}$ and the Na^+ ions, ε(Na, L), the author suggests the following emf method, using Cell 2.

$$-\ \mathrm{Ag(s), AgCl(s)}\ |\ \text{Cell solution}\ |\ \mathrm{IS\ Na^+}\ +\qquad \text{Cell 2}$$

The cell solution has the composition:

0.01 M NaCl

0.5 M $NaClO_4$

In Cell 2, IS Na^+ denotes a Na^+-selective glass electrode. The cell solution should be titrated with a solution of the composition: 0.01 M NaCl, X M Na_yL (or $Na_{y-1}HL$, $Na_{y-2}H_2L$, etc., where $y = |z_L|$), Z M $NaClO_4$ (in order to increase the ionic strength of the cell). The $[Na_yL]$ of the cell should be increased by the titration to as high value as possible. The experiences gained in this laboratory about the use of IS Na^+ electrodes of commercial Type 39 137 of the Beckman Co. and of Type 46 72 10 of the Corning Glass Co. are presented in Ref. [13]. The potential of both Na^+-selective glass electrodes drifted with time. For the use of these electrodes for accurate emf measurements, an extrapolation procedure is suggested, as described in the Experimental section.

In order to check the reliability of the Na^+-selective glass electrode, a back titration must be done. At the end of the forward titration, we decrease the volume of the test solution by sucking out a portion with a pipette. We then continue to titrate with a solution of 0.01 M NaCl.

The emf of cell 2, in mV and with molal concentrations, can be written as

$$E = E_0 + g \log_{10}(m_{Na}\, m_{Cl}) + g \log_{10}(\gamma_{Na}\gamma_{Cl}) \tag{6.5}$$

Here, $g = (10^3\ RT\ \ln 10)/F$ and the values of the constants are given in the Definitions... often used in the text. Expressing the $\log_{10} \gamma_J$ values according to SIT [6–12], we have

$$\log_{10} \gamma_{Cl} = -D(I) + \varepsilon\,(Na, Cl)m_{Na} \tag{6.6}$$

$$\log_{10} \gamma_{Na} = -D(I) + \varepsilon\,(Na, Cl)m_{Cl} + \varepsilon(Na, ClO_4)m_{ClO4} + \varepsilon\,(Na, L)m_L \tag{6.7}$$

Substituting the functions obtained for $\log_{10} \gamma_{Cl}$ and $\log_{10} \gamma_{Na}$ into Eq. (6.5), we have

$$\begin{aligned} E^* \equiv E - g \log_{10}(m_{Na}m_{Cl}) + g2D(I) - g\varepsilon\,(Na, Cl)(m_{Cl} + m_{Na}) \\ - g\varepsilon\,(Na, ClO_4)m_{ClO4} = E_0 + g\varepsilon\,(Na, L)\, m_L \end{aligned} \tag{6.8}$$

By plotting the function E^* against m_L, the value of ε (Na, L) can be calculated from the slope of the straight line obtained. Here, we need the constants

ε(Na, Cl) [6] = 0.13 kg solvent (mol solute)$^{-}$1

$\varepsilon(Na, ClO_4)$ [14] = 0.03 kg solvent (mol solute)$^{-1}$

If we use ε''(Na, Cl) and ε'' (Na, ClO_4) in liter solution (mol solute)$^{-1}$ determined in this paper, our calculations for ε'' (Na, L) can be carried out on the molar scale as well.

This procedure was used by the author for the determination of ε'' (Na^+, $HAsc^-$).

$HAsc^-$ denotes the hydrogen ascorbate ion.

The cell solution had the composition: 0.1 M NaCl and 1.000 M $NaClO_4$. We used a titrating solution: 0.1 M NaCl, 1.000 M NaHAsc, and 2.286×10^{-2} M H_2Asc. The pH of this titrating solution is approximately 6. A Na^+-selective glass electrode, Model 84-11 ROSS, was used from the ORION Research Company, which suggests pH = 6 – 12 for the measurements of Na^+ concentration. For the protolysis constant of the ascorbic acid, the value

$$H_2Asc \leftrightharpoons HAsc^- + H^+, \log_{10} K_1 = -4.359$$

was used for the calculation of the pH. The interaction coefficient ε''(Na^+, Hasc) was determined on the molar concentration scale. The plot E* against [NaHAsc] is shown in Fig. 6.2, according to Eq. (6.8).

ε'' (Na, Cl) = 0.05 was used in the calculations. The following results were obtained.

For $0.08 \le$ [NaHAsc] ≤ 0.170 M, ε''(Na, Hasc) = 2.80 ± 0.09 and $0.170 \le$ [NaHAsc] ≤ 0.500 M, ε'' (Na, HAsc) = 0.93 ± 0.07.

For the back titration, a solution with the composition 0.100 M NaCl + 1.00 M $NaClO_4$ was used.

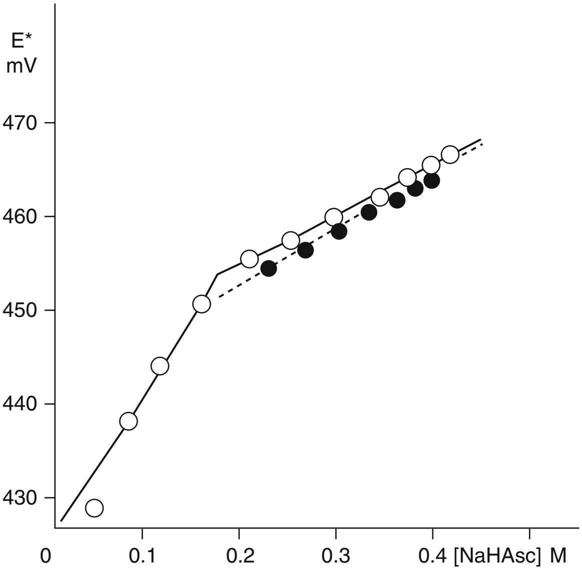


Fig. 6.2 Determination of the interaction coefficient ε''(Na^+, $HAsc^-$) according to Eq. (6.8). Filled symbols denote back titration. Reproduced with kind permission of Springer Science and Business Media from Néher-Neumann E (2003) The liquid junction potential in potentiometric titrations. VII. On emf titrations proposed for the determination of some interaction coefficients. J Solution Chem 32: 645–662 (Fig. 2)

6.2.3 Determination of *ε*″ (B, ClO$_4$)

For determination of the interaction coefficient between a metal ion, other than Na$^+$, and the ClO$_4{}^-$ ion, the emf method presented below, is suggested.

$$-\ \mathrm{LM\,ClO_4^-}\ |\ \text{Cell solution}\ |\ \mathrm{GE}\ + \qquad \text{Cell 3}$$

The cell solution has the composition:

$$0.1\ \mathrm{M\ HClO_4}$$

$$0.4\ \mathrm{M\ NaClO_4}$$

The cell solution should be titrated with a solution of the composition: 0.1 M HClO$_4$, X M B(ClO$_4$)$_{z(B)}$, Z M NaClO$_4$. The concentration c_B of the cell should be increased by titration to as high a level as possible.

The notation LM ClO$_4{}^-$ stands for a perchlorate electrode of liquid-membrane type. According to the experiences gained in this laboratory [14], the perchlorate electrodes, commercially available at present, cannot be used for precise emf measurements. On the other hand, it was noticed [15] that solutions of tetraheptylammonium bromide, iodide, nitrate or perchlorate in ethyl bromide behave as anionic liquid membranes with ideality close to 100%. A simple and useful construction for this type of electrodes is presented.

At the end of the titration in question, a back titration can be made with 0.100 M HClO$_4$ solution, after decreasing the volume of the test solution. The emf of this cell, in mV and with molar concentrations, can be written as

$$\mathrm{E} = \mathrm{E_0} + \mathrm{g}\log_{10}(c_\mathrm{H}\, c_\mathrm{ClO4}) + \mathrm{g}\log_{10}(f_\mathrm{H}\, f_\mathrm{ClO4}) \tag{6.9}$$

With the activity factor $\log_{10} f_\mathrm{ClO4}$, expressed according to SIT as follows,

$$\log_{10} f_\mathrm{ClO4} = -\mathrm{D(I)} + \varepsilon''(\mathrm{Na, ClO_4})c_\mathrm{Na} + \varepsilon''(\mathrm{B, ClO_4})c_\mathrm{B} + \varepsilon''(\mathrm{H, ClO_4})c_\mathrm{H} \tag{6.10}$$

and with $\log_{10} f_\mathrm{H}$, given by Eq. (6.2), we obtain

$$\begin{aligned}\mathrm{E}^* \equiv \mathrm{E} - \mathrm{g}\log_{10}(c_\mathrm{H}\, c_\mathrm{ClO4}) + 2\mathrm{g\,D(I)} - \mathrm{g}\varepsilon''(\mathrm{H, ClO_4})(c_\mathrm{H} + c_\mathrm{ClO4})\\ - \mathrm{g}\varepsilon''(\mathrm{Na, ClO_4})c_\mathrm{Na} = \mathrm{E_0} + \mathrm{g}\varepsilon''(\mathrm{B, ClO_4})c_\mathrm{B}\end{aligned} \tag{6.11}$$

Plotting the function E* against c_B, the value of ε'' (B, ClO$_4$) can be calculated from the slope of the straight line obtained. Here, we need the value ε'' (Na, ClO$_4$) $\cong \varepsilon$ (Na, ClO$_4$) = 0.03 kg solvent (mol solute)$^{-1}$ [14].

An alternative cell for determining ε'' (B, ClO$_4$) is discussed in Appendix C (Chapter 6).

6.2.4 Determination of ε'' (H, L)

We can use Cell 4 for the determination of ε'' (H, L).

$$-\ \text{Ag(s), AgCl(s)} \mid \text{Cell solution} \mid \text{GE} + \qquad \text{Cell 4}$$

The cell solution has the composition:

$$0.010\ \text{M NaCl}$$

$$2.990\ \text{M NaClO}_4$$

$$[\text{H}^+] = 0.001\ \text{M HClO}_4$$

The emf of this cell, in mV, can be written as

$$E = E_0 + g\log_{10}\{h[\text{Cl}^-]\} + g\log_{10}(f_H f_{Cl}) \tag{6.12*}$$

where h denotes the hydrogen ion concentration at equilibrium. v_0 ml of the cell solution should be titrated with solution of the composition: 0.010 M NaCl, 0.300 M HL, 1.000 M NaL, and 1.990 M $NaClO_4$. For the back titration, after decreasing the volume of the test solution, the following solution can be used: 0.010 M NaCl + 2.990 M $NaClO_4$.

The HAcetate (HAc) – NaAc system can be taken as an example. For the protolysis of the acid HL, we write

$$\text{HL} \leftrightharpoons \text{H}^+ + \text{L}^- \text{ with the protolysis constant } K_a$$

$$\log_{10} h = \log_{10} K_a - \log_{10}(c_{salt}/c_{acid}) \tag{6.12}$$

In the calculation of E, the following approximations can be used for the buffer system in question:

$$[\text{H}_y\text{L}] \cong [\text{H}_y\text{L}]_F \equiv c_{acid}\ \text{M and } [\text{L}^{y-}] \cong [\text{Na}_y\text{L}]_F \equiv c_{salt}\ \text{M}$$

Here, c_{acid} and c_{salt} are the weight, analytical ($\equiv$ formal) concentrations.

With the ionic activity coefficients, expressed according to SIT [6–12], we have

$$\log_{10} f_H = -D(I) + \varepsilon''(\text{H, Cl})[\text{Cl}^-] + \varepsilon''(\text{H, ClO}_4)[\text{ClO}_4^-] + \varepsilon''(\text{H, L})[\text{L}^{y-}] \tag{6.13}$$

$$\log_{10} f_{Cl} = D(I) + \varepsilon''(\text{Na, Cl})[\text{Na}^+] + \varepsilon''(\text{H, Cl})h \tag{6.14}$$

and we obtain

$$\begin{aligned} E^* \equiv{}& E - g\log_{10}(c_{acid}/c_{salt}) + 2g\,D(I) - g\,\varepsilon''(\text{H, ClO}_4)[\text{ClO}_4^-] - SL(\text{H, HAc})c_{acid} \\ & - g\varepsilon''(\text{H,Cl})h = \text{constant} + g\,\varepsilon''(\text{H, Ac})[\text{NaAc}]_F \end{aligned} \tag{6.15a}$$

where

$$\text{constant} = E_{0H} + g\log_{10} K_a + g\log_{10}[Cl^-] + g\varepsilon''(H, Cl)\,[Cl^-] + g\varepsilon''(Na, Cl)\,[Na^+] \tag{6.15b}$$

Here, SL(H, HAc) = 8.4 mV/ M HAc, determined in a test solution containing 3 M $NaClO_4$ ionic medium and 50 mM $HClO_4$, is kept constant. We titrate with the solution of the composition X M HAc + 50 mM $HClO_4$ + 3 M $NaClO_4$. Plotting the function E_H – 59.16 $\log_{10}$ h versus $[HAc]_F$, the slope is identical with SL(H, HAc).

Plotting the function E* vs. $[L^{y-}]_F$, the value of ε'' (H, L) can be calculated from the slope of the straight line obtained.

The determination of ε'' (H, Ac) was done by the author. The plot of E* vs. $[NaAc)_F$ is shown in Fig. 6.3. The result ε'' (H, Ac) = 0.07 ± 0.01 liter solution (mol solute)$^{-1}$ was obtained.

In Fig. 6.3, the position of the E* values are uncertain below [NaAc] = 0.100 M. The reason for this may be that in this range the measured changes are too small in comparison to the experimental uncertainty.

Another determination of ε'' (H, Ac) was also done at $[Na^+]$ = 3 M, and [HAc] = 10 mM, both kept constant. The plot in question is shown in Fig. 6.4. The following results were obtained.

	ε''(H, Ac) liter solution (mol solute)$^{-1}$
$0 \le [NaAc] \le 0.070$ M	0
$0.070 \le [NaAc] \le 0.350$ M	0.07 ± 0.01
$0.350 \le [NaAc] \le 0.470$ M	0.11 ± 0.01

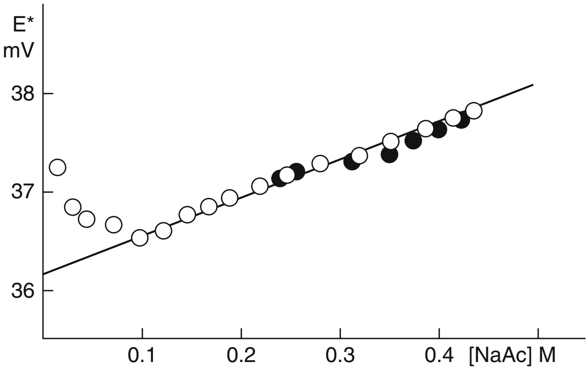


Fig. 6.3 Determination of the interaction coefficient $\varepsilon''(H^+, Ac^-)$ at constant ratio c_{acid}/c_{salt} = 0.300 / 0.97771 M. Filled symbols denote back titration. Reproduced with kind permission of Springer Science and Business Media from Néher-Neumann E (2003) The liquid junction potential in potentiometric titrations. VII. On emf titrations proposed for the determination of some interaction coefficients. J Solution Chem 32: 645–662 (Fig. 3)

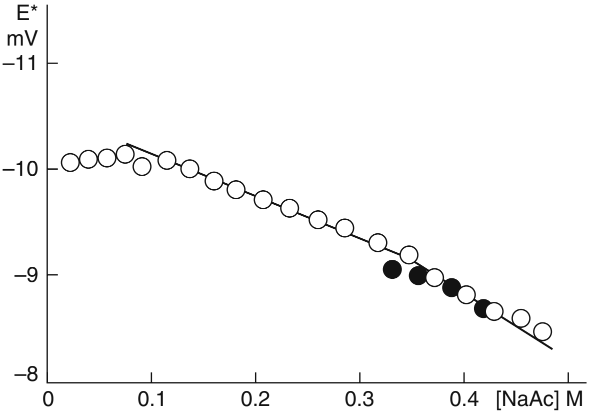


Fig. 6.4 Determination of the interaction coefficient $\varepsilon''(H^+, Ac^-)$ with $[HAc]_F = 0.0100$ M, is kept constant. Filled symbols denote back titration. Reproduced with kind permission of Springer Science and Business Media from Néher-Neumann E (2003) The liquid junction potential in potentiometric titrations. VII. On emf titrations proposed for the determination of some interaction coefficients. J Solution Chem 32: 645–662 (Fig. 4)

Cell 4 can also be used in cases where L^{y-} is an anion of a strong acid. For the back titration, a solution of composition 0.010 M NaCl + 2.990 M $NaClO_4$ was used.

The procedure suggested above can also be used for the determination of the interaction coefficients of the type ε'' (H^+, $HL^{z(an)-}$), ε'' (H^+, $H_2L^{z(an)-}$). Here, z(an) = – z_L + u, where u is the number of H atoms present in the anions in question.

6.2.5 Determination of ε'' (A, Cl)

Cell 2 can also be used for the determination of the interaction coefficient ε'' (A, Cl), by using a cell solution of composition 0.5 M ACl. This value should be increased to as high value as possible, by the addition of X M ACl. In this case, the following equation is valid

$$E^* \equiv E - g\log_{10}\{[A^+]\,[Cl^-]\} + 2g\,D(I) = E_0 + g\varepsilon''(A, Cl)\{[Cl^-] + [A^+]\} \qquad (6.16)$$

Plotting the function E* vs. $\{[Cl^-] + [A^+]\}$, the interaction coefficient ε'' (A, Cl) can be calculated from the slope of the straight line obtained. For the back titration, pure water was used.

The interaction coefficient ε'' (Na, Cl) was determined by the author in a broad concentration range. v_0 ml cell solution with the composition 0.170 M NaCl was titrated with 3.00620 M NaCl. The plots are presented in Fig. 6.5.

The following results were obtained.

ε''(Na, Cl) liter solution/mol solute

$0.170 \le [NaCl] \le 0.300$ M -0.014

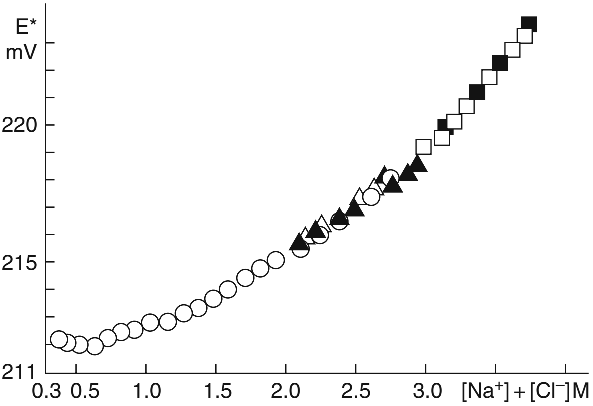


Fig. 6.5 Determination of the interaction coefficient $\varepsilon''(\text{Na}^+, \text{Cl}^-)$ in the concentration range $[\text{NaCl}] = 0.170-1.90$ M. Filled symbols denote back titration. The Symbols Δ, ▲ are shifted along the E* mV axes by −4.36 mV and the symbols □, ■ by −4.98 mV units. Reproduced with kind permission of Springer Science and Business Media from Néher-Neumann E (2003) The liquid junction potential in potentiometric titrations. VII. On emf titrations proposed for the determination of some interaction coefficients. J Solution Chem 32: 645–662 (Fig. 5)

$0.300 \leq [\text{NaCl}] \leq 0.650$ M	0.027 ± 0.001
$0.650 \leq [\text{NaCl}] \leq 1.050$ M	0.053 ± 0.002
$1.050 \leq [\text{NaCl}] \leq 1.300$ M	0.053 ± 0.009
$1.300 \leq [\text{NaCl}] \leq 1.900$ M	0.102 ± 0.003

It is seen from the results that at low ionic strength, $[\text{NaCl}] \prec 0.300$ M, the interaction coefficient ε'' (Na, Cl) is not constant and it has a negative value. In this region, the Debye–Hückel term of the activity coefficients dominates, which results in quite different values for ε'' (Na, Cl). The condition of the SIT is that the interaction coefficients are constant within the range $0.5 \leq \text{I} \leq 3.00$ M.

The given ranges of uncertainty correspond to ± 0.10 respective ± 0.20 mV errors in E* values.

6.2.6 Determination of ε'' (A, ClO_4)

Cell 2 can also be used for the determination of the interaction coefficient ε'' (A, ClO_4), by using an A^+ ion-sensitive glass electrode and a titrating solution of the composition 0.01 M ACl + ca. 5 M $AClO_4$. The interaction coefficient ε'' (Na, ClO_4) was determined by the author.

The cell solution had the composition 0.010 M NaCl + 0.69953 M $NaClO_4$. The titrating solution had the composition 0.010 M NaCl + 2.990 M $NaClO_4$. In this case, the following equation is valid

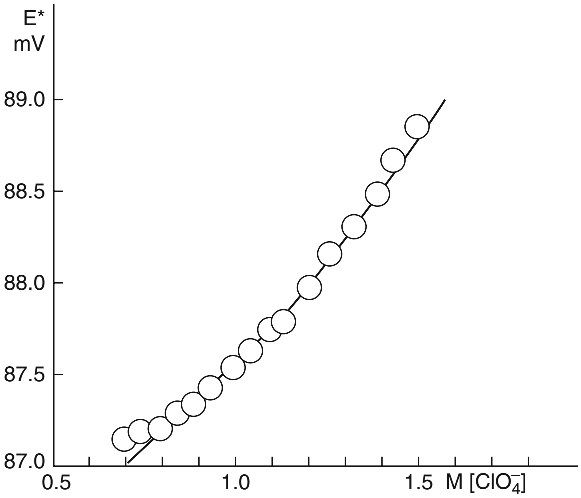


Fig. 6.6 Determination of the interaction coefficient $\varepsilon''(Na^+, ClO_4^-)$ in the concentration range 0.70 < $[NaClO_4]$ < 1.50 M. Reproduced with kind permission of Springer Science and Business Media from Néher-Neumann E (2003) The liquid junction potential in potentiometric titrations. VII. On emf titrations proposed for the determination of some interaction coefficients. J Solution Chem 32: 645–662 (Fig. 6)

$$\begin{aligned} E^* &\equiv E - g\log_{10}\{[A^+]\,[Cl^-]\} + g2\,D(I) - g\varepsilon''(A, Cl)\{[Cl^-] + [A^+]\} \\ &= E_0 + g\varepsilon''(A, ClO_4)\,[ClO_4^-] \end{aligned} \tag{6.17}$$

Plotting the function E* vs. $[ClO_4^-]$, the interaction coefficient ε'' (A, ClO_4) can be calculated from the slope. This plot is shown in Fig. 6.6. The following results were obtained:

$$0.70 \le [ClO_4^-] \le 1.125\ M \quad \varepsilon''(Na, ClO_4) = 0.030 \pm 0.006$$

$$1.125 \le [ClO_4^-] \le 1.50\ M \quad \varepsilon''(Na, ClO_4) = 0.045 \pm 0.004$$

6.2.7 Determination of *ε″ (H, Y)*

We can use emf Cell 5, defined below.

$$-\ Ag(s), AgCl(s)\ |\ \text{Cell solution}\ |\ GE + \qquad \text{Cell 5}$$

The cell solution has the composition:

0.01 M NaCl
0.05 M HY strong acid
0.5 M AY

The cell solution should be titrated with a solution of the composition 0.01 M NaCl + 0.05 M HY + ca. 5 M AY. The concentration of [AY] in the cell should be increased to as high a value as possible.

The emf of the cell (in mV) can be given as

$$E = E_0 + g \log_{10}\{[H^+]\,[Cl^-]\} + g[\log_{10} f_{Cl} + \log_{10} f_H] \tag{6.18}$$

We can write, according to SIT [6–12],

$$\log_{10} f_{Cl} = -D(I) + \varepsilon''(H, Cl)\,[H^+] + \varepsilon''(Na, Cl)\,[Na^+] \tag{6.19}$$

$$\log_{10} f_H = -D(I) + \varepsilon''(H, Cl)\,[Cl^-] + \varepsilon''(H, Y)\,[Y^-] \tag{6.20}$$

Therefore, we have

$$\begin{aligned} E^* \equiv E - g \log_{10}\{[H^+]\,[Cl^-]\} + g2\,D(I) - g\varepsilon''(H, Cl)\{[H^+] + [Cl^-]\} \\ - g\varepsilon''(Na, Cl)\,[Na^+] = E_0 + g\varepsilon''(H, Y)\,[Y^-] \end{aligned} \tag{6.21}$$

Plotting the function E^* vs. $[Y^-]$, the interaction coefficient ε'' (H, Y) can be calculated from the slope. The values of ε'' (H, Cl) and ε'' (Na, Cl) should be known.

6.2.8 *Determination of* $\boldsymbol{\varepsilon''}$ *(H, Cl)*

Cell 5 can also be used for the determination of ε'' (H, Cl) with the composition for the cell solution 0.5 M HCl. This value should be increased by titration (X M HCl) to as high value as possible. For this cell, we have

$$E^* \equiv E - g \log_{10}\{[H^+]\,[Cl^-]\} + 2g\,D(I) = E_0 + g\varepsilon''(H, Cl)\{[H^+] + [Cl^-]\} \tag{6.22}$$

Plotting the function E^* vs. $\{[H^+] + [Cl^-]\}$, the interaction coefficient ε''(H, Cl) can be obtained from the slope. Ag(s) and AgCl(s) electrodes can be prepared according to Brown [16].

6.3 The Dependence of the Interaction Coefficients on the Ionic Strength

The potentiometric titrations presented above show the ionic strength dependence of these coefficients also. When determining the interaction coefficients, the total ionic strength during the titrations should include the $[A^+] = C$ M, or $[Y^-] = C$ M or $I = C$ M value, used at the complex formation study.

In order to keep the interaction coefficients constant during the complex formation studies, we should look over which the I values depend on.

The ionic strength in cells with complex formation can be defined as follows. According to definition

$$\mathrm{I} = (1/2)\Sigma_\mathrm{J}\, \mathrm{c_J}\, \mathrm{z_J^2} \tag{6.23}$$

The species which are present are: A^+, Y^-, H^+, $B^{z(B)+}$, L^{y-}, $L_k{}^{z(Lk)-}$, $N_j{}^{z(Nj)-}$, $P_i{}^{z(Pi)+}$. Therefore,

$$\mathrm{I} = (1/2)\Sigma_\mathrm{J}[\mathrm{c_A} + \mathrm{c_Y} + \mathrm{h} + \mathrm{b\, z_B^2} + \mathrm{l\, y^2} + \mathrm{l_k\, z(Lk)^2} + \mathrm{n_j\, z(Nj)^2} + \mathrm{p_i\, z(Pi)^2}] \tag{6.24}$$

The ion concentrations involved are given in Chapter 4.1.2. Assuming that A_yL is used as complexing agent and AOH was used during the determination of the experimental constant E_{0H} through an acid–base titration for increasing the pH, we have the following I functions.
For $[A^+] = C$ M, is kept constant:

$$\mathrm{I_A} = (1/2)\Sigma_\mathrm{J}(\mathrm{C} + \mathrm{C} + \Delta \mathrm{c_Y} + \Sigma \text{ equilibrium terms}) \tag{6.25}$$

where

$$\Delta \mathrm{c_Y} = \mathrm{c_Y} - \mathrm{C} = -\mathrm{AOH_T} - \mathrm{y\, L_T} + \mathrm{HY_T} + \mathrm{z_B\, B_T} \tag{6.26}$$

$$\Sigma \text{ equilibrium terms} = \mathrm{h} + \mathrm{b\, z_B^2} + \mathrm{l\, y^2} + \mathrm{l_k z(Lk)^2} + \mathrm{n_j\, z(Nj)^2} + \mathrm{p_i\, z(Pi)^2} \tag{6.27}$$

which gives

$$\mathrm{I_A} = \mathrm{C} + (1/2)\Sigma_\mathrm{J}(\Delta \mathrm{c_Y} + \Sigma \text{ equilibrium terms}) \tag{6.28}$$

For $[Y^-] = C$ M, is kept constant:

$$\mathrm{I_Y} = (1/2)\Sigma_\mathrm{J}(\mathrm{C} + \Delta \mathrm{c_A} + \mathrm{C} + \Sigma \text{ equilibrium terms}) \tag{6.29}$$

where

$$\Delta \mathrm{c_A} = \mathrm{c_A} - \mathrm{C} = -\mathrm{HY_T} - \mathrm{z_B\, B_T} + \mathrm{y\, L_T} + \mathrm{AOH_T} \tag{6.30}$$

and

$$\mathrm{I_Y} = \mathrm{C} + (1/2)\Sigma_\mathrm{J}(\Delta \mathrm{c_A} + \Sigma \text{ equilibrium terms}) \tag{6.31}$$

For $I = C$ M, is kept constant:

$$\mathrm{I} = ((1/2)\Sigma_\mathrm{J}(\mathrm{C} + \Delta \mathrm{c_A} + \mathrm{C} + \Delta \mathrm{c_Y} + \Sigma \text{ equilibrium terms})) \tag{6.32}$$

where

$$\Delta \mathrm{c_A} = \mathrm{c_A} - \mathrm{C} = -\mathrm{HY_T} - (1/2)(\mathrm{z_B^2} + \mathrm{z_B})\mathrm{B_T} - (1/2)(\mathrm{y^2} + \mathrm{y})\, \mathrm{L_T} + \mathrm{y\, L_T} + (1/2)\mathrm{AOH_T} \tag{6.33}$$

on the basis of Eqs. (4.10), (4.11), (4.14), (4.15) and (4.16).

$$\Delta c_Y = c_Y - C = z_B\,B_T - (1/2)(z_B^2 + z_B)B_T - (1/2)(y^2 + y)\,L_T - (1/2)AOH_T \quad (6.34)$$

and

$$I = C + (1/2)\Sigma_J(\Delta c_A + \Delta c_Y + \Sigma \text{ equilibrium terms}) \quad (6.35)$$

In order to keep the interaction coefficients constant, at planning the complex formation studies, we should choose the total concentrations B_T and L_T so that the change of the ionic strength is on a minimum level:

$$\Delta I_A = I_A - C,\ \Delta I_Y = I_Y - C, \text{ and } I - C.$$

6.4 Experimental

$NaClO_4$ stock solution was prepared from solid $NaClO_4$ (p.a. Merck). The stock solution was free from Cl^- impurity. Its concentration was analysed by drying a weighed amount of a sample until a constant weight was obtained.

$Cd(ClO_4)_2$ stock solution was prepared and analysed as given in Ref. [17].

Ascorbic acid test solutions were prepared fresh, from the solid compound (Merck p.a.).

The emf of the cells studied was measured with FLUKE Multimeter, Type 8840A. The experiments were carried out in a silicon oil thermostat at 25°C. Cleaned $N_2(g)$ was bubbled through the test solution, which was saturated with the ionic medium used. The cleaning procedure is described in Ref. [17] and Appendix 1 of Chapter 8.

The amalgam electrode was prepared according to Refs. [17–19].

Two different Na^+-selective glass electrodes were used. The potentials of both were drifted with time. The emf of the cells was measured every 5 min over a period of one-half hour.

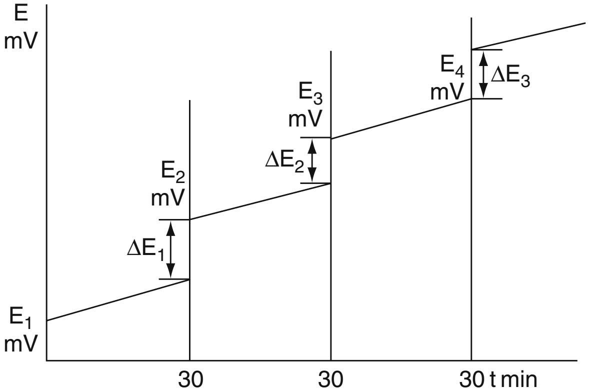


Fig. 6.7 Scheme of emf readigs. Reproduced with kind permission of Springer Science and Business Media from Néher-Neumann E (2003) The liquid junction potential in potentiometric titrations. VII. On emf titrations proposed for the determination of some interaction coefficients. J Solution Chem 32: 645–662 (Fig. 7)

The recorded potentials were plotted on millimetre paper and extrapolated to the times of burette additions. The potential differences so obtained were then summarized, as shown in the scheme of Fig. 6.7. We obtained

$$E_2 = E_1 + \Delta E_1 \text{mV}$$

$$E_3 = E_2 + \Delta E_2 = E_1 + \Delta E_1 + \Delta E_2 \text{ mV}$$

and so on. As the position of the points from a forward and back titration agreed quite well, this procedure seems to be useful.

Appendix 1

The use of an ion-selective indicator electrode for the determination of ε'' (B, ClO_4).

An alternative cell is presented for the determination of the interaction coefficient ε'' (B, ClO_4) with the help of an ion-selective electrode denoted IS $B^{z(B)+}$.

We propose the following emf cell:

$$- \text{Ag(s), AgCl(s) | Test solution | IS } B^{z(B)+} + \quad \text{Cell 6}$$

The test solution has the composition:

$$0.050\text{M NaCl}$$

$$c_B = 0.030 \text{ M } B(ClO_4)_{z(B)}$$

$$c_H = 0.020 \text{ M } HClO_4$$

$$0.50 - z_B\, c_B \text{ M } NaClO_4$$

v_0 ml solution of the test solution should be titrated with a solution of the composition: 0.050 M NaCl + 0.030 M $B(ClO_4)_{z(B)}$ + 0.020 M $HClO_4$ + 3 M $NaClO_4$. The total cell emf (in mV) can be given as

$$E = E_0 + (g/z_B)\log_{10} c_B + (g/z_B)\log_{10} f_B + g\log_{10}[Cl^-] + g\log_{10} f_{Cl} \quad (6.36)$$

where

$$\log_{10} f_B = -z_B^2\, D(I) + \varepsilon''(B, ClO_4)\,[ClO_4^-] + \varepsilon''(B, Cl)\,[Cl^-] \quad (6.37)$$

$$\log_{10} f_{Cl} = -D(I) + \varepsilon''(B, Cl)c_B + \varepsilon''(Na, Cl)\,[Na^+] + \varepsilon''(H, Cl)c_H \quad (6.38)$$

These equations result in

$$\mathrm{E} + \mathrm{g}\, \mathrm{D(I)}(\mathrm{z_B}+1) - \mathrm{g}\varepsilon''(\mathrm{Na, Cl})[\mathrm{Na^+}] = \mathrm{constant} + (\mathrm{g/z_B})\varepsilon''(\mathrm{B, ClO_4})\ [\mathrm{ClO_4^-}]\mathrm{mV} \tag{6.39}$$

where

$$\begin{aligned}\mathrm{constant} = \mathrm{E_0} &+ (\mathrm{g/z_B})\log_{10}\mathrm{c_B} + (\mathrm{g/z_B})\ \varepsilon''(\mathrm{B, Cl})\ [\mathrm{Cl^-}] + \mathrm{g}\log_{10}[\mathrm{Cl^-}] \\ &+ \mathrm{g}\varepsilon''(\mathrm{B, Cl})\ \mathrm{c_B} + \mathrm{g}\varepsilon''(\mathrm{H, Cl})\mathrm{c_H}\end{aligned} \tag{6.40}$$

Plotting $\mathrm{E} + \mathrm{g}\ \mathrm{D(I)}\ (\mathrm{z_B} + 1) - \mathrm{g}\varepsilon''\ (\mathrm{Na, Cl})\ [\mathrm{Na^+}]$ vs. $[\mathrm{ClO_4}^-]$, the interaction coefficient ε'' (B, $\mathrm{ClO_4}$) can be calculated from the slope of the plot. For the back titration, the following solution can be used: 0.050 M NaCl + 0.030 M $\mathrm{B(ClO_4)_{z(B)}}$ + 0.020 M $\mathrm{HClO_4}$.

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Chapter 7
Emf Titrations Proposed for the Determination of Certain Transport Numbers [1]

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7.1 Introduction

Some useful emf titrations, for cells with large liquid junction potentials, are proposed for the determination of the transport numbers of strong electrolytes of the following types:

(1) The strong electrolytes A_eH_u L or A_yL (used as complexing agent) with the absolute values for the anionic charges $y = e + u = 1, 2$ or 3. The pK_a values of the corresponding acid H_yL must be well separated. The method was tested in sodium hydrogen ascorbate solutions.
(2) Pure electrolyte $BY_{z(B)}$, where the cation $B^{z(B)+}$ can form an amalgam.
(3) Metal perchlorates.

In this publication, we study the total potential anomalies ΔE_J appearing across liquid junctions of the type: AY | AY + HY + $BY_{z(B)}$ and AY | AY + HY + $BY_{z(B)}$ + A_yL.

The total cell emf is given by

$$E_J = E_{0J} + (g/z_J)\log_{10} c_J + \Delta E_J \tag{7.1}$$

where the total potential anomalies are

$$\Delta E_J = (g/z_J)\log_{10} f_{JTS2} + E_D + E_{Df} \tag{7.2}$$

For these studies, the ionic molar conductivities in the transition layer have to be known. For the interpretation of conductivity measurements in the several system studied [2–4], the transport numbers and the molar conductivities of the electrolyte

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components used are needed. These components are AY, $BY_{z(B)}$, HY, A_eH_uL, and A_yL, at the concentration level C/ $|z_J|$M.

For example, this is the case in the estimation of the deviations of the conductivity $10^3\ \kappa$ from additivity. Moreover, in order to determine the ionic molar conductivities in mixtures, a combination of a graphical treatment and a curve-fitting procedure, carried out by a computer program, has been used [4]. In the computer treatment, the ionic molar conductivities measured on the pure electrolytes used as components, at concentration C/z_B or C/y M, can be used as initial values. For the calculation of $\lambda_B{}^{tr}$, λ_A, λ_Y, $\lambda_H{}^{tr}$ and $\lambda_L{}^{tr}$, the molar conductivities and the transport numbers of the electrolytes have to be known. Here, superscript tr denotes trace.

In the proposed emf cells, the appearance of the liquid junction potential is used for the determination of the transport numbers of a single electrolyte. These cells are of unusual composition. In the bridge and test solutions, only one electrolyte may be present (at different concentrations), for which the transport numbers are to be determined.

In the discussion below, the standard state is defined in such a way, in the calculation of the activity coefficients, that $f_J \rightarrow 1$ when ionic strength $I \rightarrow 0$.

7.2 Survey of Emf Cells for the Determination of Transport Numbers

7.2.1 *Determination of Transport Numbers in Strong Electrolyte A_eH_uL or A_yL with Anionic Charges $y = e + u = 1, 2$ or 3*

The transport numbers of pure electrolytes can be determined with the help of either the classical moving boundary method or emf cells. Biedermann and Douhéret [5] introduced cells of different types for determination of transport numbers of the 1:1 electrolytes $HClO_4$, $LiClO_4$, $NaClO_4$, and NaCl over a broad concentration range. They used measured mean activity coefficients in their calculations. Here, we shall use the SIT approach [6–13].

We shall propose emf cells as well for the determination of transport numbers in the strong electrolytes given above. The pK_{an} values of the corresponding acid, H_yL, should be separated by several pK_{an} units. Hence, we can expect only one dominating anionic species. The composition of the cell should be

$$- \text{Reference half-cell} \mid\mid \text{Bridge solution} \mid\mid \text{Test solution} \mid \text{GE} - A^+ + \text{Cell } 6^x$$

where the composition of the bridge solution is:

$$\text{TS1},\ \ x = 0,$$

$$\mathrm{C/y\ M = [salt]_1}$$

$$\mathrm{[A^+] = C\ M}$$

$$\text{ionic strength } \mathrm{I_1}$$

The composition of the test solution is:

$$\mathrm{TS2,\ x = 1,}$$

$$\mathrm{c_{s2}\ M = [salt]_2} \text{ is varied,}$$

$$\text{ionic strength } \mathrm{I_2}$$

Here, salt denotes the strong electrolyte $\mathrm{A_eH_uL}$ or $\mathrm{A_yL}$ and GE – $\mathrm{A^+}$ stands for an $\mathrm{A^+}$ ion-selective glass electrode.

The reference half-cell can have the composition

$$\mathrm{Ag(s), AgCl(s)\ |\ 0.010\ M\ ACl, C - 0.010\ M\ AClO_4, [A^+] = C\ M.}$$

The salt concentration in the test solution should be varied by titration within the limits:

$$\mathrm{0.5 \le c_{s2} \le C/y\ M.}$$

For the ion concentrations, we can write, for example in $\mathrm{A_yL}$,

$$\mathrm{c_L = [L^{y-}] = [salt]}$$

$$\mathrm{c_A = [A^+] = y[salt] \equiv yc_L}$$

The total emf of this cell, in mV and with molar concentrations, can be written as

$$\mathrm{E = E_0 + g\log_{10} c_{A(TS2)} + g\log_{10} f_{A(TS2)}} - g\int_{TS1}^{TS2} \Sigma_J \mathrm{(t_J/z_J)d\log_{10} a_J} \tag{7.3}$$

where the symbols $\mathrm{t_J}$ and $\mathrm{a_J}$ denote characteristic properties of the transition layer (the mixture of TS1 and TS2). $\mathrm{t_J}$ denotes the transport number of ion J with the electric charge $\mathrm{z_J}$ (the sign of the charge must also be given), $\mathrm{a_J}$ is the activity and

$$\mathrm{a_J = c_Jf_J} \tag{7.4}$$

$$\mathrm{c_J = x\ c_{J(TS2)} + (1 - x)\ c_{J(TS1)}} \tag{7.5}$$

In the following, subscripts 1 and 2 are abbreviations for TS1 and TS2, respectively.

For the present cell, Eq. (7.3) has the form

$$E = E_0 + g\log_{10} c_{A2} + g\log_{10} f_{A2} - g\int_{c(A1)}^{c(A2)} [-(t_L/y)d\log_{10}(c_L f_L) + t_A d\log_{10}(c_A f_A)] \tag{7.6}$$

Introducing $t_A = 1 - t_L$ and $c_L = c_A/y$ into Eq. (7.6), we obtain

$$\begin{aligned} E = E_0 + g\log_{10} c_{A1} + g\log_{10} f_{A1} + (gt_L/y)\int_{c(A1)}^{c(A2)} \big\{d[\log_{10}(c_A/y) \\ + \log_{10} f_L] + d(\log_{10} {c_A}^y + \log_{10} {f_A}^y)\big\} \end{aligned} \tag{7.7}$$

The constancy of t_L is assumed within the limits of the integration. The necessary ionic activity coefficients are estimated with the help of the simple specific interaction theory [6–13]. For the actual ions in the transition layer, we can write

$$\log_{10} f_L = -{z_L}^2 D(I) + \varepsilon''(A, L)\, c_A \tag{7.8}$$

$$\log_{10} f_A = -D(I) + \varepsilon''(A, L)\, c_A/y \tag{7.9}$$

where D(I) denotes the Debye–Hückel term and is given by Eq. (2). For the ionic strength I in the transition layer, we have

$$I = x\, I_2 + (1 - x)\, I_1 \tag{7.10}$$

The interaction coefficient $\varepsilon''(A, L)$ is assumed to be constant for the integration. This constancy is well established for 1:1, 1:2 and 2:1 electrolytes in the range of ionic strength $0.5 \le I \le 3$ M. For the cationic charge = 3, the validity of the simple specific interaction theory (SIT) has been proved by Spahiu [11] for C = 0.3, 0.9, 1.5 and 3 M, for the yttrium carbonate system. Therefore, we proposed our cells for use with a maximum charge of 3.

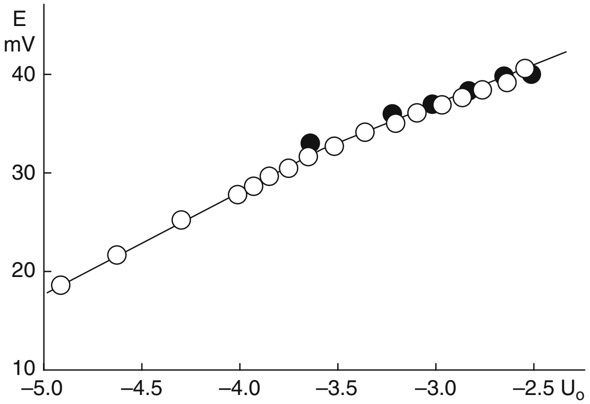
Substituting the values of $\log_{10} f_A$ and $\log_{10} f_L$ into Eq. (7.7), we can integrate to obtain

$$E = E_0 + g\log_{10} c_{A1} + gD(I)_1 + g\varepsilon''(A, L)\, c_{A1}/y + (gt_L/y)\, U_0 \tag{7.11}$$

The first four members of Eq. (7.11) are constant and

$$U_0 = (1 + y)\log_{10}(c_{A2}/c_{A1}) - (y + y^2)\,[D(I)_2 - D(I)_1] + 2\varepsilon''(A, L)\,[c_{A2} - c_{A1}] \tag{7.12}$$

Fig. 7.1 Determination of the transport number ^{t}HAsc according to Eqs. (7.11) and (7.12). Reproduced with kind permission of Springer Science and Business Media from Néher-Neumann E (2003) The liquid junction potential in potentiometric titrations. VIII. Emf titrations proposed for the determination of certain transport numbers. J Solution Chem 32: 753–764 (Fig. 1)



By plotting E vs. U_0, the transport number of the anion L^{y-} can be calculated from the slope.

We used this method for the experimental determination of the transport number t_L in sodium hydrogen ascorbate solutions (NaHAsc). Concentrations $[\text{salt}]_1 = 1.99967$ M and $0.180 \leq [\text{salt}]_2 \leq 1$ M were used in the cell studied. The plot obtained is presented in Fig. 7.1 according to Eqs. (7.11) and (7.12). The following result was obtained. In the range of U_0

$$-5.30 \leq U_0 \leq -3.60$$

which corresponds to

$$0.18 \leq [\text{NaHAsc}]_2 \leq 0.6\,\text{M}$$

we have

$$t_{\text{Hasc}} = 0.175 \pm 0.001$$

In the range of U_0,

$$-\,3.60 \leq U_0 \leq -2.50$$

which corresponds to

$$0.60 \leq [\text{NaHAsc}]_2 \leq 1\ \text{M}$$

we have

$$t_{\text{Hasc}} = 0.120 \pm 0.003$$

7.2.2 *The Determination of the Transport Numbers in the Strong Electrolyte $BY_{z(B)}$ Containing An Amalgam-Forming Cation*

We shall discuss two emf cells combined with a titration technique.

7.2.2.1 Cell 7

The concentration cell given below (cell 7) is very useful, if the mean activity factor of the electrolyte $BY_{z(B)}$ or the interaction coefficient $\varepsilon''(B, Y)$ is known. The composition of cell 7 is

$$- B - Hg \mid \text{Solution TS1} \mid\mid \text{Solution TS2} \mid B - Hg + \qquad \text{Cell 7}$$

where the composition of Solution TS1 is:

$$[BY_{z(B)}] = c_{B1}$$

$$[Y1] = z_B c_{B1}$$

The composition of Solution TS2 is:

$$[BY_{z(B)}] = c_{B2} = 3/z_B \text{ M}$$

$$[Y2] = z_B c_{B2} = 3 \text{ M}$$

$$c_{B2} \succ c_{B1}$$

We can use either dilute amalgam electrodes (0.01 wt.%), which can be prepared in the solution in question with the help of a coulometric circuit [14–17] or saturated ones [18]. The concentration of the solution TS1 should be varied within the range $0.5 \leq c_{B1} \leq 3/z_B$M. Cell 7 can be realized by measuring the emf values of the following cells:

$$- Ag(s), AgCl(s) \mid\mid 3 \text{ M AY} \mid\mid \text{Cell sol.TS2} \mid B - Hg + \qquad \text{Cell 7a}$$

Reference
half-cell

$$- Ag(s), AgCl(s) \mid\mid 3 \text{ M AY} \mid\mid \text{Cell sol.TS1} \mid B - Hg + \qquad \text{Cell 7b}$$

Reference
half-cell

First, we can have the concentration $c_{B2} \succ c_{B1}$ in the test solution. The measured emf is denoted E_{7a}. We can then dilute this solution by titrating with H_2O. We now measure the emf values E_{7b}. Hence, the emf of cell 7 will be $E = E_{7a} - E_{7b}$. Moreover, E can be written, in mV, on the molal concentration scale (m_J), as

$$E = (g/z_B)\log_{10}(m_{B2}\gamma_{B2}/m_{B1}\gamma_{B1}) - g\int_{TS1}^{TS2} \Sigma_J(t_J/z_J)\, d\log_{10} a_J \qquad (7.13)$$

where γ_B denotes the molal activity coefficient of the ion B. For the present cell, Eq. (7.13) has the form

$$E = (g/z_B)\log_{10}(m_{B2}\,\gamma_{B2}/m_{B1}\,\gamma_{B1}) - g\int_{m(B1)}^{m(B2)}[(t_B/z_B)\,d\log_{10}(m_B\,\gamma_B) - t_Y\,d\log_{10}(m_Y\gamma_Y)] \tag{7.14}$$

Introducing $t_B = 1 - t_Y$ and $m_Y = z_B\, m_B$ into Eq. (7.14), we obtain

$$E = (g/z_B)\int_{m(B1)}^{m(B2)} t_Y\, d\log_{10}[{z_B}^{z(B)}{m_B}^{z(B)+1}\gamma_B{\gamma_Y}^{z(B)}] \tag{7.15}$$

According to the definition of the mean activity coefficient $\gamma\pm$ for the electrolyte $BY_{z(B)}$, we can write

$$E = (gt_Y/z_B)\int_{m(B1)}^{m(B2)} d\log_{10}[{z_B}^{z(B)}{m_B}^{z(B)+1}\gamma{\pm}^{z(B)+1}] \tag{7.16}$$

After integration, when $t_Y \equiv t_{ClO4}$ is considered to be constant, we obtain

$$E = [g(z_B + 1)t_Y/z_B]\log_{10}[m_{B2}\gamma \pm (TS2)/m_{B1}\gamma \pm (TS1)] \tag{7.17}$$

By plotting the measured E, in mV, versus $\log_{10}[m_{B2}\ \gamma\pm TS2)/m_{B1}\ \gamma\pm (TS1)]$, the transport number of anion Y can be calculated from the slope.

If the mean activity coefficient of the electrolyte $BY_{z(B)}$ is not measured, the activity coefficients involved in Eq. (7.15) can be expressed with the help of SIT [6–13]. Now, it is advantageous to use the molar concentration scale.

Hence, we write for an intermediate plan in the transition layer

$$\log_{10} f_B = -{z_B}^2 D(I) + \varepsilon''(B, Y)\,[Y] \tag{7.18}$$

$$\log_{10} f_Y = -D(I) + \varepsilon''(B, Y)\,c_B \tag{7.19}$$

Introducing $[Y] = z_B\, c_B$ and substituting the values of $\log_{10} f_J$ into Eq. (7.15), we obtain after integration

$$\begin{aligned} E = (gt_Y/z_B)\{&(z_B + 1)\log_{10}(c_{B2}/c_{B1}) - ({z_B}^2 + z_B)[D(I)_2 - D(I)_1] \\ &+ 2z_B\varepsilon''(B, Y)(c_{B2} - c_{B1})\} \end{aligned} \tag{7.20}$$

Plotting E, in mV, versus $(z_B + 1)\log_{10}(c_{B2}/c_{B1}) - ({z_B}^2 + z_B)\,[D(I)_2 - D(I)_1] + 2z_B\varepsilon''(B, Y)\,(c_{B2} - c_{B1})$, the transport number of the anion Y is calculated from the slope. The interaction coefficient $\varepsilon''(\mathrm{B, Y})$ involved can be determined with the help of an emf titration as well, as suggested in Ref. [19].

7.2.2.2 Cell 8

Cell 8 can also be used for the determination of the transport numbers in the strong electrolyte $\mathrm{BY}_{\mathrm{z(B)}}$, if the interaction coefficient $\varepsilon''(\mathrm{B, Y})$ is known.

−B − Hg | Test solution, TS1 | | Bridge solution, TS2 | | Reference +
half-cell, Cell 8

The composition of the test solution (TS1) is:

$$[\mathrm{BY}_{\mathrm{z(B)}}]_1 = \mathrm{c}_{\mathrm{B1}}$$

$$[\mathrm{Y1}] = \mathrm{z}_{\mathrm{B}}\mathrm{c}_{\mathrm{B1}}$$

The composition of the bridge solution (TS2) is:

$$[\mathrm{BY}_{\mathrm{z(B)}}]_2 = \mathrm{c}_{\mathrm{B2}} = 3/\mathrm{z}_{\mathrm{B}}\,\mathrm{M}$$

$$[\mathrm{Y2}] = \mathrm{z}_{\mathrm{B}}\mathrm{c}_{\mathrm{B2}} = 3\,\mathrm{M}$$

In this cell $[\mathrm{B}^{\mathrm{z(B)+}}] = [\mathrm{BY}_{\mathrm{z(B)}}]$.

The composition of the test solution should be varied by titration within the range $0.5 \leq \mathrm{c}_{\mathrm{B1}} \leq 3 / \mathrm{z}_{\mathrm{B}}$ M.

The total emf of this cell, in mV and with molar concentrations, can be written as

$$\mathrm{E} = \mathrm{E}_0 - (\mathrm{g}/\mathrm{z}_{\mathrm{B}})\log_{10}(\mathrm{c}_{\mathrm{B1}}\mathrm{f}_{\mathrm{B1}}) - \mathrm{g}\int_{c(B1)}^{c(B2)} \{(\mathrm{t}_{\mathrm{B}}/\mathrm{z}_{\mathrm{B}})\,\mathrm{d}\log_{10}(\mathrm{c}_{\mathrm{B}}\mathrm{f}_{\mathrm{B}}) - \mathrm{t}_{\mathrm{Y}}\,\mathrm{d}\log_{10}([\mathrm{Y}]\mathrm{f}_{\mathrm{Y}})\} \tag{7.21}$$

Introducing $\mathrm{t}_{\mathrm{B}} = 1 - \mathrm{t}_{\mathrm{Y}}$ and $[\mathrm{Y}] = \mathrm{z}_{\mathrm{B}}\,\mathrm{c}_{\mathrm{B}}$, we obtain

$$\mathrm{E} = \mathrm{E}_0 - (\mathrm{g}/\mathrm{z}_{\mathrm{B}})\log_{10}\mathrm{c}_{\mathrm{B2}} - (\mathrm{g}/\mathrm{z}_{\mathrm{B}})\log_{10}\mathrm{f}_{\mathrm{B2}} + (\mathrm{g}\,\mathrm{t}_{\mathrm{Y}}/\mathrm{z}_{\mathrm{B}})\int_{c(B1)}^{c(B2)} \mathrm{d}\{\log_{10}\left[\mathrm{z}_{\mathrm{B}}^{\mathrm{z(B)}}\mathrm{c}_{\mathrm{B}}^{(1+\mathrm{z(B)})}\right] + \log_{10}\mathrm{f}_{\mathrm{B}} + \mathrm{z}_{\mathrm{B}}\log_{10}\mathrm{f}_{\mathrm{Y}}\} \tag{7.22}$$

Expressing $\log_{10}\mathrm{f}_{\mathrm{B}}$ and $\log_{10}\mathrm{f}_{\mathrm{Y}}$ according to SIT [6–13] as given by Eqs. (7.18) and (7.19), respectively, we obtain, after integration

$$\mathrm{E} = \mathrm{E}_0 - (\mathrm{g}/\mathrm{z}_{\mathrm{B}})\log_{10}\mathrm{c}_{\mathrm{B2}} + \mathrm{g}\mathrm{z}_{\mathrm{B}}\mathrm{D(I)}_2 - \mathrm{g}\varepsilon''(\mathrm{B, Y})\,\mathrm{c}_{\mathrm{B2}} + (\mathrm{g}\mathrm{t}_{\mathrm{Y}}/\mathrm{z}_{\mathrm{B}})\,\mathrm{U}_1 \tag{7.23}$$

Here, the first four members of Eq. (7.23) are constant and

$$U_1 = (1 + z_B)\log_{10}(c_{B2}/c_{B1}) - (z_B + z_B{}^2)[D(I)_2 - D(I)_1] + 2z_B\varepsilon''(B, Y)(c_{B2} - c_{B1}) \tag{7.24}$$

The transport number of anion Y can be calculated from the slope of a plot of E vs. U_1.

7.2.3 *The Determination of the Transport Numbers in Metal Perchlorate Solutions*

We can determine the transport numbers of metal perchlorates, often needed in the estimation of ionic molar conductivities, by measuring the emf value of the following cells using titration technique.

7.2.3.1 Cell 9

We can use the concentration cell given below if we know either the mean activity factor of the electrolyte $BY_{z(B)}$ or the interaction coefficient $\varepsilon''(B, Y)$. The later can be determined using an emf titration as well, in a cell without a liquid junction, as suggested in Ref. [19]. Here, we use the notation $Y = ClO_4{}^-$.

$$-\ \mathrm{LM\ Y}\ |\ \text{Solution TS1}\ |\ |\ \text{Solution TS2}\ |\ \mathrm{LMY}\ +\qquad \text{Cell 9}$$

The composition of Solution TS1 is:

$$[B^{z(B)+}]_1 = c_{B1} = 3/z_B\ M$$

$$[Y1] = z_B c_{B1} = 3\ M$$

$$c_{B1} \succ c_{B2}$$

The composition of Solution TS2 is:

$$[B^{z(B)+}]_2 = c_{B2}$$

$$[Y2] = z_B c_{B2}$$

In cell 9, the concentration c_{B2} should be varied within the range $0.5 \le c_{B2} \le 3/z_B$ M. Here, LM Y denotes a perchlorate electrode of liquid membrane type [20].

Cell 9 can be realized by measuring emf values of the following cells:

$$-\ \mathrm{LM\ ClO_4^-}\ |\ \mathrm{TS1}\ |\ |\ \mathrm{C\ M\ AY}\ |\ |\ \mathrm{Ag(s), AgCl(s)}\ \text{ref. half-cell}\ +\ \text{Cell 9a}$$

Here, we measure the emf value E_{9a}. Then, we add water to TS1 from a burette, in order to prepare TS2. We measure E_{9b} for the following cell

$$- \mathrm{LM\ ClO_4^-}\ |\ \mathrm{TS2}\ |\ |\ \mathrm{C\ M\ AY}\ |\ |\ \mathrm{Ag(s), AgCl(s)\ ref.\ half\text{-}cell} + \mathrm{Cell\ 9b}$$

The emf for cell 9 can then be obtained as $E = E_{9a} - E_{9b}$.

The total emf of cell 9 can be written, in mV and with molal concentrations, as

$$E = g\log_{10}(m_{Y1}\gamma_{Y1}/m_{Y2}\gamma_{Y2}) - g\int_{TS1}^{TS2} \Sigma_J(t_J/z_J)\, d\log_{10} a_J \tag{7.25}$$

where a_J denotes the activity of the ion J present in the transition layer.

For the present cell, Eq. (7.25) has the form

$$E = g\log_{10}(m_{Y1}\gamma_{Y1}/m_{Y2}\gamma_{Y2}) - g\int_{m(Y1)}^{m(Y2)} [(t_B/z_B)\, d\log_{10}(m_B\gamma_B) - t_Y d\log_{10}(m_Y\gamma_Y)] \tag{7.26}$$

Introducing $t_B = 1 - t_Y$ and $m_B = m_Y/z_B$ into Eq. (7.26) we obtain

$$\begin{aligned} E = {} & (g/z_B)\log_{10}\{{m_{Y1}}^{1+z(B)}{\gamma_{Y1}}^{z(B)}\gamma_{B1}/[{m_{Y2}}^{1+z(B)}{\gamma_{Y2}}^{z(B)}\gamma_{B2}]\} \\ & + (gt_Y/z_B)\int_{m(Y1)}^{m(Y2)} \{d\log_{10}[{m_Y}^{1+z(B)}/z_B]\gamma_B\} + d\log_{10}{\gamma_Y}^{z(B)} \end{aligned} \tag{7.27}$$

According to the definition of the mean activity coefficient $\gamma\pm$ for the electrolyte $BY_{z(B)}$, we can write

$$\begin{aligned} E = {} & [g(1 + z_B)/z_B]\log_{10}\,[m_{Y1}\gamma\,\pm_{(TS1)}\,/(m_{Y2}\,\gamma \pm (TS2))] \\ & + (gt_Y/z_B)\int_{m(Y1)}^{m(Y2)} [d(1 + z_B)\log_{10}(m_Y/z_B) + d(1 + z_B)\log_{10}\gamma\pm] \end{aligned} \tag{7.28}$$

After integration, we obtain

$$F_2 \equiv E - [g(1 + z_B)/z_B]\log_{10}[m_{Y1}\gamma \pm (TS1)/(m_{Y2}\,\gamma \pm (TS2))] = (gt_Y/z_B)U_2 \tag{7.29}$$

where

$$U_2 = (1 + z_B)\log_{10}(m_{Y2}/m_{Y1}) + (1 + z_B)\log_{10}[\gamma \pm (TS2)/\gamma \pm (TS1)] \tag{7.30}$$

Plotting the function F_2 vs. U_2, the transport number of the Y ion can be calculated from the slope.

If the mean activity coefficient of the electrolyte $BY_{z(B)}$ is not measured, the activity coefficients involved in Eq. (7.27) can be expressed with the help of SIT [6–13], as given by Eqs. (7.18) and (7.19). Now, we continue the deductions on the molar concentration scale.

Introducing the $\log_{10} f_Y$ and $\log_{10} f_B$ values into Eq. (7.27), we obtain, after integration

$$\begin{aligned} F_3 \equiv E - [g(1 + z_B)/z_B] \log_{10}\{[Y1]/[Y2]\} - (g/z_B)\{z_B[D(I)_2 - D(I)_1] \\ + z_B^2[D(I)_2 - D(I)_1] + 2\varepsilon''(B, Y)\{[Y1] - [Y2]\}\} = (g\, t_Y/z_B)U_3 \end{aligned} \qquad (7.31)$$

where

$$U_3 = (1+z_B) \log_{10}\{[Y2]/[Y1]\} - (z_B + z_B^2)\,[D(I)_2 - D(I)_1] + 2\varepsilon''(B, Y)\,\{[Y2] - [Y1]\} \qquad (7.32)$$

Plotting the function F_3 vs. U_3, the transport number of the anion Y can be calculated from the slope.

7.2.3.2 Cell 10

Cell 10 can also be used for the determination of the transport numbers in the strong electrolyte $BY_{z(B)}$, if the interaction coefficient ε''(B, Y) is known.

−LMY | Test solution TS1 | | Bridge solution TS2 | | Reference half-cell+
Cell 10

The Test solution TS1 has the composition:

$$[BY_{z(B)}]_1 = c_{B1}$$

$$[Y1] = z_B c_{B1}$$

The Bridge solution TS2 has the composition:

$$[BY_{z(B)}]_2 = c_{B2} = 3/z_B\ M$$

$$[Y2] = z_B c_{B2} = 3\ M$$

In cell 10, $[B^{z(B)+}] = [BY_{z(B)}]$. The composition of the test solution should be varied by titration within the range $0.5 \le c_{B1} \le 3\,/\,z_B$ M. The total emf of this cell, in mV and with molar concentrations, can be written as

$$E = E_0 + g \log_{10}\{[Y1]f_{Y1}\} - g \int_{TS1}^{TS2} \Sigma_J(t_J/z_J)\, d\log_{10} a_J \qquad (7.33)$$

For the present cell, it will give the following equation

$$E = E_0 + g \log_{10}\{[Y1]f_{Y1}\} - g \int_{[Y1]}^{[Y2]} \{(t_B/z_B)\, d\log_{10}[c_B f_B] - t_Y\, d\log_{10}\{[Y]f_Y\}\} \qquad (7.34)$$

Introducing $t_B = 1 - t_Y$ and $c_B = [Y]/z_B$ into Eq. (7.34), we obtain

$$\begin{aligned} E = E_0 &+ g\log_{10}[Y1] + g\log_{10} f_{Y1} - (g/z_B)\log_{10}\{[Y2]/[Y1]\} \\ &- (g/z_B)\,[\log_{10} f_{B2} - \log_{10} f_{B1}] + (g t_Y/z_B)\int_{[Y1]}^{[Y2]} \{d\,\{\log_{10}([Y]/z_B) \\ &+ \log_{10} f_B\} + d\{\log_{10}[Y]^{z(B)} + \log_{10} f_Y{}^{z(B)}\}\} \end{aligned} \tag{7.35}$$

Expressing $\log_{10} f_B$ and $\log_{10} f_Y$ according to SIT, as given by Eqs. (7.18), (7.19), we obtain, after integration

$$\begin{aligned} F_4 \equiv E &- g\log_{10}[Y1] + gD(I)_1 - g\varepsilon''(B, Y)\{[Y1]/z_B\} \\ &+ (g/z_B)\log_{10}\{[Y2]/[Y1]\} + (g/z_B)\{z_B{}^2[D(I)_1 - D(I)_2] \\ &+ \varepsilon''(B, Y)\,\{[Y2] - [Y1]\}\} = E_0 + (g\,t_Y/z_B)U_4 \end{aligned} \tag{7.36}$$

where U_4 is identical to U_3.

Plotting F_4 vs. U_4, the transport number of the anion Y can be calculated from the slope.

The experiments were carried out as described in Chapter 6.

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Chapter 8

Studies on Emf Cells Where Strong Complexes Are Formed Using Liquid Junctions of the Type AY | AY + $BY_{z(B)}$ + HY + A_yL AT $[Y^-]$ = C M, Constant, and – $\log_{10}[H^+] \geq 7$ [1]

8.1 Introduction

Potential functions have been derived for the calculation of the total cell emf (E_B and E_H) for emf cells with liquid junctions and containing the system $AOH - BY_{z(B)} - H_yL - AY$. At first, the presence of the species H^+, OH^-, $B^{z(B)+}$, L^{y-}, A^+, Y^- is considered. A weak or strong electrolyte is considered to be used as complexing agent (H_yL). $B^{z(B)+}$ denotes the central metal ion and Y^- is the common anion of the ionic medium (A^+, Y^-). The cells have indicator electrodes reversible to $B^{z(B)+}$ (cell B) and H^+ ions (cell H), respectively.

The total emf for cell H, during a titration of strong acid–strong base (*for the determination of* E_{0H} *on the acid side*, in the system HY – AOH – AY), is *in the acid range*

$$\begin{aligned} E_{Ha} &= E_{0Ha} + g\log_{10}[H^+] + g\log_{10} f_{HTS2} + E_D + E_{Df} \\ &= E_{0Ha} + g\log_{10}[H^+] - g[D(I) - D(C)] + SL(H, c_H)c_H + \text{corr} \end{aligned} \tag{8.1}$$

In the alkaline range, introducing $[H^+] = K_W/[OH^-]$, we have

$$\begin{aligned} E_{Hb} &= E_{0Ha} + g\{\log_{10} K_w - \log_{10}[OH^-] + \log_{10} f_{HTS2}\} + E_D + E_{Df} \\ &= E_{0Ha} + g\log_{10} K_w - g\log_{10}[OH^-] - SL(H, c_{OH})c_{OH} \\ &\quad - g\,[D(I) - D(C)] + \text{corr} \end{aligned} \tag{8.2}$$

During the complex formation study, we have in the alkaline range

$$\begin{aligned} E_{Hcpx} = {} & E_{0Hacpx} + g\log_{10} K_w - g\log_{10}[OH^-] - g\,[D(I) - D(C)] \\ & + \Sigma_V\, Q(H, V)V + \text{corr} \end{aligned} \tag{8.3}$$

where $V = [OH^-]$, b, l, Δc_A

In cells with complex formation, the composition change of the ionic medium, $\Delta\, c_A$, results in a quite high liquid junction effect. On the basis of this phenomenon, the cell with the condition $[Y^-]$ = CM, constant, results in the smallest potential anomalies [2]. Therefore, this cell was chosen for the study of the potentials across liquid junctions in alkaline solutions.

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The cells are defined in Section 1.2. Symbols and definitions used throughout this book are defined in Chapter 1. The special symbols used in equilibrium studies are presented in Chapter 4.

We assume that the equilibrium processes (I)–(III) take place in the cells.

$$\text{(I)}\quad \mathrm{qH + rL^{y-} \rightleftharpoons H_qL_r}$$

$$\text{(II)}\quad \mathrm{pB + qH + rL^{y-} \rightleftharpoons B_pH_qL_r}$$

$$\text{(III)}\quad \mathrm{pB + qH_2O \rightleftharpoons B_p(OH)_q + qH}$$

If$-\log_{10} h \leq 9$, a glass electrode can be used as indicator electrode and the functions derived for $-\log_{10} h \leq 7$ are valid. In more alkaline solutions, the use of a H_2(g) electrode is necessary. A new electrode of this kind is presented in the Appendix 1 (Chapter 8).

The composition of the test solution, TS2, in the system $BY_{z(B)} + HY + AOH + AY + A_yL$ at equilibrium are given, if strong complexes are formed with a ligand from a weak acid, in Section 4.1.2. The concentration of the ions of the ionic medium is as follows.

$$c_Y = [Y^-] = C\,M,\ \text{is kept constant} = [AY] + HY_T + z_B\,B_T \tag{8.4}$$

$$c_A = [A^+] = C + AOH_T + y\,L_T - HY_T - z_B\,B_T\,M = C + \Delta c_A \tag{8.5a}$$

where the composition change of the ionic medium is

$$\Delta c_A = c_A - C = AOH_T - HY_T + y\,L_T - z_B\,B_T \tag{8.5b}$$

Here, T denotes total, analytical concentration.

The different equilibrium concentrations can be calculated from the corresponding equilibrium constants determined preliminarily, using an incomplete ΔE_J function, and from the known, actual total concentrations, moreover, h and b.

The test solution can be prepared in different ways. Some possibilities are given in Appendix 1 of Chapter 4.

First, the constants E_{0B} and E_{0H} should be determined (cf. Chapter 2). In the case of E_{0Ha}, a solution containing $\approx$25 mM strong acid should be titrated with a solution containing AOH. $c_Y = C$ M should be kept constant. The titration should be finished at $[HY] \cong 10^{-3}$M. Then the main titration follows by adding solutions containing the complexing agent A_yL and $BY_{z(B)}$, moreover, AY. For other cases (using H_yL and AOH), mentioned in the Appendix 1 of Chapter 4, the term L_T should be set to zero in the functions of c_A and Δc_A.

8.2 The Presentation of the Potential Functions

For the calculation of the preliminary chemical model and preliminary equilibrium constants, we assume the species H^+, $B^{z(B)+}$, L^{y-}, $OH^-$and A^+, Y^- to be present in the test solution. This mixture can be treated as mixture of strong electrolytes. The ion concentration of the reacting ions H^+, OH^-, $B^{z(B)+}$ and L^{y-} at some intermediate plane in the transition layer of the junction can be written according to the principle of the continuous mixture junction and the model of linear mixing (cf. Eq. (1.58)) as

$$h^* = x\,h,\ [OH^-]^* = x\,[OH^-],\, b^* = x\,b,\, l^* = x\,l$$

Here, h, $[OH^-]$, b and l are the free, equilibrium concentrations, calculated preliminarily. The concentrations of the ions of the ionic medium in the transition layer are

$$c_Y{}^* = C\ M,\ \text{constant},$$

$$c_A{}^* = C + x\,(AOH_T - HY_T + y\,L_T - z_B\,B_T) = C + x\Delta c_A \tag{8.6}$$

The conductance of uncharged molecules is supposed to be zero. Therefore, such species are not taking part in the potential functions. Anyhow, the uncharged molecules, H_yL, can have some influence on the emf values when using a glass or a $H_2(g)$ electrode, due to for example adsorption. This must be checked in a separate experiment at constant [HY], as discussed in Chapter 4 "The Total emf of Cell H for Small Values of w/a".

The ionic strength in the test solution is

$$I = C + (1/2)(h + [OH^-] + bz_B{}^2 + \Delta c_A + \Sigma_k\, l_k\, z_L{}^2 + \Sigma_j\, n_j\, z_{Nj}{}^2 + \Sigma_i\, p_i\, z_{Pi}{}^2) \tag{8.7}$$

The necessary functions for the calculation of the potential terms E_D and E_{Df}, and the final results are given below.

8.2.1 The Calculation of the Ideal Diffusion Potential Term, E_D

According to the general deduction presented in Ref. [3] by Eqs. (15–22) and Section 4.1.5, for the calculation of the potential term E_D, we must know the following functions

$$U_{TS2} - U_{TS1} = h\lambda_H + b\lambda_B + \Delta c_A\lambda_A - l\lambda_L - [OH^-]\lambda_{OH} \tag{8.8}$$

$$S_{TS2} - S_{TS1} = h\lambda_H + bz_B\lambda_B + \Delta c_A\lambda_A + y\,l\,\lambda_L + [OH^-]\lambda_{OH} = w \tag{8.9}$$

$$S_{TS2} = h\lambda_H + bz_B\lambda_B + \Delta c_A\lambda_A + y\ l\lambda_L + [OH^-]\lambda_{OH} + C(\lambda_A + \lambda_Y) = w + a \tag{8.10}$$

$$S_{TS1} = C(\lambda_A + \lambda_Y) = a \tag{8.11}$$

The function E_D obtained is presented in Eq. (21) of Ref. [3]. For small values of w/a, using the approximation $\ln[(w/a) + 1] \cong w/a$, we obtain, according to Eq. (22) in Ref. [3]

$$E_D = -g\,F_0(h\lambda_H + b\lambda_B + \Delta c_A\lambda_A - l\lambda_L - [OH^-]\lambda_{OH}) \tag{8.12}$$

where

$$F_0 = 1/[2.303\,C(\lambda_A + \lambda_Y)] \tag{8.13}$$

In Eq. (8.12), the terms $h\lambda_H$ and $b\lambda_B$ are probably negligible.
For every potentiometric titration, one should investigate if the condition for the approximation is fulfilled.

8.2.2 The Calculation of the Activity Factor Contribution to the Ideal Diffusion Potential, E_{Df}

For the preliminary data treatment, we assume the same species to be present as in the calculation of E_D. Forming the term E_{Df}, according to Eq. (23) in Ref. [3], with the ion concentrations at some intermediate plane in the transition layer, we obtain

$$\begin{aligned} E_{Df} = -\,g \int_{x=0}^{x=1} (1/N)\big\{ & x\,h\lambda_H\,d\log_{10} f_H + x\,b\lambda_B\,d\log_{10} f_B \\ & + (C + x\Delta c_A)\lambda_A\,d\log_{10} f_A - C\lambda_Y\,d\log_{10} f_Y - x\,l\lambda_L\,d\log_{10} f_L \\ & - x\,[OH^-]\lambda_{OH}\,d\log_{10} f_{OH}\big\} \end{aligned} \tag{8.14}$$

where

$$N = wx + a \tag{8.15}$$

We define $\log_{10} f_J$ in general, according to the specific interaction theory (SIT) [4–11] cf. Eqs. (12), (13). The reference state is chosen in such a way that $f_J^{tr} \rightarrow 1$ as $c_J \rightarrow 0$ in C M AY as solvent. Here, tr denotes trace. The SIT approach can be used in the range $0.5 \leq I \leq 3$ M if $z_B \leq 3$, with a moderate accuracy of $\pm 0.01 \log_{10}$ unit [9, 12]. This is acceptable in most cases in solution chemistry. Hence, we can write for some intermediate plane in the transition layer

$$\begin{aligned} \log_{10} f_J^* = & -z_J^2[D(I^*) - D(C)] + \{\varepsilon''(J, L)l^* + \varepsilon''(J, OH)[OH^-]^*\}_{ca} \\ & + \{\varepsilon''(J, H)h^* + \varepsilon''(J, B)b^* + \varepsilon''(J, A)(c_A^* - C)\}_{an} \end{aligned} \tag{8.16}$$

Here $\{\ldots\}_{ca}$ = the terms to be used if J is a cation and
$\{\ldots\}_{an}$ = the terms to be used if J is an anion.

Considering Eq. (8.16) and the actual ion concentrations in the transition layer, we obtain for example for the H^+ and OH^-ions

$$\log_{10} f_H{}^* = -[D(I^*) - D(C)] + \varepsilon''(H, L)x\,l \tag{8.17a}$$

$$d\log_{10} f_H{}^* = [-dD(I^*)/dx + \varepsilon''(H, L)\,l]dx \tag{8.17b}$$

$$\log_{10} f_{OH}{}^* = -\,[D(I^*) - D(C)] + \varepsilon''(B, OH)x\,b + \varepsilon''(A, OH)\,(C + x\Delta c_A - C) \tag{8.18a}$$

$$d\log_{10} f_{OH}{}^* = [-dD(I^*)/dx + \varepsilon''(B, OH)b + \varepsilon''(A, OH)\Delta c_A]dx \tag{8.18b}$$

The $d\log_{10} f_J$ values for the other ions involved can be obtained in the same way. Substituting these values for $d\log_{10} f_J$ into Eq. (8.14), we should rearrange it in such a way that it can be integrated in the form given by Eq. (30) in Ref. [3]. Hence, we obtain

$$\Phi_1(x) = x\,\{-h\lambda_H - z_B{}^2 b\lambda_B - \Delta c_A\lambda_A + z_L{}^2 l\lambda_L + [OH^-]\lambda_{OH}\} + C(\lambda_Y - \lambda_A) \tag{8.19}$$

$$\begin{aligned}\Phi_2 = {} & b\varepsilon''(B, L)l\lambda_B + b\varepsilon''(B, OH)[OH^-]\lambda_B + \Delta c_A\lambda_A\{\varepsilon''(A, L)l \\ & + \varepsilon''(A, OH)[OH^-]\} - l\lambda_L\{\varepsilon''(H, L)h + \varepsilon''(B, L)b + \varepsilon''(A, L)\Delta c_A\} \\ & - [OH^-]\lambda_{OH}[\varepsilon''(B, OH)b + \varepsilon''(A, OH)\Delta c_A] + h\varepsilon''(H, L)l\lambda_H\end{aligned} \tag{8.20}$$

$$\begin{aligned}\theta_1 = {} & C\lambda_A\{\varepsilon''(A, L)l + \varepsilon''(A, OH)[OH^-]\} - C\lambda_Y\{\varepsilon''(A, Y)\Delta c_A \\ & + \varepsilon''(H, Y)h + \varepsilon''(B, Y)b\}\end{aligned} \tag{8.21}$$

The result of the integration of Eq. (8.14) is given by Eq. (31) in Ref. [3]. For small values of w/a, we can write, according to Eq. (33) in Ref. [3]

$$\begin{aligned}E_{Df} = \mathrm{corr} - g\theta_1/a = {} & \mathrm{corr} - g\,t_A\{\varepsilon''(A, L)l + \varepsilon''(A, OH)[OH^-]\} \\ & + g\,t_Y\{\varepsilon''(A, Y)\Delta c_A + \varepsilon''(H, Y)h + \varepsilon''(B, Y)b\}\end{aligned} \tag{8.22}$$

The term corr is defined according to Eqs. (1.23)–(1.25). In Eq. (8.22), the terms $\varepsilon''(H, Y)$ h and $\varepsilon''(B, Y)$ b can probably be neglected.

When planning the titrations, one should be careful with the choice of the experimental total concentrations. If the condition $\ln[(w/a) + 1] \cong w/a$ is not fulfilled due to an improper choice of B_T and L_T, the complete functions for E_D and E_{Df}, given by Eqs. (21) and (31) in Ref. [3], respectively, have to be considered, which are rather complicated for practical use.

8.2.3 The Total Emf of Cell B in Alkaline Solutions, with a $B^{z(B)+}$ Ion-Selective Indicator Electrode and for Small Values of w/a

We can write for the total cell emf, as in earlier studies,

$$E_B = E_{0B} + (g/z_B)\log_{10}(b\,f_{BTS2}) + E_D + E_{Df} \tag{8.23}$$

Considering the definition of the total potential anomalies, ΔE_B,

$$\Delta E_B = (g/z_B)\log_{10} f_{BTS2} + E_D + E_{Df} \tag{8.24}$$

we can also write

$$E_B = E_{0B} + (g/z_B)\log_{10} b + \Delta E_B \tag{8.25}$$

Expressing $\log_{10} f_{BTS2}$ according to Eq. (8.16) with $x = 1$, we have

$$\log_{10} f_{BTS2} = -{z_B}^2[D(I) - D(C)] + \varepsilon''(B, L)l + \varepsilon''(B, OH)[OH^-] \tag{8.26}$$

Here D(I) is the Debye–Hückel term for the test solution. Substituting E_D and E_{Df} into Eq. (8.23) by Eqs. (8.12), (8.13) and (8.22) respectively, moreover Eq. (8.26), we obtain

$$E_B = E_{0B} + (g/z_B)\log_{10} b - gz_B[D(I) - DC] + \Sigma_V\, Q(B, V)V + \text{corr} \tag{8.27}$$

where, V denotes all the changing concentration terms which appear in Eq. (8.27) = h, b, l. Δc_A, $[OH^-]$.

Q(B, V) is a function which defines a constant in terms of some interaction coefficients and ionic molar conductivities measured in the equilibrium solution studied. The functions $\Sigma_V Q(B, V)V$ give the potential contributions of the ions present in the transition layer, to ΔE_B, reduced by the Debye–Hückel terms. They cannot be determined experimentally, but they can be calculated. The functions Q(B, V) can be given as follows.

$$Q(B, h) = -g\, F_0\lambda_H + gt_Y\varepsilon''(H, Y) \tag{8.28}$$

$$Q(B, l) = (g/z_B)\varepsilon''(B, L) + g\, F_0\lambda_L - g\, t_A\varepsilon''(A, L) \tag{8.29}$$

$$Q(B, b) = -g\, F_0\lambda_B + g\, t_Y\varepsilon''(B, Y) \tag{8.30}$$

$$Q(B, \Delta c_A) = -g\, F_0\lambda_A + g\, t_Y\varepsilon''(A, Y) \tag{8.31}$$

$$Q(B, [OH^-]) = (g/z_B)\varepsilon''(B, OH) + g\, F_0\lambda_{OH} - g\, t_A\varepsilon''(A, OH) \tag{8.32}$$

Comparing Eq. (8.27) with Eq. (8.25), it is obvious that

$$\Delta E_B = -gz_B[D(I) - D(C)] + \Sigma_V\, Q(B, V)V + \text{corr} \tag{8.33}$$

As is seen, Eq. (8.27) is the correct function for the calculation of the free, equilibrium concentration of the metal ion, b, for small values of w/a. This can be done by successive approximations knowing E_{0B} and the functions Q(B, V). The determination of the constant E_{0B} is discussed in Chapter 2. It is important to remember that a conditional constant, denoted either E_{0B1} or E_{0B2} and $E_{0B}{}^*$, cannot be used here. The functions Q(B, V) can be estimated as given in Chapter 4 “The Estimation of the Functions Q(H, b) Respective Q(B, b)”.

We can emphasize, again, that the total potential anomalies depend on the ion concentrations and the deviation of the cation concentration of the ionic medium from the composition of the ionic medium, and not on total concentrations, as clearly is seen from Eq. (8.27). In this equation, the term corr gives only a minor contribution to the total potential anomalies, if the composition of the ionic medium is not changed drastically. It has been proved to be negligible, e.g. in the cell containing mixtures of strong electrolytes at the experimental condition $[A^+] = CM$, constant (cf. Ref. [3]).

The equations derived above are valid also for the cases where the ligand is coming from a strong acid. When using the functions obtained, the poles of the cell must be considered. For cells which have poles opposite to those ones defined here, for cell B and H, the functions E_B and E_H must be taken with the opposite sign.

8.2.4 The Total Emf of cell H, in Alkaline Solutions, with a H^+ Ion-Sensitive Indicator Electrode and for Small Values of w/a

The total cell emf, for alkaline solutions and for a $H_2(g)$ indicator electrode, can be written as

$$E_H{}^x = E_{Ha} + E_P = E_{0Ha} + g\{\log_{10} K_w - \log_{10}[OH^-] + \log_{10} f_{HTS2}\} + E_D + E_{Df} \tag{8.34a}$$

Here E_P is the pressure correction of the $H_2(g)$ electrode in mV:

$$E_P = (g/2)\log_{10} p(H_2) \tag{8.34b}$$

$p(H_2)$ is the partial pressure of the $H_2(g)$ in atmospheres and K_w is the ionic product of water. The corrected total cell emf will be given as $E_H{}^x$.

The preparation and the way of functioning of the hydrogen electrode is discussed in Appendix 1 (Chapter 8).

Substituting the functions $\log_{10} f_H$ with $x = 1$, E_D and E_{Df} into Eq. (8.34a), we obtain

$$\begin{aligned} E_H{}^x &= E_{0Ha} + g\log_{10} K_w - g\log_{10}[OH^-] - g[D(I) - D(C)] + g\varepsilon''(H, L)l \\ &\quad - gF_0\{h\lambda_H + b\lambda_B + \Delta c_A\lambda_A - l\lambda_L - [OH^-]\lambda_{OH}\} - gt_A\{\varepsilon''(A, L)l \\ &\quad + \varepsilon''(A, OH)[OH^-]\} + gt_Y\{\varepsilon''(A, Y)\Delta c_A + \varepsilon''(H, Y)h \\ &\quad + \varepsilon''(B, Y)b\} + corr \end{aligned} \tag{8.34c}$$

Equation (8.34c) can also be written in the following form

$$E_H{}^x = E_{0Ha} + g\log_{10} K_w - g\log_{10}[OH^-] - g\,[D(I) - D(C)] + \Sigma_V\, Q(H, V)V + corr, \tag{8.35}$$

where $V = h, l, b, \Delta c_A$ and $[OH^-]$.

The function Q(H, V) denotes a function with a constant value, again, in terms of some interaction coefficients and ionic molar conductivities measured in the equilibrium solution. The functions Q(H, V), valid for the present cell, can be given as follows.

$$Q(H, h) = -g\ F_0\lambda_H + g\ t_Y\varepsilon''(H, Y) \tag{8.36}$$

$$Q(H, l) = g\varepsilon''(H, L) + g\ F_0\lambda_L - g\ t_A\varepsilon''(A, L) \tag{8.37}$$

$$Q(H, b) = -g\ F_0\lambda_B + g\ t_Y\varepsilon''(B, Y) \tag{8.38}$$

$$Q(H, \Delta c_A) = -g\ F_0\lambda_A + g\ t_Y\varepsilon''(A, Y) \tag{8.39}$$

$$Q(H, [OH^-]) = g\ F_0\lambda_{OH} - g\ t_A\varepsilon''(A, OH) \tag{8.40}$$

For the total potential anomalies, we have

$$\Delta E_H = g \log_{10} f_{HTS2} + E_D + E_{Df} \tag{8.41}$$

and

$$\Delta E_H = -g\ [D(I) - D(C)] + \Sigma_V\ Q(H, V)V + \text{corr} \tag{8.42}$$

If it was found in some separate experiment that the cell emf is influenced by the presence of the H_yL molecules as well, Eq. (8.35) should be extended as follows.

$$\begin{aligned} E_H{}^x = {} & E_{0Ha} + g \log_{10} K_w - g \log_{10}[OH^-] - g\ [D(I) - D(C)] \\ & + \Sigma_V\ Q(H, V)V + SL(H, \text{acid})[H_yL]_F + \text{corr} \end{aligned} \tag{8.43}$$

Here SL(H, acid) denotes the slope of the plot $E_H - g \log_{10} [H^+]$ versus $[H_yL]_F$, at constant [HY] and $[Y^-] = C$ M, constant. The equations presented above are valid also in the cases when the ligand comes from a strong acid and strong complexes are formed.

As is seen, Eq. (8.35) or (8.43) is the correct function for the calculation of the free, equilibrium concentration of the OH^- ions, for small values of w/a. This can be done by successive approximations knowing the constant E_{0Ha} and the functions Q(H, V). The determination of E_{0Ha} is discussed in Chapter 2. We should remember that a conditional constant, denoted either E_{0H1} or E_{0H2} and $E_{0H}{}^*$ cannot be used here. The functions Q(H,V) can be estimated in the same way as the functions Q(B, V) in Chapter 4.

If hydrogen gas electrode cannot be used, because of the presence of an oxidizing substance, a glass electrode can be used, which is calibrated against a H_2(g) electrode. This procedure will be discussed in Appendix 1 (Chapter 8).

8.2.5 *Emf Titration Suggested for the Determination of the Experimental Slope Function SL(H, l) and $\log_{10}K_l$ Value of the Weak Acid HL*

First, the constant E_{0Ha} should be determined by titrating v_0 ml solution S_0 with v_1 ml solution T_1. The composition of the solutions is

$$S_0 : 25.10^{-3}\ \mathrm{M\ HY}$$

$$C - 25.10^{-3}\ \mathrm{M\ AY}$$

$$c_Y = C\ \mathrm{M,\ constant}$$

$$T_1 : 20.10^{-3}\ \mathrm{M\ AOH}$$

$$C\ \mathrm{M\ AY}$$

During this so-called E_0-titration, the H^+ ion concentration of the test solution can be given as

$$[H^+] = HY_T - AOH_T$$

$[H^+]$ is formally identical with c_H defined in Chapter 2. Hence, the cell can be treated in the same way as it has been done for cell H in the mixture of strong electrolytes, considering $c_B = 0$. This case was discussed in Chapter 2. Therefore, the following potential function is valid

$$E_H{}^x = E_{0Ha} + g \log_{10}[H^+] - g\,[D(I) - D(C)] + SL(H, c_H)[H^+] + \mathrm{corr} \quad (8.44)$$

The intercept of the plot $E_H{}^x - g \log_{10} [H^+] + g[D(I) - DC] - \mathrm{corr}$ versus $[H^+]$ will result in E_{0Ha}. The slope of this plot is $SL(H, c_H)$.

At the end of the E_0-titration, solution S contains $\cong 1.10^{-3}$ M HY and $C - 1.10^{-3}$ M AY. Then totally v_2 ml solution T_2 should be added to $v_0{}^*$ ml test solution, in several steps. Solution T_2 is a HL–AL buffer couple, with the composition

$$T_2 : 0.1\ \mathrm{M\ HL},\ 1.8\ \mathrm{M\ AL} = L_T \text{ and } C\ \mathrm{M\ AY}$$

Now, we have the following species in the test solution: OH^-, L^-, HL, A^+, Y^-, H^+. In this buffer system, $\log_{10} [H^+]$ of the test solution can be calculated as

$$\log_{10}[H^+] \equiv \log_{10} K_w - \log_{10}[OH^-] = \log_{10} K_l - \log_{10}(c_{salt}/c_{acid}) \quad (8.45)$$

Here K_l is the protolysis constant for the reaction

$$\mathrm{HL} \rightleftharpoons \mathrm{H}^+ + \mathrm{L}^-$$

Now, we have for the composition of the ions of the ionic medium

$$c_Y = [Y^-] = C\ M,\ \text{is kept constant,} = [AY] + HY_T \tag{8.46}$$

$$c_A = [A^+] = [AY] + AOH_T + y\ L_T = C - HY_T + AOH_T + y\ L_T \tag{8.47a}$$

$$\Delta c_A = c_A - C = AOH_T - HY_T + y\ L_T \tag{8.47b}$$

The necessary equations for the deduction of the value of ΔE_H, valid in this system, can be obtained from those ones presented in sections 8.2.1 and 8.2.2. Here, we give only the final results for some important functions. If we have the acid H_yL, the pK_a values must be well separated. Considering the composition of the test solution, we have, now

$$I = C + (1/2)\{[OH^-] + \Delta c_A + y^2 L_T\} \tag{8.48}$$

w is given by Eq. (8.9) with b = 0 and $l = L_{T,}$
$\log_{10} f_{OH}$ is given by Eq. (8.18a) with b = 0 and I,
$\Phi_1(x)$ is given by Eq. (8.19) with b = 0.

For small values of w/a, we obtain for the buffer system

$$\begin{aligned} E_H{}^x &= E_{0Ha} + g\log_{10} K_1 - g\log_{10}(c_{salt}/c_{acid}) - g\,[D(I) - D(C)] \\ &\quad + g\varepsilon''(H, L)L_T - gF_0\{h\lambda_H + \lambda_A \Delta c_A - L_T\lambda_L - [OH^-]\lambda_{OH}\} \\ &\quad - g\ t_A\{\varepsilon''(A, L)L_T + \varepsilon''(A, OH)[OH^-]\} + gt_Y\{\varepsilon''(A, Y)\Delta c_A \\ &\quad + \varepsilon''(H, Y)h\} + \text{corr} \end{aligned} \tag{8.49}$$

where F_0 is given by Eq. (8.13), t_A and t_Y by Eq. (2–6).

According to the earlier treatment of the problem, we have, considering $h \cong 0$

$$\begin{aligned} E_H{}^x &= E_{0Ha} + g\log_{10} K_1 - g\log_{10}(c_{salt}/c_{acid}) - g\,[D(I) - D(C)] + SL(H, l)l \\ &\quad + gF_0[OH^-]\lambda_{OH} - g\ t_A\varepsilon''(A, OH)[OH^-] \end{aligned} \tag{8.50}$$

$$\begin{aligned} \Delta E_H &= g\log_{10} f_{HTS2} + E_D + E_{Df} = -g\,[D(I) - D(C)] + SL(H, l)l \\ &\quad + g\ F_0[OH^-]\lambda_{OH} - g\ t_A\varepsilon''(A, OH)[OH^-] \end{aligned} \tag{8.51}$$

SL(H, l) is the slope of the plot E_H'' versus $l = L_T$.

$$\begin{aligned} E_H'' &= E_H{}^x + g\log_{10}(c_{salt}/c_{acid}) + g\,[D(I) - D(C)] \\ &\quad - g\ F_0[OH^-]\lambda_{OH} + g\ t_A\varepsilon''(A, OH)[OH^-] - \text{corr} = E_{0Ha} \\ &\quad + g\log_{10} K_1 + SL(H, l)L_T \end{aligned} \tag{8.52a}$$

$$\text{The intercept} = \mathrm{E_{0Ha}} + \mathrm{g}\log_{10}\mathrm{K_l} \tag{8.52b}$$

from which the protolysis constant $\log_{10} \mathrm{K_l}$ can be calculated.

The calculated slope function can be obtained as (cf. Eq. (8.49))

$$\begin{aligned}\mathrm{SL(H, l)} = {} & \mathrm{dE_H''/d\,l} = -\mathrm{g}\varepsilon''(\mathrm{H, L}) - \mathrm{g\,F_0y}\lambda_\mathrm{A} + \mathrm{g\,F_0}\lambda_\mathrm{L} \\ & -\mathrm{g\,t_A}\varepsilon''(\mathrm{A, L}) + \mathrm{g\,t_Y}\varepsilon''(\mathrm{A, Y})\mathrm{y}\end{aligned} \tag{8.53}$$

If we want to recalculate SL(H, l) into the function Q(H, l), we should calculate the difference function given below

$$\mathrm{Q(H, l) - SL(H, l) = Eq.\ (8.37) - Eq.\ (8.53)} = \mathrm{g\,F_0y}\lambda_\mathrm{A} - \mathrm{g\,t_Y}\varepsilon''(\mathrm{A, Y})\mathrm{y} \tag{8.54}$$

Then, we have

$$\mathrm{Q(H, l)} = \mathrm{SL(H, l)_{exp}} + \mathrm{g\,F_0}\lambda_\mathrm{A}\mathrm{y} - \mathrm{g\,t_Y}\varepsilon''(\mathrm{A, Y})\mathrm{y} \tag{8.55}$$

Here, exp denotes experimental.

If it was found in a separate experiment that the molecules HL contribute to the cell potential, $\mathrm{E_H}^{x}$, the equations (8.49), (8.50) and (8.52) should be extended with the term SL(H, acid)$[\text{acid}]_\mathrm{F}$ (cf. Chapter 4 “The Total emf of Cell H for Small Values of w/a”).

For the estimation of the calculated slope function SL(H, l), we need ionic molar conductivities determined in the present mixture. It can be done in a similar way as discussed in Chapter 4 “Estimation Through Conductivity Measurements”. The interaction coefficients ε'' (A, L) and ε'' (H, L) can be determined by an emf titration, as it is suggested by the author in Chapter 6. For the determination of ε'' (A, OH), another emf titration will be suggested below.

The experimental value for SL(H, l) can be obtained through the graphical treatment discussed above. For the improvement of the constancy of the ionic molar conductivities involved in the slope function SL(H, l), the linearity of the experimental slope function is to be checked.

The determination of the interaction coefficient ε'' (A, OH).

The author proposes the following emf cell, free from liquid junction, for the determination of ε'' (A, OH).

$$-\ \mathrm{Pt/H_2(g)}\ |\ \text{Cell solution } \mathrm{S_0}\ |\ \mathrm{IS\ Na^+}\ + \qquad \text{Cell 11}$$

The cell solution $\mathrm{S_0}$ has the composition:

0.050 M NaOH

0.500 M $\mathrm{NaClO_4}$

In cell 11, IS $\mathrm{Na^+}$ denotes a $\mathrm{Na^+}$-selective glass electrode. $\mathrm{v_0}$ = 50.0 ml cell solution $\mathrm{S_0}$ should be titrated with a solution of the composition: 0.050 M NaOH, 3 M

$NaClO_4$. The $[Na^+]$ of the cell should be increased by the titration to as high value as possible. The emf value of this cell, in mV, can be written as

$$\begin{aligned} E^x &= e_{Na^+} - e_{OH^-} = E_0 + g\log_{10}[Na^+] + g\log_{10} f_{Na} \\ &\quad + g\log_{10}[OH^-] + g\log_{10} f_{OH} + E_P \end{aligned} \tag{8.56}$$

where e denotes the potential of a single electrode.

Expressing the $\log_{10} f_{Na}$ and $\log_{10} f_{OH}$ values according to SIT [4–11], again, we have

$$\log_{10} f_{Na} = -D(I) + \varepsilon''(Na, OH)[OH^-] + \varepsilon''(Na, ClO_4)[ClO_4{}^-] \tag{8.57}$$

$$\log_{10} f_{OH} = -D(I) + \varepsilon''(Na, OH)[Na^+] \tag{8.58}$$

Inserting these activity coefficients into Eq. (8.56), we obtain

$$\begin{aligned} E^* \equiv E^x &-g\log_{10}[Na^+] - g\log_{10}[OH^-] + 2g\,D(I) - g\varepsilon''(Na, ClO_4)[ClO_4{}^-] \\ &- E_P = \text{constant} + g\varepsilon''(Na, OH)[Na^+] \end{aligned} \tag{8.59}$$

where

$$\text{constant} = E_0 + g\varepsilon''(Na, OH)[OH^-] \tag{8.60}$$

Plotting the function E^* against $[Na^+]$, the value of ε'' (Na, OH) can be calculated from the slope.

If the concentration of the formed complexes cannot be neglected when we calculate the total potential anomalies of a cell, a method of graphical integration should be used, as discussed in Chapter 5. For the calculation of the $\log_{10} f_J$ values we have

$$\begin{aligned} \log_{10} f_J{}^* = &- z_J{}^2[D(I^*) - D(C)] + \{\Sigma_k\varepsilon''(J, L_k)l_k{}^* + \Sigma_j\varepsilon''(J, N_j)n_j{}^* \\ &+ \varepsilon''(J, OH)[OH^-]^*\}_{ca} + \{\varepsilon''(J, H)h^* + \varepsilon''(J, B)b^* \\ &+ \varepsilon''(J, A)\,(c_A{}^* - C) + \Sigma_i\varepsilon''(J, P_i)p_i{}^*\}_{an} \end{aligned} \tag{8.61}$$

When defining the ideal diffusion potential, E_D, the term – λ_{OH} $d[OH^-]^*$ dx should be added to Eq. (4–28) in Chapter 4.

When defining the contribution of the activity coefficients to E_D, namely E_{Df}, the term – $[OH^-]^*$ λ_{OH} $d\log_{10} f_{OH}$ should be added to Eq. (4–34b) in Chapter 4.

The estimation of the function Q{H, $[OH^-]$}.

First, we should determine the experimental slope function SL{H, $[OH^-]$}$_{exp.}$ We can use cell H with a $H_2(g)$ indicator electrode. For the solution S_0, we can have $\approx 2.10^{-3}$ M NaOH + 3 M $NaClO_4$. We can titrate with a solution: 0.1 M NaOH + 3 M $NaClO_4$. For the total cell emf, we have

$$
\begin{aligned}
E_H{}^x &= E_H + E_P = E_{0Hb} - g\log_{10}[OH^-] + g\,[D(I) - D(C)] - g\varepsilon''(A, OH)\Delta c_A \\
&\quad + g\,F_0[OH^-]\lambda_{OH} - g\,t_A\varepsilon''(A, OH)[OH^-] + \text{corr}
\end{aligned}
\tag{8.62}
$$

where E_{0Hb} is the experimental constant determined on the alkaline side.

$SL\{H, [OH^-]\}_{exp}$ is the slope of the plot $E_H{}^x + g\log_{10}[OH^-] - g[D(I) - D(C)] - \text{corr}$ vs. $[OH^-]$, where corr is neglected:

$$
\begin{aligned}
SL\{H, [OH^-]\} &= d\left\{E_H{}^x + g\log_{10}[OH^-] - g\,[D(I) - D(C)]\right\}/d[OH^-] \\
&= g\,F_0\lambda_{OH} - g\varepsilon''(A, OH)(t_A + 1)
\end{aligned}
\tag{8.63}
$$

as $\Delta c_A = AOH_T\, M \equiv [OH^-]$.

Calculating the difference function: Eq. (8.40)–(8.63), we have

$$
Q\{H, [OH^-]\} - SL\{H, [OH^-]\} = g\varepsilon''(A, OH) \tag{8.64}
$$

Knowing the experimental slope function, we obtain

$$
Q\{H, [OH^-]\} = SL\{H, [OH^-]\}_{exp} + g\varepsilon''(A, OH) \tag{8.65}
$$

8.2.6 The Protolysis of H_2L in Alkaline Solutions

We use the same treatment as in Section 4.3.1.4 (cf Ref. [2]). We study the equilibrium processes

$$
H_2L \rightleftharpoons HL^- + H^+ \quad K_1 = [HL^-]\,[H^+]/[H_2L]
$$

$$
HL^- \rightleftharpoons H^+ + L^{2-} \quad K_2 = [H^+]\,[L^{2-}]/[HL^-]
$$

First, we determine E_{0H} through an acid–base titration, in the absence of the ligand at $[Y^-] = C$ M, constant. During the main titration, we titrate with the buffer system: 0.2 M AHL + 1 M A_2L + C M AY. In the equilibrium solution, the following ions are present: H^+, OH^-, $[HL^-] = c_{acid} = HL_T$, $l = [L^{2-}] = c_{salt} = L_T$, Y^- and A^+.

The total cell emf was deduced in Ref. [2]. The following result was obtained. [cf. Eqs. (8.12), (8.22), (6.59) in Ref. [3], and (8.6)].

$$
\begin{aligned}
E_H{}^x = {} & E_{0Ha} + g\log_{10} h - g\,[D(I) - D(C)] + L_T[g\varepsilon''(H, L) + g\,F_0(\lambda_L - y\lambda_A) \\
& - g\,t_A\varepsilon''(A, L) + g\,yt_Y\varepsilon''(A, Y)] + HL_T[g\varepsilon''(H, HL) + g\,F_0(\lambda_{HL} - \lambda_A) \\
& - g\,t_A\varepsilon''(A, HL) + g\,t_Y\varepsilon''(A, Y)] + [OH^-]\,[g\,F_0\lambda_{OH} - g\,t_A\varepsilon''(A, OH)] \\
& + h[-g\,F_0\lambda_H + g\,t_Y\varepsilon''(H, Y)]
\end{aligned}
\tag{8.66}
$$

where the last term will be neglected.

For pK_2 – p$K_1 \geq$ 5.

Inserting Eq. (4.135) into Eq. (8.66), we can form E_H''.

$$\begin{aligned} E_H'' \equiv E_H^x + g\log_{10}(c_{salt}/c_{acid}) + g\,[D(I) - D(C)] - SL\{H, l \\ =[HL^-]\}HL_T - g[OH^-]\,[F_0\lambda_{OH} - t_A\varepsilon''(A, OH)] = E_{0Ha} \\ +g\log_{10} K_2 + SL\{H, l = [L^{2-}]\}L_T \end{aligned} \tag{8.67}$$

The slope function $SL\{H, l = [HL^-]\}$ is given by Eqs. (8.52), (8.53). Knowing this experimental slope function, we can plot the function E_H'' versus L_T. Then $\log_{10} K_2$ can be calculated from the intercept (= E_{0Ha} + g $\log_{10} K_2$). The slope of this plot is $SL\{H, l = [L^{-2}]\}$. For the theoretical slope we obtain from Eq. (8.66)

$$SL\{H, l = [L^{2-}]\} = g\varepsilon''(H, L) + g\,F_0(\lambda_L - y\lambda_A) - g\,t_A\varepsilon''(A, L) + g\,yt_Y\varepsilon''(A, Y) \tag{4.143}$$

When dilute NaOH and a H_2L containing solution, or A_2L are used at the study of the protolysis of H_2L, the slope function $SL\{H, l = [L^{2-}]\}$ should be recalculated into $Q\{H, l = [L^{2-}]\}$. Hence, we form the difference function

$$\begin{aligned} Q\{H, l = [L^{2-}]\} - SL\{H, l = [L^{2-}]\} = \text{Eq. (4.53)} - \text{Eq.(4.143)} \\ = gyF_0A - g\,y\,t_Y\,\varepsilon''(A, Y) \end{aligned} \tag{4.144}$$

And knowing the experimental slope function, we have

$$Q\{H, l = [L^{2-}]\} = SL\{H, l = [L^{2-}]\}_{exp} + \text{the difference function (4.144)} \tag{4.145}$$

For $pK_2 - pK_1 < 5$

The procedure of Chapter 4 “Deducation for $pK_2 - pK_1 < 5$” or a curve-fitting computer program should be used.

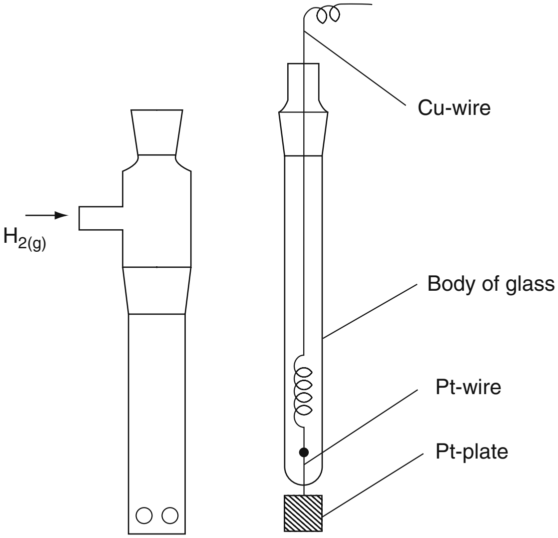
Appendix 1 (Chapter 8)
The Hydrogen Electrode [13]

At present, hydrogen, quinhydrone and glass electrodes are used as H^+-sensitive indicator electrodes. In alkaline solutions, the hydrogen electrode should be used. In theory, the hydrogen electrode is best, but often it cannot be used since it reduces some substances in the equilibrium solution. In this case, glass electrode should be used which is calibrated against hydrogen electrode. The hydrogen electrode looks as shown in Fig. 8.1. It can be prepared either by electrolysis or thermally [13].

The Preparation of the Hydrogen Electrode by Electrolysis

The Pt foil (wire) should be cleaned in conc. HNO_3 (or aqua regia for a short time), water and ethanol, and then ignited in an ethanol flame. Then it should be coated with Pt, Pd or Ir black by electrolysis. For example, using *Platinum black*: dissolve

Fig. 8.1 The hydrogen electrode



1 g $PtCl_4$ in 30 ml H_2O, add 0.1 ml 0.1 M HCl and 20 mg Pb Ac_2. Electrolyse (as catode) 1–3 minutes with 0.3–0.15 A (Sirkka), 0.4–0.2 A (Bates, pH 1954, pp. 166 – 167), 0.01 A/cm^2 (Georg II). Sometimes, no black cover is obtained, it then helps to add more Pb Ac_2 (Sirkka). Finally, the foil should be electrolysed (as catode) in 0.1 M H_2SO_4 (Georg II), 10 % H_2SO_4 (Sirkka, Nils) for 20 – 30 minutes with the same current density as before. When the last electrolysis was cut down to 5 min, equally good results were obtained (Sirkka). The lead acetate does not influence the electrode (Georg II). The electrode is rinsed with distilled water before it goes into the equilibrium solution. We can also wipe it off with filter paper.

Old Pt black is removed with aqua regia. When this has been repeated a number of times, the Pt surface becomes etched and dull, and it is time to reject it (Nils).

For each new titration, a new electrode should be made.

The hydrogen gas must be made free from oxygen. Let it pass through a series of six wash bottles: the first three should contain acid $CrCl_2$ solution in contact with amalgamated zinc for complete removal of oxygen by oxidation to Cr(III), the fourth a 10 % KOH solution to remove carbon dioxide, the fifth water and the sixth C M ionic medium.

The H_2(g) stream should be divided into two (regulated by a pincher): one stream bubbles through the electrode tube and the other one enters below the surface of the solution. Before the titration, first bubble O_2-free N_2 for at least 30 min, then H_2 (O_2-free) for about an hour or until changes in the rate of bubbling (always slow) do not influence E. The outlet for H_2 should be under water and the titration vessel should be tight, and not unnecessarily large. It may be a good idea to have the apparatus standing with N_2 or H_2 bubbling overnight, after a titration, and to check E the next morning (Nils).

In alkaline solutions which do not cotain O_2 or other oxidizing substances, equilibrium is obtained within 30–60 min for each point (Nils).

The Thermal Preparation of the Hydrogen Electrode [14]

The thin Pt-plate electrode should be placed in aqua regia and boiled for 1–5 min depending on the condition of the metal. The electrode should then be washed immediately with doubly distilled water, dried and stored under conditions where no deposits can be formed on the metal surface.

The sensing surface can be prepared as follows. We prepare a 1–2% solution of hexachloroplatinic acid by dissolving platinum metal in aqua regia. A drop of this solution is applied to the sensor body so as to cover its entire surface. The metal plate is the heated gently in an ordinary spirit flame. A yellow deposit is formed as the liquid evaporates. The heating should be continued until the yellow colour just disappear, forming a layer of platinum black on the sensor body surface. The procedure should be repeated until an even layer covers the surface. Excessive heating should be avoided as this results in a layer of greyish appearance and a deactivated electrode. The prepared electrode should be used immediately, to avoid contamination from the air.

The Total Emf of Cell H with a Hydrogen Indicator Electrode

The electrode reaction of cell H is at the platinized platinum electrode surface
$\frac{1}{2}\,H_2 \rightleftharpoons H^+ + e^-$
and at the surface of the reference electrode

$$e^- + AgCl(s) \rightleftharpoons Ag(s) + Cl^-$$

The potential of the hydrogen electrode is

$$e_H = e_H{}^0 + g\log_{10}[(a(H^+)/p(H_2)^{1/2})] \tag{8.68}$$

The potential of the reference electrode is

$$e_{ref} = e_{AgCl,Ag^0} - g\log_{10}[Cl^-] \tag{8.69}$$

and the total emf of cell H will be

$$E_H{}^x \equiv E_H + (g/2)\log_{10} p(H_2) = E_{0H} + g\log_{10}[a(H^+)] \tag{8.70}$$

where

E_H = the measured emf, in mV, of cell H with the partial pressure of hydrogen $p(H_2)$, in atmospheres,

$E_H{}^x$ = the corrected emf which we would have if the partial pressure of hydrogen were one atmosphere,
$e_H{}^0$ and $e_{AgCl,\,Ag}{}^0$ are the normal potentials,
$a(H^+)$ = the activity of the hydrogen ions,
$p(H_2)$ = the partial pressure of hydrogen, is obtained by subtracting the vapour pressure of C M ionic medium from the observed barometric pressure.

If the pressure is measured in Pascal (Pa), we have

$$1\text{Normal atmosphere } (p_0) = 1.01325 \times 10^5 \text{ Pa } (\text{Nm}^{-2})$$

$$e_H = e_H{}^0 + g \log_{10} a(H^+) + g \log_{10}(1.01325 \times 10^5/p(H_2)^{1/2}) \text{ mV} \tag{8.71}$$

$$E_H{}^x = E_H - g \log_{10}(1.01325 \times 10^5/p(H_2)^{1/2}) = E_{0H} + g \log_{10} a(H^+)\text{mV} \tag{8.72}$$

where $p(H_2)$ is given in Pa.

Table 8.1 presents some values [15, 16] for the ionic product of water (- $\log_{10} K_w$) at 25°C for the equilibrium

$$H_2O \rightleftharpoons H^+ + OH^-$$

and

$$[H^+]\,[OH^-] = K_w \tag{8.73}$$

Table 8.1 Survey of some values [15, 16] for the ionic product of water ($-\log_{10} K_W$) for the equilibrium $H_2O \rightleftharpoons H^+ + OH^-$ and $[H^+]\,[OH^-] = K_W$, at 25°C in different ionic media, measured by hydrogen indicator electrode

Ionic medium M	0.5	1	2	3
Na $Cl0_4$	13.73 m units Na($Cl0_4$)	13.77 (I=1)	14.08 (Na) $Cl0_4$	14.15 (Na) $Cl0_4$
				14.22 (Na) $Cl0_4$ 14.03 Na ($Cl0_4$) m units 14.17 ($I = 3$)
	13.74 ($I = 0.5$)	13.80 ($I = 1$) 13.95 1 (Na $Cl0_4$)	13.97 ($I = 2$)	14.20 ($I = 2.99$)
Na Cl	13.70 m units Na(Cl)	13.73 (I =1)		14.03 ($I = 3$)
KNO_3		13.73 ($I = 1.01$)	13.88 ($I = 2$)	
KC1	13.76 ($I = 0.5$)	13.80 ($I = 1$) 13.96 1 (KCl)	13.96 ($I = 2$)	

Notations to Table 8.1

2 ($NaClO_4$): ionic strength held constant at the value stated (2 mol liter^{-1}) by addition of the inert salt shown in parenthesis.
I ($NaClO_4$): measurements made at a series of ionic strength (I) with sodium perchlorate as the inert salt.
2 (Na)ClO_4: concentration of the anion (ClO_4^-) held constant at the value stated (2 mol liter $^{-1}$) with the ion shown in parenthesis as the inert cation.
3 Na(ClO_4): concentration of the cation of the ionic medium held constant at the value stated (3 mol liter^{-1}) with the ion shown in parenthesis as the inert anion.

Presentation of a New Calibration Method for the Glass Electrode Against the Hydrogen Electrode in Alkaline Solutions

We should use the following cell construction

– Ref. half-cell || Bridge sol. || Test sol. | H_2(g), Pt and GE electrodes +

The bridge solution is C M $NaClO_4$. In the test solution $[ClO_4^-] = C$ M, constant. In the reference half-cell, we should have two reference electrodes, one separate for each indicator electrode. They should be connected to two potentiometers. For the glass electrode circuit, we need a digital voltmeter (DVM) suitable for electrodes of high resistance (glass electrode). The connection of the glass electrode to the DVM cannot be disconnected during the measurement, because the value of $E_{0\,gl}$ will change. For the hydrogen electrode of law resistance, we can have a Vernier potentiometer (a potentiometer with Wheaston bridge).

The calibration procedure consists of the following steps.

(1) The determination of the experimental constants E_{0Ha}(for the hydrogen electrode) and E_{0gla} (for the glass electrode), respectively, through an acid–base titration.
In the case of for example $NaClO_4$ ionic medium, $v_0 = 50.0$ ml 0.010 M $HClO_4$ + 2.99 M $NaClO_4$ should be titrated with totally 24.5 ml 0.020 M NaOH containing 3 M $NaClO_4$.
The emf of the cells can be described by Eq. (8.1) before the equivalence point. For example, for the hydrogen electrode, the intercept of the plot $E_H^x - g \log_{10}[H^+] + g[D(I) - D(C)]$ versus $[H^+]$ will give the constant E_{0Ha} and the slope SL(H, c_H). And the same plot should be done for the cell with the glass electrode.

(2) Then we continue the titration with the calibration, by adding $v_{T2} = 50.00$ ml 0.040 M NaOH + 3 M $NaClO_4$. We measure the potentials of the indicator electrodes after each burette addition. Now, Eq. (8.2) describes the emf of the

cells after the equivalence point has passed. As the sodium error appears in the potential of the glass electrode, the measured $[OH^-]_{gl}$ by it will be erroneous. The $[OH^-]_H$ measured by the hydrogen electrode is correct. On the basis of Eq. (8.2), we can define the measured potentials $E_H{}^x$ and E_{gl}. Then we plot the function for example for the hydrogen electrode: $E_H{}^x + g \log_{10} [OH^-]_H - g \log_{10} K_w + g[D(I) - D(C)]$ vs. $[OH^-]_H$. The intercept will be the constant E_{0Ha}, the slope $SL^x(H, [OH^-]_H)$. Similarly, we obtain for the glass electrode: the intercept E_{0gla} and the slope $SL(H, [OH^-]_{gl})$.

(3) Then we form the difference function $\Delta E_{corr} = E_H{}^x - E_{gl}$. We obtain

$$\begin{aligned}\Delta E_{corr} = E_H{}^x - E_{gl} = E_{0Ha} - E_{0gla} + g\log_{10}[OH^-]_{gl} - g\log_{10}[OH^-]_H \\ + SL(H, [OH^-]_{gl})[OH^-]_{gl} - SL^x(H, [OH^-]_H)[OH^-]_H \text{ mV}\end{aligned} \tag{8.74}$$

Then we plot the correction function ΔE_{corr} vs. E_{gl} mV on a millimetre paper.

(4) The use of the correction.

We study the complex formation reaction with a glass electrode and measure the emf $E_{gl,cpx}$ which defines $[OH^-]_{gl}$. This is described by Eq. (8.3). First, the experimental constant E_{0gla} should be determined. Now, we have $E_{0gl,cpx}$ experimental constant. We read the correction term from the diagram at the $E_{gl,cpx}$ value measured and form the function

$$\Delta E_{corr} + E_{gl,px} = \text{Eq. (8.74)} + \text{Eq. (8.3)}.$$

From here, we can express the real $[OH^-]_H$ as

$$\begin{aligned}\log_{10}[OH^-]_H = -(1/g)(\Delta E_{corr} + E_{gl,cpx}) + (1/g)\,(E_{0Ha} - E_{0gla} + E_{0gl,cpx}) \\ + \log_{10} K_w - [D(I) - D(C)] + (1/g)\Sigma_V Q(H, V)V + (1/g)\text{corr}\end{aligned} \tag{8.75}$$

as the terms $(1/g)\,\{SL(H, [OH^-]_{gl})\,[OH^-]_{gl} - SL^x(H, [OH^-]_H)[OH^-]_H\} \cong 0$.

Here, $V = [OH^-]_{gl}$, b, l Δ c_A. The concentration $[OH^-]_{gl}$ can be calculated from $E_{gl,cpx}$ using Eq. (8.3) by successive approximations. The term "corr" is negligible.

The calibration curve should be determined for every new experimental condition used ($[A^+]$ = C M, constant, I = C M, constant) and new potential functions must be deduced.

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Notation to Appendix 2 in Chapter 4

In the procedure suggested above for the determination of E_{0B} and E_{0H}, simultaneously, the concentrations both c_B and c_H are varied. Therefore, the graphical determination of these constants, suggested in Chapter 2, is not possible. Only by numerical calculations. In this experiment, separate reference electrode and potentiometer should be used for each indicator electrode.

We should remember that during the determination of E_{0B} and E_{0H}, the total cell emf can be calculated in general as for cell B:

$$\begin{aligned} E_B = {} & E_{0B} + (g/z_B)\log_{10} c_B - gz_B[D(I) - D(C)] + gd_1c_B + gd_2c_H \\ & + SL(B, H_yL)[H_yL] + corr \end{aligned} \tag{4.234b}$$

where for $[A^+] = C$ M, constant, d_1 is given by Eq. (2.3) and d_2 by Eq. (2.4). The slope function involved should also be determined. Moreover,

For Cell H:

$$E_H = E_{0H} + g\log_{10} c_H - g[D(I) - D(C)] + gd_3c_B + gd_4c_H + SL(H, H_yL)[H_yL] + corr \tag{4.234c}$$

where for $[A^+] = C$ M, constant, d_3 is given by Eq. (2.14a) and d_4 by Eq. (2.14b).

A non-conditional constant for E_{0B} can be calculated from Eq. (4.34b), after conductivity measurements. The same kind of constant for E_{0H} can be obtained from Eq. (2.34c), having the necessary conductivity data (cf. Chapters 2 and 3). The slope function SL (B, H_yL) can be determined according to Section 4.1.8.1., SL (H, H_yL) according to Section 4.1.8.2.

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