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The Liquid Junction Potential in Potentiometric Titrations. 1. The Calculation of Potentials Across Liquid Junctions of the Type $AY\,|\,BY_{z(B)}+HY+AY$ for Cells with Mixtures of Strong Electrolytes

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Equations were derived, in a general form, for practical emf cells with the experimental conditions $[A^+]=C$ M, constant, $[Y^-]=C$ M, constant, and I (the ionic strength) $=C$ M, constant, containing three strong electrolytes, for calculation of the total cell emf:

$E_J = E_{OJ} + (g/z_J)\log c_J f_{JTS2} + E_D + E_{Df}$ mV

Here, (A^+, Y^-) is the ionic medium (constant ionic medium method), $B^{z(B)+}$ is the metal ion, E_D is the ideal diffusion potential (Henderson equation) E_{Df} is the contribution of the activity coefficients to the diffusion potential, E_J is the total cell emf for measuring electrodes reversible to the ions J. f_{JTS2} denotes the activity coefficients in the terminal solution TS2. The concentration of a chosen ion of the ionic medium, C, should be in the range $0.5 \leqslant C \leqslant 3$ mol dm^{-3}. The charge of the metal ion $B^{z(B)+}$ is restricted to $\leqslant 3$. The cells considered, have electrodes reversible either to $B^{z(B)+}$ or H^+ ions, cells B and H, respectively. The theory is tested on emf cells containing the mixtures of $Cd(ClO_4)_2+HClO_4+NaClO_4$ at the three experimental conditions defined above. The total potential anomalies in the cells are

$\Delta E_J = (g/z_J)\log f_{JTS2} + E_D + E_{Df}$

Measured slope functions of the type $E_J' \equiv E_J - (g/z_J)\log c_J$ versus c_H or c_B were compared with the calculated ones. The agreement was good: $\leqslant 1.6$ mV/M $[Cd^{2+}]$ or $[H^+]$. The determination of the constants of the Nernst equations, E_{OJ}, is discussed.

The series entitled 'The Liquid Junction Potential in Potentiometric Titrations' concerns the calculation of potentials across liquid junctions in emf cells most frequently used in potentiometric titrations under different experimental conditions. The present paper is a summary of the revised parts 1–5 of Ref. 1.

The ionic medium present in the cells studied can be used in three ways: (i) $[A^+]=C$ M, is kept constant, (ii) $[Y^-]=C$ M, is kept constant, or (iii) $I=C$ M, is kept constant.

The cells studied, can be described as follows.

– RE	Solution 3 ‖	Bridge soln. TS1 AY CM $x=0$ ‖	Test soln. TS2 $x=1$	Electrodes + reversible to H^+ and $B^{z(B)+}$ ions
	$E_{j(1,3)}$	$E_{j(1,2)}$		Cell H Cell B

Here, $E_{j(1,3)}$ and $E_{j(1,2)}$ are the liquid junction terms. The term $E_{j(1,3)}$ is constant and is included in the value of the constants E_{OH} and E_{OB} of the cells. $E_{j(1,2)}$ is split into

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

RE denotes the reference electrode, which is Ag(s), AgCl(s). The total emf of these cells is

$$E_J = E_{OJ} + (g/z_J)\log c_J f_{JTS2} + E_D + E_{Df} \tag{2}$$

For most chemists, the expression 'liquid junction potential' denotes all potential anomalies appearing in an emf cell with liquid junction, denoted ΔE_J. We define ΔE_J as

$$\Delta E_H = g\log f_{HTS2} + E_D + E_{Df}, \quad \text{for cell H} \tag{3}$$

$$\Delta E_B = (g/z_B)\log f_{BTS2} + E_D + E_{Df}, \quad \text{for cell B} \tag{4}$$

Neglect of ΔE_J could result in erroneous interpretation of emf data as far as the minor species and the formation of weak complexes are concerned.

Use of least-squares optimization programs is customary[2] in the treatment of emf data. In this procedure, species are suggested until the theoretical and experimental titration data agree within, say, 0.01 mV. Systematic errors in the data may show up, for instance, as the formation of polynuclear species. 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, which depend on *all* ion concentrations present in the test solution and the salt bridge used in emf cells.

It should be emphasized that it is not possible to give one explicit function which describes the ΔE_J in every kind of emf cell. The complexity of the problem is increased by the fact that for the calculation of ΔE_J the ionic molar conductivities in the transition layer of the junction are needed. As it will be shown, these are constant only under given experimental conditions.

The goal of the current series is to show how to solve the problems of emf titrations connected to the presence of liquid junctions.

Definitions and symbols

All concentrations are expressed in mol dm^{-3}.

Latin symbols

a — a part of the potential functions E_D and E_{Df}, defined by eqn. (19)

A_γ — theoretical Debye–Hückel coefficient[3] equal to 0.5115 mol$^{-1/2}$ dm$^{3/2}$ for water at 25 °C

C — concentration of a chosen ion of the ionic medium, which is kept constant during the potentiometric titration

$D(I)$

$$= \frac{A_\gamma \sqrt{I}}{1 + 1.5\sqrt{I}} \qquad (5)$$

$D(I^*)$ — function $D(I)$ in the transition layer

E_D — ideal diffusion potential[4]

$$E_D = -g \int_{TS1}^{TS2} \sum_J \frac{t_J^*}{z_J} \, d \log c_J^* \qquad (6)$$

E_{Df} — activity coefficient contribution to E_D

$$E_{Df} = -g \int_{TS1}^{TS2} \sum_J \frac{t_J^*}{z_J} \, d \log f_J \qquad (7)$$

E_j — liquid junction potential[5,6]

$$E_j = -g \int_{TS1}^{TS2} \sum_J \frac{t_J^*}{z_J} \, d \log(c_J^* f_J)$$

$$= E_D + E_{Df} \qquad (8)$$

$\log f_J$ — log of the ionic activity coefficient of the ion J on the molar concentration scale, can be expressed according to the specific interaction theory[7–14]

For cations (R)

$$\log f_R = -z_R^2 D(I) + \sum_X \tilde{\varepsilon}(R, X) c_X \qquad (9)$$

where X denotes anions, and the first term is the Debye–Hückel term[3,15]

For anions

$$\log f_X = -z_X^2 D(I) + \sum_R \tilde{\varepsilon}(R, X) c_R \qquad (10)$$

F_C — Faraday constant[16] = 9.648 530 9(29) × 10^4 Coulomb mol^{-1}

g — $RT \ln 10/F_C$ = 59.159 mV at 25 °C

$h = [H^+]$ — concentration of the H^+ ions at equilibrium

I — total ionic strength, in general and in the test solution

$$I = (1/2) \sum_J c_J z_J^2 \qquad (11)$$

$I(C)$ — ionic strength in the bridge solution of C mol dm^{-3} AY

$L^{Y^-} \equiv L^{z(L)}$ — ligand in the complex formation reaction

R — gas constant[16] = 8.314 510(70) J mol^{-1} K^{-1}

t_J^* — transport number[17,18] of the constituent J in the transition layer

$$t_J^* = \frac{\lambda_J^* c_J^* |z_J|}{\sum_J \lambda_J^* c_J^* |z_J|} \qquad (12)$$

T — temperature in K

T subscript — denotes total, analytical concentration

TS1 — composition of the terminal solution 1 with the mixing fraction $x = 0$ at one end of the junction in the cell studied

TS2 — composition of the terminal solution 2 with the mixing fraction $x = 1$ at the other end of the junction in the cell studied, being in contact with the positive pole of the cell[17,18]

x — mixing fraction at some intermediate plane in the transition layer of the junction, $0 \leqslant x \leqslant 1$

y — $= |z_L|$, the absolute value of the charge number for the ligand

$z_J \equiv z(J)$ — the algebraic charge number (with its algebraical sign in the equations) of ion J

$|z_J|$ — the absolute value of the charge number

w — a part of the potential function E_D and E_{Df}, defined by eqn. (18)

$*$ — superscript, denotes a property of the transition layer

Greek symbols

$\tilde{\varepsilon}(J, K)$ — interaction coefficient between the ions J and K, on the amount concentration scale, in dm^3 solution (mol solute)$^{-1}$

$\varepsilon(J, K)$ — interaction coefficient between the ions J and K on the molarity scale, in kg solvent (mol solute)$^{-1}$

The interaction coefficient used by

	Guggenheim, β, are related to ε by $\varepsilon = 2\beta/\ln 10$.
κ	conductivity of the test soution in $S\,cm^{-1}$ κ = cell constant of the conductivity cell (cm^{-1})/R (Ω), where R is the measured resistance of the solution in question
$10^3\kappa$	$= \sum_J \lambda_J \lvert z_J \rvert c_J$ (13)
λ_J^*	the ionic molar conductivity of ion J of charge number z_J and concentration c_J^* in the transition layer, in $S\,cm^2\,mol^{-1}$
$\Lambda_{R,X}$	$= \lambda_R + \lambda_X$, the molar conductivity of the electrolyte RX, in $S\,cm^2\,mol^{-1}$

Ionic charges in subscripts are omitted for simplicity and double subscripts are avoided. Therefore, e.g., the notation λ_{Lk} is used instead of λ_{L_k}, or $BY_{z(B)}$ instead of BY_{z_B}.

Potential functions for cells containing mixtures of strong electrolytes

General assumptions. The special conditions assumed to be fulfilled for the deductions are as follows.

(1) The liquid junctions are of the continuous mixture type. This means that the concentration of the ion J, c_J, at some intermediate plane in the transition layer, can be calculated as

$$c_J^* = [c_J^*] = x c_{JTS2} + (1-x) c_{JTS1} \tag{14}$$

(2) The ionic molar conductivities in the transition layer (λ_J^*) are assumed to be constants. They are not known, but in the calculations approximate values measured experimentally in the test solution studied (λ_J) have been used. The trace ionic molar conductivities are used for the ions present in minor concentrations, $c_J \leqslant 0.1\,mol\,dm^{-3}$, in the ionic medium used.

(3) The ionic activity coefficients are calculated by means of the specific ionic interaction theory, SIT,[7–14] as defined by eqns. (9) and (10) which proved to be useful even in the case of complex formation. The interaction coefficients are considered to be constant throughout the junction.

Deduction of the potential functions.

1. *The calculation of the ideal diffusion potential,* E_D. The expression for the calculation of the ideal diffusion potential has been suggested by Henderson, Planck, Lewis and Sargent[4,17,18] and is given by eqn. (6). Integration of this equation and assuming a linear concentration profile in the transition layer yields[4,17,18]

$$E_D = -\frac{g}{2.303}\frac{U_{TS2}-U_{TS1}}{S_{TS2}-S_{TS1}}\ln\frac{S_{TS2}}{S_{TS1}} \tag{15}$$

where

$$U = \left(\sum_J c_J\lambda_J\right)_{\text{cations}} - \left(\sum_J c_J\lambda_J\right)_{\text{anions}} \tag{16}$$

$$S = \left(\sum_J c_J \lvert z_J\rvert \lambda_J\right)_{\text{cations}} + \left(\sum_J c_J \lvert z_J\rvert \lambda_J\right)_{\text{anions}} \tag{17}$$

Deduction of eqn. (15) can be found in most textbooks on electrochemistry. Introducing

$$S_{TS2} - S_{TS1} \equiv w \tag{18}$$

and

$$S_{TS1} \equiv a = C(\lambda_A + \lambda_Y) \tag{19}$$

moreover

$$S_{TS2} \equiv w + a \tag{20}$$

we obtain

$$E_D = -\frac{g}{2.303}\frac{U_{TS2}-U_{TS1}}{w}\ln\left(\frac{w}{a}+1\right) \tag{21}$$

For small values of w/a we can write, using the approximation $\ln[(w/a)+1] \cong w/a$

$$E_D \cong -\frac{g}{2.303}\frac{U_{TS2}-U_{TS1}}{a} \tag{22}$$

The same equations can also be obtained with the formulae of Baes and Mesmer.[19] The validity of the approximation must be checked for every system studied.

2. *The deduction of the activity factor contribution to the diffusion potential,* E_{Df}. The deduction is based upon the definition of E_{Df} obtained by the combination of eqns. (7) and (12). This function can always be written in the form

$$E_{Df} = -g\int_{TS1,x=0}^{TS2,x=1} \sum_J \left(\frac{1}{N}\lambda_J c_J^* \frac{\lvert z_J\rvert}{z_J}\,d\log f_J\right) \tag{23}$$

where the concentrations refer to a plane in the transition layer and

$$N = wx + a \tag{24}$$

We calculate $\log f_J$ from the specific ionic interaction theory,[7–14] as given in eqns. (9) and (10). In the current calculations, the activity coefficient of the ion J defined in such a way that the trace activity coefficient, f_J^{tr}, is 1 when $c_J \to 0$ in $C\,mol\,dm^{-3}$ AY, the pure ionic medium as solvent. The choice of the reference state is also convenient because $\Delta E_J = 0$ if $c_J \to 0$. Hence, we obtain

$$\log f_J^{tr} = 0 = -z_J^2 D(C) + \tilde{\varepsilon}(J, Y)C \quad \text{for cations} \tag{25}$$

$$\log f_J^{tr} = 0 = -z_J^2 D(C) + \tilde{\varepsilon}(J, A)C \quad \text{for anions.} \tag{26}$$

Therefore, the activity coefficient for a cation, J, in the medium AY at constant concentration of $[A^+] = C\ \mathrm{mol\ dm^{-3}}$ can be written, according to eqns. (9) and (25), as

$$\log f_J = -z_J^2[D(I) - D(C)] + \sum_{\text{anions},X} [\tilde{\varepsilon}(J, Y)(c_Y - C) + \tilde{\varepsilon}(J, X')c_{X'}] \quad (27)$$

For an anion, J, we obtain in a similar way

$$\log f_J = -z_J^2[D(I) - D(C)] + \sum_{\text{cations},R} [\tilde{\varepsilon}(A, J)(c_A - C) + \tilde{\varepsilon}(J, R')c_{R'}] \quad (28)$$

The ionic strength at some intermediate plane in the transition layer can be calculated according to the principle of the continuous mixture junction:

$$(I^*) = xI(\text{TS2}) + (1 - x)I(\text{TS1}) \equiv xI + (1 - x)I(C) \quad (29)$$

Eqn. (23) can be rewritten in the form

$$E_{\text{Df}} = -g \int_{x=0}^{x=1} \left(\frac{\phi_1(x)}{wx + a} \frac{dD(I^*)}{dx} + \frac{\phi_2 x}{wx + a} + \frac{\theta_1}{wx + a} \right) dx \quad (30)$$

where $\phi_1(x)$ is a function of x, and ϕ_2 and θ_1 are independent of x. These terms will be given in the different experimental cells studied. The result of the integration is

$$E_{\text{Df}} = \text{corr} - \frac{g\phi_2}{w} + \frac{g(\phi_2 a - \theta_1 w)}{w^2} \ln\left(\frac{w}{a} + 1\right) \quad (31)$$

where

$$\text{corr} = -g \int_{x=0}^{x=1} \frac{dD(I^*)}{dx} \frac{\phi_1(x)\, dx}{wx + a} \quad (32)$$

For small values of w/a we can write

$$E_{\text{Df}} \cong \text{corr} - \frac{g\theta_1}{a} \quad (33)$$

Inserting the derivative $dD(I^*)/dx$ into eqn. (32), as defined below,

$$\frac{dD(I^*)}{dx} = \frac{dD(I^*)}{dI^*} \frac{dI^*}{dx} = \frac{0{\cdot}5115}{2\sqrt{I^*}(1 + 1.5\sqrt{I^*})^2} \frac{dI^*}{dx} \quad (34)$$

the term corr can be integrated graphically. It summarizes the Debye–Hückel terms of the contribution of the activity coefficients. These terms are generally negligible at the use of high concentrations for the ionic medium and $c_H \leqslant 0.1\ \mathrm{mol\ dm^{-3}}$, $c_B \leqslant 0.1\ \mathrm{mol\ dm^{-3}}$.

Emf cells where $[A^+] = C$ M, is kept constant

In this section, the calculation of the total potential anomalies and the total cell emf values are presented for emf cells containing the mixture of three strong electrolytes with the liquid junction type $AY \mid AY + HY + BY_{z(B)}$, at the experimental condition $[A^+] = C$ M, is kept constant. The composition of the test solution studied can be given as

TS2 ($x = 1$)

$c_B = [B^{z(B)+}] = [BY_{z(B)}]$ M

$c_H = [H^+] = [HY]$ M

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

$c_Y = [Y^-] = C + c_H + z_B c_B$ M

and $I = C + c_H + c_B(z_B^2 + z_B)/2$

The total emf of cell B with an amalgam indicator electrode and for small values of w/a. The total cell emf E_B is given by eqn. (2). For the ideal diffusion potential we obtained for small values of w/a, using the approximation $\ln(w/a + 1) = w/a$

$$E_D \cong -gF_0[c_B(\lambda_B - z_B\lambda_Y) + c_H(\lambda_H - \lambda_Y)] \quad (35a)$$

where

$$F_0 = 1/[2.303C(\lambda_A + \lambda_Y)] \quad (35b)$$

For E_{Df}, eqn. (30) yields

$$\phi_1(x) = x[c_B z_B(\lambda_Y - z_B\lambda_B) + c_H(\lambda_Y - \lambda_H)] + C(\lambda_Y - \lambda_A) \quad (36)$$

$$\phi_2 = (c_H + z_B c_B)[\tilde{\varepsilon}(B, Y)c_B(\lambda_B - \lambda_Y) + \tilde{\varepsilon}(H, Y)c_H(\lambda_H - \lambda_Y)] \quad (37)$$

$$\theta_1 = (c_H + z_B c_B)C\lambda_A\tilde{\varepsilon}(A, Y) - C\lambda_Y[\tilde{\varepsilon}(B, Y)c_B + \tilde{\varepsilon}(H, Y)c_H] \quad (38)$$

and eqn. (33) results in

$$E_{\text{Df}} \cong \text{corr} - g(c_H + z_B c_B)t_A\tilde{\varepsilon}(A, Y) + gt_Y[\tilde{\varepsilon}(B, Y)c_B + \tilde{\varepsilon}(H, Y)c_H] \quad (39a)$$

where

$$t_A = \lambda_A/(\lambda_A + \lambda_Y) \quad \text{and} \quad t_Y = \lambda_Y/(\lambda_A + \lambda_Y) \quad (39b)$$

The term 'corr' is given by eqn. (32) and can be estimated by graphical integration. The magnitude of this term was estimated for Mixture 1 (the composition of it is given in the section 'The comparison of the calculated ...'), as a test solution at $x = 1$, and it was found to be negligible.

Hence, we have for the total cell emf E_B

$$E_B \cong E_{OB} + (g/z_B)\log c_B - gz_B[D(I) - D(C)] + gd_1 c_B + gd_2 c_H + \text{corr} \quad (40)$$

where

$$d_1 = \tilde{\varepsilon}(B, Y) - \frac{\lambda_B - z_B\lambda_Y}{2.303C(\lambda_A + \lambda_Y)} - z_B t_A\tilde{\varepsilon}(A, Y) + t_Y\tilde{\varepsilon}(B, Y) \quad (41)$$

$$d_2 = \frac{\tilde{\varepsilon}(B, Y)}{z_B} - \frac{\lambda_H - \lambda_Y}{2.303C(\lambda_A + \lambda_Y)} - t_A\tilde{\varepsilon}(A, Y) + t_Y\tilde{\varepsilon}(H, Y) \quad (42)$$

On the basis of eqn. (40), the constant E_{OB} can be determined through a potentiometric titration where c_B is varied and c_H is kept constant, as a plot of $E_B-(g/z_B)\log c_B + gz_B[D(I)-D(C)]-\text{corr}$ versus c_B, at constant c_H. The intercept of this plot is a conditional constant, which depends on c_H.

$$E_{OB\alpha} = E_{OB} + gc_H d_2 \quad (43)$$

The slope of this plot is

$$\text{SL}(B, c_B)_\alpha = gd_1 \text{ mV/M} \quad (44)$$

Its calculation can be used for checking the theory.

E_{OB} should be calculated from eqn. (43), by subtracting the term $gc_H d_2$. This can be estimated by using the ionic molar conductivities measured in the mixture studied and the necessary interaction coefficients involved. This plot is the most convenient way for the determination of E_{OB} and is introduced for the first time here.

The conditional constant $E_{OB\alpha}$ cannot be used in the function E_B, valid for cells with complex formation. Its use results in a change in the stability constants with $[H^+]$, which may be interpreted as the formation of polynuclear complexes.

The total emf of cell H for small values of w/a. In cell H, a H^+ ion-sensitive indicator electrode is used. For E_H we obtained [cf. eqns. (2), (35a), (35b), (27) (28), (39a) and (39b)]

$$E_H = E_{OH} + g\log c_H - g[D(I) - D(C)] + gc_B d_3 + gc_H d_4 + \text{corr} \quad (45)$$

where

$$d_3 = z_B\tilde{\varepsilon}(H, Y) - \frac{\lambda_B - z_B\lambda_Y}{2.303C(\lambda_A + \lambda_Y)} - z_B t_A\tilde{\varepsilon}(A, Y) + t_Y\tilde{\varepsilon}(B, Y) \quad (46)$$

$$d_4 = \tilde{\varepsilon}(H, Y) - \frac{\lambda_H - \lambda_Y}{2.303C(\lambda_A + \lambda_Y)} - t_A\tilde{\varepsilon}(A, Y) + t_Y\tilde{\varepsilon}(H, Y) \quad (47)$$

Equation (45) can be used for the determination of E_{OH}, in a potentiometric titration where c_H is varied and c_B is kept constant. If we plot the function $E_H - g\log c_H + g[D(I)-D(C)]-\text{corr}$ versus c_H, at constant c_B, the intercept will be a conditional constant which depends on c_B.[20]

$$E_{OH\alpha} = E_{OH} + gc_B d_3 \quad (48)$$

E_{OH} can be calculated from the intercept, by subtracting the term $gc_B d_3$. This can be done by knowing some ionic molar conductivities, measured in the mixture studied, and some interaction coefficients. This is the easiest way to get E_{OH}. The slope of this plot is

$$\text{SL}(H, c_H)_\alpha = gd_4 \quad (49)$$

Its calculation can be used for checking the theory.

Again, the use of the conditional constant E_{OH} in equilibrium studies will result in the variation of the equilibrium constants ($\beta_{p,q,r}$) with c_B. This may be interpreted as the formation of additional polynuclear complexes.

Comparison of the calculated and experimental slope functions. As the experimental slope functions are the results of the real changes of the ion concentrations and the ionic molar conductivities which exist in the transition layer, a comparison of the measured and calculated slopes is a measure of the correctness of the theory presented here.

Slope functions have been measured in the mixtures of $Cd(ClO_4)_2 + HClO_4 + 3$ mol dm^{-3} $NaClO_4$. The slope functions defined below have been studied at different experimental conditions, using both a Cd amalgam and a glass electrode in Mixture 1 and a glass electrode in Mixture 2. The composition of these mixtures was as follows.

Mixture 1: $c_H = 0.025$ mol dm^{-3} is kept constant, $[AY] = 3$ mol dm^{-3} is kept constant, c_B is varied within the range 0–0.180 mol dm^{-3}.

Mixture 2: $c_B = 0.050$ mol dm^{-3} is kept constant, $[AY] = 3$ mol dm^{-3} is kept constant, c_H is varied within the range 0.004–0.100 or 0.200 mol dm^{-3}.

Here, $B = Cd^{2+}$, $Y^- = ClO_4^-$, $AY = NaClO_4$.

(1) The measured slope of the plot $E'_B \equiv E_B - (g/z_B)\log c_B$ versus c_B, at constant c_H, often used in the current practice, resulting in the slope function $\text{SL}(B, c_B)_\beta$, was compared with the calculated one defined by eqn. (52a) below. The result is given in Table 1. This plot is shown in Fig. 1.

In order to prove the usefulness of the presented theory, the study of the total contribution of the Cd^{2+} ions to E_B and E_H was chosen, which is described by the slope functions denoted $\text{SL}(B, c_B)_\beta$ and $\text{SL}(H, c_B)_\beta$ [cf. eqns. (52a) and (57a) below] for cell B and H, respectively. In this chapter, the subscripts will be omitted for simplicity. The mathematical description of these functions is more complicated than that of the slopes denoted with the subscripts α. However, this choice was made because the corresponding plots have belonged to the standard methods used in emf studies until now.

For the graphical study of these slope functions, the contribution of every independent variable (c_B, c_H and C) to E_B and E_H must be separated. Hence, these functions must be redefined as total differentials. The functions for the total cell emf, redefined as total differentials in terms of the integrals of the partial derivatives of the independent variables, are given by eqn. (50) for E_B and by eqn. (56a) for E_H. Hence, we have for the

Table 1. Survey of the calculated and measured slopes in mV $dm^3 mol^{-1}$ for cells B and H with the experimental condition $[Na^+]=3$ mol dm^{-3}, constant, in Mixture 1. The graphical results for the ionic molar conductivities of Table 3 in Part 2,[21] were used. The term corr was neglected.

	Slope SL(B, c_B) cf. eqn. (52a)	Slope SL(H, c_B) cf. eqn. (57a)
$\left(\frac{(g/z_J)\,\partial \log f_J}{\partial c_B}\right)_{c_H}$	$-3.77+23.66=19.89$	$-1.88+21.29=19.41$
$\left(\frac{\partial E_D}{\partial c_B}\right)_{c_H}$	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

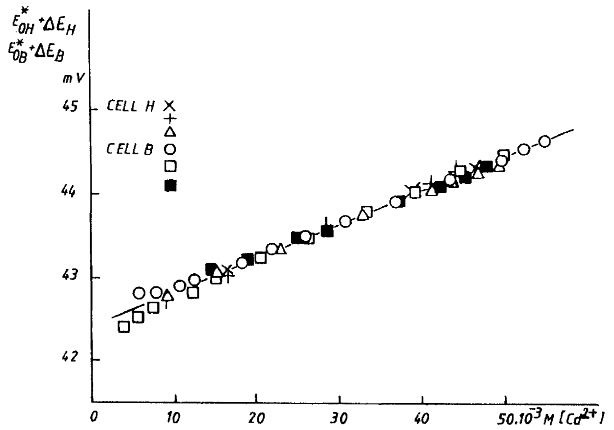

Fig. 1. Determination of the experimental slope function SL(B, c_B) and the conditional constant $E_{OB\beta}=E^x_{OB}+F(B, c_H)$. Moreover, the slope function SL(H, c_B) is determined and the conditional constant $E_{OH\beta}=E^x_{OH}+F(H, c_H)$, for Mixture 1, where $[Na^+]=3$ M, is kept constant. Points with symbols △ 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.

plot in Fig. 1 and Mixture 1

$$E_B = E^x_{OB} + (g/z_B)\log c_B + \int_0^{c_B}\left(\frac{\partial E'_B}{\partial c_B}\right)_{c_H} dc_B + \int_0^{c_H}\left(\frac{\partial E'_B}{\partial c_H}\right)_{c_B=0} dc_H \qquad (50)$$

$$E'_B \equiv E_B - (g/z_B)\log c_B = E_{OB} + \Delta E_B \equiv E^x_{OB} + F(B, c_H) + \int_0^{c_B} SL(B, c_B)\, dc_B \qquad (51)$$

where the slope of this plot is

$$SL(B, c_B) \equiv \left(\frac{\partial E'_B}{\partial c_B}\right)_{c_H} = -g z_B\, dD(I)(z_B^2 + z_B)/2 + g d_1 + \left(\frac{\partial \text{corr}}{\partial c_B}\right)_{c_H} \qquad (52a)$$

For the intercept we obtain a conditional constant

$$E_{OB\beta} = E^x_{OB} + F(B, c_H) \qquad (52b)$$

The involved F function represents the contribution of the H^+ ions to E_B and is given by eqn. (53) in Table 2. Moreover

$$dD(I) = \left(\frac{\partial D(I)}{\partial I}\right)_{c_B, c_H, \ldots} = \frac{0.5115}{2I^{1/2}(1+1.5I^{1/2})^2} \qquad (54)$$

The constant E^x_{OB} is defined in Table 2. It was proved that the last term of eqn. (52a) is neglibible in the present mixture.

The value of $g\,dD(I)$ was calculated as follows. As seen from eqn. (51), the term $\int_0^{c_B}[g\,dD(I)]_{c_H}\,dc_B$ appears there. The value of this integral was estimated by graphical integration for several mixtures. For Mixture 1 we obtained

$$\int_0^{c_B}[g\,dD(I)]_{c_H}\,dc_B = 0.63 c_B \text{ mV} \qquad (55)$$

The derivative of eqn. (55), with respect to c_B, gives $g\,dD(I) = 0.63$ mV $dm^3 mol^{-1}$.

(2) Similarly, the measured slope of the plot $E'_H \equiv E_H - g\log c_H$ versus c_B, at constant c_H, in Mixture 1, results in the slope function SL(H, c_B), was compared with the calculated one defined by eqn. (57a). The result is given in Table 1. This plot is presented in Fig. 1. For this plot we have

$$E_H = E^x_{OH} + g\log c_H + \int_0^{c_H}\left(\frac{\partial E'_H}{\partial c_H}\right)_{c_B} dc_H + \int_0^{c_B}\left(\frac{\partial E'_H}{\partial c_B}\right)_{c_H=0} dc_B \qquad (56a)$$

$$E'_H \equiv E_H - g\log c_H = E_{OH} + \Delta E_H \equiv E^x_{OH} + F(H, c_H) + \int_0^{c_B} SL(H, c_B)\, dc_B \qquad (56b)$$

Table 2. Survey of the functions F appearing in the conditional constants $E_{OB\beta}$ and $E_{OH\beta}$, moreover, the functions E^{x}_{OB} and E^{x}_{OH}, at $[A^+] = C$ M, constant.

$$F(\mathrm{B}, c_H) \equiv \int_0^{c_H} \left(\frac{\partial E'_B}{\partial c_H}\right)_{c_B=0} dc_H = -z_B \int_0^{c_H} [g\, dD(I)]_{c_B=0}\, dc_H + g d_2 c_H + \int_0^{c_H} \left(\frac{\partial \mathrm{corr}}{\partial c_H}\right)_{c_B=0} dc_H \tag{53}$$

$$F(\mathrm{H}, c_H) \equiv \int_0^{c_H} \left(\frac{\partial E'_H}{\partial c_H}\right)_{c_B} dc_H = -\int_0^{c_H} [g\, dD(I)]_{c_B}\, dc_H + g c_H d_4 + \int_0^{c_H} \left(\frac{\partial \mathrm{corr}}{\partial c_H}\right)_{c_B} dc_H \tag{58}$$

$$F(\mathrm{H}, c_B) \equiv \int_0^{c_B} \left(\frac{\partial E'_H}{\partial c_B}\right)_{c_H=0} dc_B = -\frac{z_B^2 + z_B}{2} \int_0^{c_B} [g\, dD(I)]_{c_H=0}\, dc_B + g c_B d_3 + \int_0^{c_B} \left(\frac{\partial \mathrm{corr}}{\partial c_B}\right)_{c_H=0} dc_B \tag{61}$$

$$E^{x}_{OB} = E_{OB} + f_1(C) \tag{64}$$

$$f_1(C) = -g z_B \int_0^{C} \left(\frac{\partial D(I)}{\partial I}\frac{\partial I}{\partial C}\right)_{c_B, c_H} dC + \int_0^{C} \left(\frac{\partial \mathrm{corr}}{\partial C}\right)_{c_B, c_H} dC + g z_B D(C) \tag{65}$$

$$E^{x}_{OH} = E_{OH} + f_3(C) \tag{66}$$

$$f_3(C) = -g \int_0^{C} \left(\frac{\partial D(I)}{\partial I}\frac{\partial I}{\partial C}\right)_{c_B, c_H} dC + \int_0^{C} \left(\frac{\partial \mathrm{corr}}{\partial C}\right)_{c_B, c_H} dC + g D(C) \tag{67}$$

where the slope of this point is

$$\mathrm{SL}(\mathrm{H}, c_B) \equiv \left(\frac{\partial E'_H}{\partial c_B}\right)_{c_H} = -(z_B^2 + z_B) g\, dD(I)/2 + g d_3 + \left(\frac{\partial \mathrm{corr}}{\partial c_B}\right)_{c_H}. \tag{57a}$$

For the intercept we have

$$E_{OH\beta} = E^{x}_{OH} + F(\mathrm{H}, c_H) \tag{57b}$$

The involved F function represents the contribution of the H^+ ions to E_H and is given by eqn. (58) in Table 2. It was proved that the last term of eqn. (57a) is negligible in this mixture. The constant E^{x}_{OH} is defined in Table 2.

(3) The measured slope of the plot $E'_H \equiv E_H - g \log c_H$ versus c_H, at constant c_B, in Mixture 2, was compared with the calculated one defined by eqn. (60a), denoted SL(H, c_H). The result is shown in Table 3. This plot is given in Fig. 2. This plot is based on the following potential functions

$$E'_H \equiv E_H - g \log c_H = E_{OH} + \Delta E_H \equiv E^{x}_{OH} + F(\mathrm{H}, c_B) + \int_0^{c_H} \mathrm{SL}(\mathrm{H}, c_H)\, dc_H \tag{59}$$

where the slope of this plot is

$$\mathrm{SL}(\mathrm{H}, c_H) \equiv \left(\frac{\partial E'_H}{\partial c_H}\right)_{c_B} = -g\, dD(I) + g d_4 + \left(\frac{\partial \mathrm{corr}}{\partial c_H}\right)_{c_B} \tag{60a}$$

For the intercept we have

$$E_{OH\beta} = E^{x}_{OH} + F(\mathrm{H}, c_B) \tag{60b}$$

The involved F function represents the contribution of the $B^{z(B)+}$ ions to E_H and is given by eqn. (61) in Table 2. The last term in eqn. (60a) is negligible in this mixture, and the value of $g\, dD(I)$ was estimated as before. Hence, we obtained

$$\int_0^{c_H} [g\, dD(I)]_{c_B}\, dc_H = 0.62 c_H \tag{62}$$

and consequently, $g\, dD(I) = 0.62$ mV dm^3 (mol H^+)$^{-1}$.

(4) The slope of the plot $E'_B \equiv E_B - (g/z_B) \log c_B$ versus c_H, at constant c_B, in Mixture 2, giving the slope function SL(B, c_H), defined by eqn. (63) below, was calculated. The result is given in Table 3. For this slope, we have

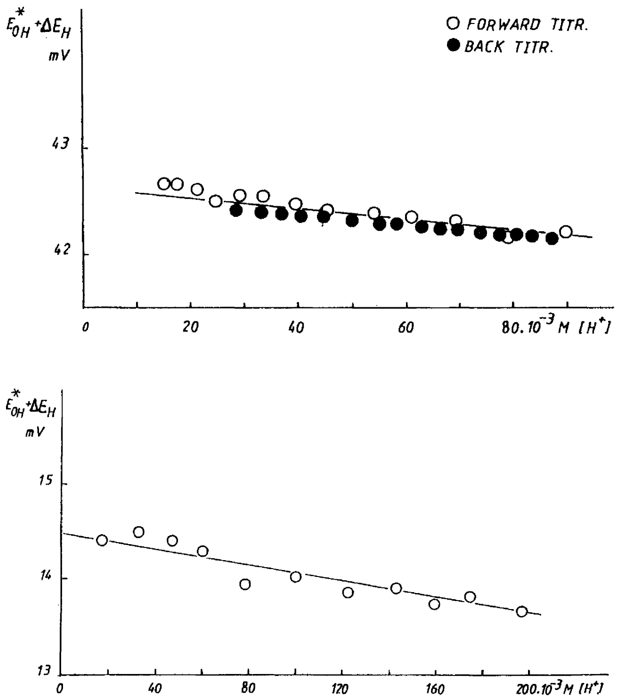

Fig. 2. Determination of the experimental slope function SL(H, c_H) and the conditional constant $E_{OH\beta} = E^{x}_{OH} + F(\mathrm{H}, c_B)$, for Mixture 2, where $[Na^+] = 3$ M is kept constant.

Table 3. Survey of the calculated and measured slopes in mV $dm^3\ mol^{-1}$ for cells H and B with the experimental condition $[Na^+]=3$ mol dm^{-3}, constant, in Mixture 2. The ionic molar conductivities, given in Table 4 in Part 2,[21] 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. eqn. (60a)	Slope SL(B, c_H) cf. eqn. (63)
$\left(\frac{(g/z_J)\,\partial \log f_J}{\partial c_H}\right)_{c_B}$	$-0.62+10.65=10.03$	$-1.24+11.83=10.59$
$\left(\frac{\partial E_D}{\partial c_H}\right)_{c_B}$	-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	

the following potential function

$$SL(B, c_H) \equiv \left(\frac{\partial E'_B}{\partial c_H}\right)_{c_B} = -gz_B\, dD(I) + gd_2 + \left(\frac{\partial \text{corr}}{\partial c_H}\right)_{c_B} \qquad (63)$$

The last term is negligible, again, in the present mixture.

The ionic molar conductivities, which are necessary for the calculation of the slope functions in question, were measured in the mixtures $HClO_4$–$Cd(ClO_4)_2$–$NaClO_4$ (in Mixture 1 and Mixture 2, as given in Tables 3 and 5 in Part 2, to be published), at $[Na^+]=3$ M, is kept constant, by accurate conductivity measurements. Moreover, the value $\Lambda[Cd(ClO_4)_2]$ was determined in the range 0–1.5 M $Cd(ClO_4)_2$. The anionic transport numbers of some electrolytes often used in emf measurements, as well as the molar conductivities of some pure electrolytes often used as ionic media in emf measurements, are presented in Tables 4 and 5, respectively.

Table 4. Survey of the anionic transport numbers[22a] for some electrolytes often used in emf measurements.

Electrolyte	Concentration range/mol kg^{-1}	$t_Y{}^-$ (anionic)
$HClO_4$	0.100–3.47_5	0.17 (3.5–2.5 mol kg^{-1})
		0.16 (2.5–1.5 mol kg^{-1})
		0.15 (1.5–0.1 mol kg^{-1})
$NaClO_4$	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

Table 5. The molar conductivities of some pure electrolytes[22b] often used as ionic medium in emf measurements, in S cm^2 (g mol)$^{-1}$.

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

Table 6. Survey of some interaction coefficients on the molar ($\bar{\varepsilon}$) nd the molal (ε) scale.

	$\bar{\varepsilon}$ $\frac{dm^3 \text{ solution}}{\text{mol solute}}$	Ref.	ε $\frac{\text{kg solvent}}{\text{mol solute}}$	Ref.
$NaClO_4$			0.03	23
$LiClO_4$			0.34	10
$Ca(ClO_4)_2$			0.27	14
$Mg(ClO_4)_2$			0.33	14
$NaHCO_3$	0.01	23		
$HClO_4$	0.18	[a]	0.14	14
$Cd(ClO_4)_2$	0.40		0.32	[b]
$Zn(ClO_4)_2$	0.38	[a]	0.30	11
$Pb(ClO_4)_2$	0.24	[a]	0.15	14
$Cu(ClO_4)_2$	0.39	[a]	0.32	14
$Fe(ClO_4)_3$			0.56	14

[a]Recalculated by the author from the corresponding ε values. [b]Determined by the author.

Some useful interaction coefficients can be found in Table 6.

Emf cells where $[Y^-]=C$ M, is kept constant

In this section the calculation of the total potential anomalies (ΔE_B and ΔE_H) and the total cell emf E_B and E_H is presented for emf cells containing a mixture of strong electrolytes with a liquid junction of the type

$$AY\,|\,HY + BY_{z(B)} + AY$$

at the experimental condition $[Y^-]=C$ M, is kept constant.

The composition of the test solution studied can be given as follows.

TS2 ($x=1$)

$c_B = [B^{z(B)+}] = [BY_{z(B)}]$ M

$c_H = [H^+] = [HY]$ M

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

$c_A = [A^+] = C - z_B c_B - c_H$ M

and $I = C + c_B(z_B^2 - z_B)/2$

The total emf of cell B for small values of w/a. The total cell emf E_β is defined by eqn. (2). For E_D we obtained

$$E_D \cong -gF_0[c_B(\lambda_B - z_B\lambda_A) + c_H(\lambda_H - \lambda_A)] \quad (68)$$

where F_0 is given by eqn. (35b). For the calculation of E_{Df}, the deductions yield

$$\phi_1(x) = x[z_B c_B(\lambda_A - z_B\lambda_B) + c_H(\lambda_A - \lambda_H)] + C(\lambda_Y - \lambda_A) \quad (69)$$

$$\phi_2 = 0 \quad (70)$$

$$\theta_1 = -C\lambda_Y[\tilde{\varepsilon}(B, Y)c_B + \tilde{\varepsilon}(H, Y)c_H - \tilde{\varepsilon}(A, Y)(z_B c_B + c_H)] \quad (71)$$

$$E_{Df} \cong \text{corr} + gt_Y[\tilde{\varepsilon}(B, Y)c_B + \tilde{\varepsilon}(H, Y)c_H - \tilde{\varepsilon}(A, Y)(z_B c_B + c_H)] \quad (72)$$

where t_Y is defined by eqn. (39b). On the basis of these functions, eqn. (40) is obtained for the total cell emf E_B. In this equation, the terms d_1 and d_2 have the following values

$$d_1 = -\frac{\lambda_B - z_B\lambda_A}{2.303C(\lambda_A + \lambda_Y)} + t_Y[\tilde{\varepsilon}(B, Y) - \tilde{\varepsilon}(A, Y)z_B] \quad (73)$$

$$d_2 = -\frac{\lambda_H - \lambda_A}{2.303C(\lambda_A + \lambda_Y)} + t_Y[\tilde{\varepsilon}(H, Y) - \tilde{\varepsilon}(A, Y)] \quad (74)$$

The constant E_{OB} can be determined in the same way as discussed in the previous section.

For the total emf of cell H and for small values of w/a eqn. (45) is valid. In this cell

$$d_3 = d_1 \quad (75)$$

$$d_4 = d_2 \quad (76)$$

On the basis of eqn. (45), the constant E_{OH} can be determined, as described in the previous section.

In order to check the usefulness of the equations obtained, the calculated slopes SL(H, c_B), SL(B, c_B), SL(H, c_H) and SL(B, c_H) were compared with some measured ones, in the mixtures of $Cd(ClO_4)_2$–$HClO_4$–$NaClO_4$, as was done earlier. Two mixtures were studied with the following compositions:

Mixture 1: $c_H = 0.025$ mol dm^{-3} is kept constant, c_B is varied within the range 0–0.1 mol dm^{-3}, X mol dm^{-3} AY is the anionic medium at the experimental condition, $[Y^-] = 3$ mol dm^{-3} is kept constant.

Mixture 2: $c_B = 0.05$ mol dm^{-3} is kept constant, c_H is varied within the range 0.003–0.1 mol dm^{-3}, X′ mol dm^{-3} AY is the experimental condition, $[Y^-] =$ 3 mol dm^{-3} is kept constant.

The results of this comparison are given in Tables 7 and 8. The measured slope function SL(H, c_B) is given in Fig. 3, and SL(H, c_H) in Fig. 4. The necessary ionic molar conductivities will be published in Part 3. For the slopes in question, the following potential functions are valid.

(1) For the plot $E'_H \equiv E_H - g \log c_H$ versus c_B, at constant c_H, we have, for the slope

$$\text{SL}(H, c_B) \equiv \left(\frac{\partial E'_H}{\partial c_B}\right)_{c_H} = -g\,\mathrm{d}D(I)(z_B^2 - z_B)/2 + gd_3 + \left(\frac{\partial \text{corr}}{\partial c_B}\right)_{c_H} \quad (77)$$

The intercept of this plot results in a conditional constant

$$E_{OH\beta} = E^x_{OH} + F(H, c_H) \quad (78)$$

where the function $F(H, c_H)$ is given in Table 9. The constant E^x_{OH} is defined in Table 2, the term $g\,\mathrm{d}D(I)$ by eqn. (55).

(2) For the plot $E'_B \equiv E_B - (g/z_B) \log c_B$ versus c_B, at constant c_H, we have for the slope

$$\text{SL}(B, c_B) \equiv \left(\frac{\partial E'_B}{\partial c_B}\right)_{c_H} = -gz_B\,\mathrm{d}D(I)(z_B^2 - z_B)/2 + gd_1 + \left(\frac{\partial \text{corr}}{\partial c_B}\right)_{c_H} \quad (80)$$

The intercept of this plot results in a conditional constant

$$E_{OB\beta} = E^x_{OB} + F(B, c_H) \quad (81)$$

where the function $F(B, c_H)$ is given in Table 9.

(3) For the plot $E'_H \equiv E_H - g \log c_H$ versus c_H, at constant c_B, we have, for the slope

$$\text{SL}(H, c_H) \equiv \left(\frac{\partial E'_H}{\partial c_H}\right)_{c_B} = gd_4 = gd_2 \equiv \left(\frac{\partial E'_B}{\partial c_H}\right)_{c_B} \equiv \text{SL}(B, c_H) \quad (83)$$

The intercept of this plot results in a conditional constant

$$E_{OH\beta} = E^x_{OH} + F(H, c_B) \quad (84)$$

where the function $F(H, c_B)$ is given in Table 9. This function gives the potential contribution of the $B^{z(B)+}$ ions to E_H.

(4) For the plot $E'_B \equiv E_B - (g/z_B) \log c_B$ versus c_H, at constant c_B, we have, for the slope

$$\text{SL}(B, c_H) \equiv \left(\frac{\partial E'_B}{\partial c_H}\right)_{c_B} = gd_2 + \left(\frac{\partial \text{corr}}{\partial c_H}\right)_{c_B} \quad (86)$$

The intercept of this plot results in a conditional constant

$$E_{OB} = E^x_{OB} + F(B, c_B) \quad (87)$$

where the function $F(B, c_B)$ is given in Table 9. This function gives the potential contribution of the $B^{z(B)+}$ ions to E_B.

Emf cells where $I = C$ M, is kept constant

The calculation of the total potential anomalies (ΔE_B and ΔE_H) and the total cell emf E_B and E_H is presented for emf cells containing mixtures of strong electrolyes with the liquid junction type defined before, at the experimental condition $I = C$ M, is kept constant.

Table 7. Survey of the calculated and measured slopes in mV dm^3 mol^{-1} for cells B and H with the experimental condition $[ClO_4^-] = 3$ mol dm^{-3}, constant, in Mixture 1. The term 'corr' is neglected.

	Slope SL(H, c_B) cf. eqn. (77)	Slope SL(B, c_B) cf. eqn. (80)	
$\left(\frac{\partial(g \log f_H)}{\partial c_B}\right)_{c_H}$	−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
$\left(\frac{\partial(E_{Df} - \text{corr})}{\partial c_B}\right)_{c_H}$	11.64	$\left(\frac{\partial(E_{Df} - \text{corr})}{\partial c_B}\right)_{c_H}$	11.64
Calculated total slope:	18.10	Calculated total slope:	17.52
Experimental slope:	18.4	Experimental slope:	

Table 8. Survey of the calculated and measured slopes in mV dm^3 mol^{-1} for cells B and H with the experimental condition $[ClO_4^-] = 3$ mol dm^{-3}, constant, in Mixture 2. The term 'corr' is neglected.

	Slope SL(H, c_H) cf. eqn. (83)	Slope SL(B, c_H) cf. eqn. (86)	
$\left(\frac{\partial(g \log f_H)}{\partial c_H}\right)_{c_B}$	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
$\left(\frac{\partial(E_{Df} - \text{corr})}{\partial c_H}\right)_{c_B}$	5.00	$\left(\frac{\partial(E_{Df} - \text{corr})}{\partial c_H}\right)_{c_B}$	5.00
Calculated total slope:	−21.43	Calculated total slope:	−21.43
Experimental slope:	−21.8	Experimental slope:	

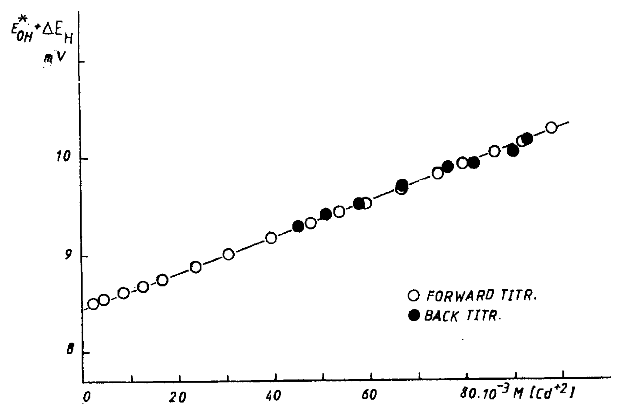

Fig. 3. Determination of the experimental slope function SL(H, c_B) and the conditional constant $E_{OH\beta} = E^{x}_{OH} + F(H, c_H)$, for Mixture 1, where $[ClO_4^-] = 3$ M is kept constant.

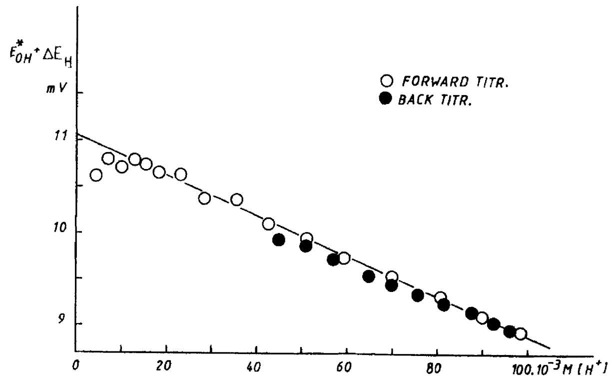

Fig. 4. Determination of the experimental slope function SL(H, c_H) and the conditional constant $E_{OH\beta} = E^{x}_{OH} + F(H, c_B)$, for Mixture 2, where $[ClO_4^-] = 3$ M is kept constant.

Table 9. Survey of functions F appearing in the expressions for the conditional constants $E_{OB\beta}$ and $E_{OH\beta}$ at $[Y^-]=C$ M constant.

$$F(H, c_H) \equiv \int_0^{c_H} \left(\frac{\partial E'_H}{\partial c_H}\right)_{c_B} dc_H = gc_H d_4 \quad (79)$$

$$F(B, c_H) \equiv \int_0^{c_H} \left(\frac{\partial E'_B}{\partial c_H}\right)_{c_B=0} dc_H = gd_2 c_H \quad (82)$$

$$F(H, c_B) \equiv \int_0^{c_B} \left(\frac{\partial E'_H}{\partial c_B}\right)_{c_H=0} dc_B = -\frac{z_B^2 - z_B}{2} \int_0^{c_B} [g\, dD(I)]_{c_H=0}\, dc_B + gc_B d_3 + \int_0^{c_B} \left(\frac{\partial \text{corr}}{\partial c_B}\right)_{c_H=0} dc_B \quad (85)$$

$$F(B, c_B) \equiv \int_0^{c_B} \left(\frac{\partial E'_B}{\partial c_B}\right)_{c_H} dc_B = -\frac{z_B(z_B^2 - z_B)}{2} \int_0^{c_B} g\, dD(I)\, dc_B + gd_1 c_B + \int_0^{c_B} \left(\frac{\partial \text{corr}}{\partial c_B}\right)_{c_H} dc_B \quad (88)$$

The composition of the test solution studied can be given as

TS2 $(x=1)$

$c_B = [B^{z(B)+}] = [BY_{z(B)}]$ M

$c_H = [H^+] = [HY]$ M

$c_A = C - c_H - c_B(z_B^2 + z_B)/2$ M AY

$c_Y = C + z_B c_B - c_B(z_B^2 + z_B)/2$ M

The total emf of cell B with an amalgam indicator electrode and for small values of w/a. The total cell emf E_B is defined by eqn. (2). For its calculation, we obtained

$$E_D \cong -gF_0[c_B(\lambda_B - z_B\lambda_Y) + c_H(\lambda_H - \lambda_A) + c_B(\lambda_Y - \lambda_A)(z_B^2 + z_B)/2] \quad (89)$$

For the calculation of E_{Df}, the deductions resulted in

$$\phi_1(x) = 0, \quad \text{because } I = C\,\text{M, constant} \quad (90)$$

$$\phi_2 = [z_B c_B - c_B(z_B^2 + z_B)/2] \times \{c_B\lambda_B\bar{\varepsilon}(B, Y) + c_H\lambda_H\bar{\varepsilon}(H, Y) - [c_H + c_B(z_B^2 + z_B)/2]\bar{\varepsilon}(A, Y)(\lambda_A - \lambda_Y) - \lambda_Y[c_H\bar{\varepsilon}(H, Y) + c_B\bar{\varepsilon}(B, Y)]\} \quad (91)$$

$$\theta_1 = C\lambda_A\bar{\varepsilon}(A, Y)[z_B c_B - c_B(z_B^2 + z_B)/2] - C\lambda_Y \times \{c_H\bar{\varepsilon}(H, Y) + c_B\bar{\varepsilon}(B, Y) - \bar{\varepsilon}(A, Y) \times [c_H + c_B(z_B^2 + z_B)/2]\} \quad (92)$$

$$E_{Df} \cong -gt_A\bar{\varepsilon}(A, Y)[z_B c_B - c_B(z_B^2 + z_B)/2] + gt_Y \times \{\bar{\varepsilon}(H, Y)c_H + c_B\bar{\varepsilon}(B, Y) - \bar{\varepsilon}(A, Y) \times [c_H + c_B(z_B^2 + z_B)/2]\} \quad (93)$$

On the basis of these functions, E_B can be obtained according to eqn. (40), where $D(I) - D(C) = 0$. The functions d_1 and d_2 are defined as follows:

$$d_1 = \bar{\varepsilon}(B, Y)(1 - z_B)/2 - [\lambda_B - z_B\lambda_Y + (\lambda_Y - \lambda_A)(z_B^2 + z_B)/2]/[2.303C(\lambda_A + \lambda_Y)] - t_A\bar{\varepsilon}(A, Y)(z_B - z_B^2)/2 + t_Y[\bar{\varepsilon}(B, Y) - \bar{\varepsilon}(A, Y)(z_B^2 + z_B)/2] \quad (94)$$

$$d_2 = -(\lambda_H - \lambda_A)/[2.303C(\lambda_A + \lambda_Y)] + t_Y[\bar{\varepsilon}(H, Y) - \bar{\varepsilon}(A, Y)] \quad (95)$$

The constant E_{OB} can be determined on the basis of eqn. (40), as described earlier, here.

For the total emf of cell H, with a H^+-sensitive indicator electrode and for small values of w/a, we have eqn. (45), where $D(I) - D(C) = 0$. In this cell, the functions d_3 and d_4 are defined as follows

$$d_3 = \bar{\varepsilon}(H, Y)(z_B - z_B^2)/2 - [\lambda_B - z_B\lambda_Y + (\lambda_Y - \lambda_A)(z_B^2 + z_B)/2]/[2.303C(\lambda_A + \lambda_Y)] - t_A\bar{\varepsilon}(A, Y)(z_B - z_B^2)/2 + t_Y[\bar{\varepsilon}(B, Y) - \bar{\varepsilon}(A, Y)(z_B^2 + z_B)/2] \quad (96)$$

$$d_4 = d_2 \quad (97)$$

because the term $\log f_H$ is independent of c_H. The constant E_{OH} can be determined as described earlier.

The measured and calculated slope functions were compared in $Cd(ClO_4)_2$–$HClO_4$–$NaClO_4$ mixtures. The compositions of Mixtures 1 and 2 are given in Tables 10 and 11, respectively. The result of the comparison for the slope functions SL(H, c_B) and SL(B, c_B) is given in Table 10, for SL(H, c_H) and SL(B, c_H) in Table 11. The experimental slope functions SL(H, c_B) and SL(H, c_H) are presented in Figs. 5 and 6, respectively. The necessary ionic molar conductivities will be published in Part 4.

For the slopes mentioned, the following potential functions are valid.

(1) For the plot $E'_H \equiv E_H - g\log c_H$ versus c_B, at constant c_H, we have, for the slope

$$\text{SL}(H, c_B) \equiv \left(\frac{\partial E'_H}{\partial c_B}\right)_{c_H} = gd_3 \quad (98)$$

and the intercept is

$$E_{OH\alpha} = E_{OH} + gd_4 c_H \quad (99)$$

(2) For the plot $E'_B \equiv E_B - (g/z_B)\log c_B$ versus c_B, at constant c_H, we have, for the slope

$$\text{SL}(B, c_B) \equiv \left(\frac{\partial E'_B}{\partial c_B}\right)_{c_H} = gd_1 \quad (100)$$

and the intercept is

$$E_{OB\alpha} = E_{OB} + gd_2 c_H \quad (101)$$

Table 10. Survey of the calculated and measured slopes in mV M^{-1}, for cells H and B, at the experimental condition $I=3$ M, constant, in Mixture 1: $[HClO_4]=0.025$ M, constant, $0 \leqslant [Cd(ClO_4)_2] \leqslant 0.1$ M and X M $NaClO_4$.

	Slope SL(H, c_B) cf. eqn. (98)	Slope SL(B, c_B) cf. eqn. (100)	
$\left(\frac{g\,\partial \log f_H}{\partial c_B}\right)_{c_H}$	−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

Table 11. Survey of the calculated and measured slopes in mV M^{-1}, for cells H and B, at the experimental condition $I=3$ M, constant, in Mixture 2: 0.05 M $Cd(ClO_4)_2$, is kept constant, $0.003 \leqslant [HClO_4] \leqslant 0.1$ M and X M $NaClO_4$.

	Slope SL(H, c_H) cf. eqn. (102)	Slope SL(B, c_H) cf. eqn. (104)	
$\left(\frac{g\,\partial \log f_H}{\partial c_H}\right)_{c_B}$	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	Experimental slope:	

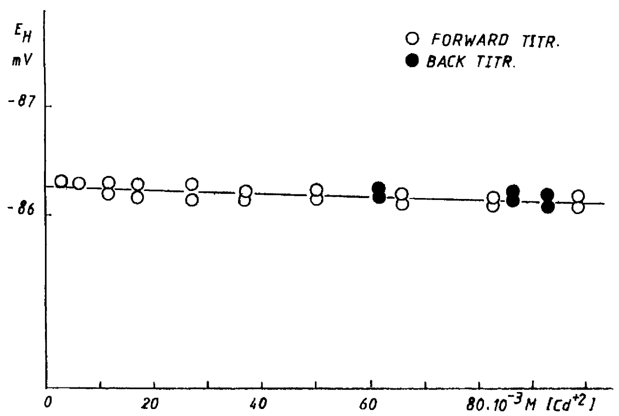

Fig. 5. Determination of the experimental slope function SL(H, c_B) and the conditional constant $E_{OH\alpha}=E_{OH}+gd_4c_H$, for Mixture 1, where $I=3$ M is kept constant.

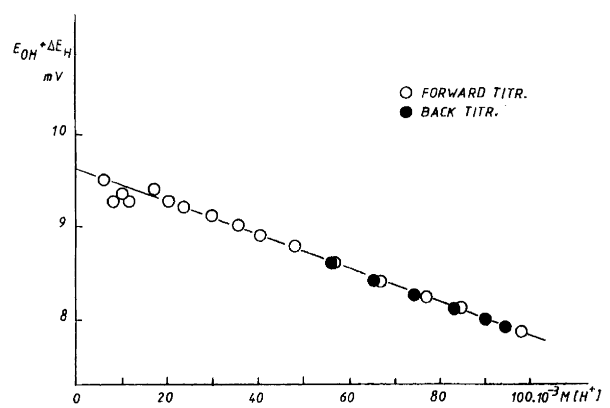

Fig. 6. Determination of the experimental slope function SL(H, c_H) and the conditional constant $E_{OH\alpha}=E_{OH}+gd_3c_B$, for Mixture 2, where $I=3$ M is kept constant.

(3) For the plot $E'_H \equiv E_H - g \log c_H$ versus c_H, at constant c_B, we have, for the slope

$$SL(H, c_H) \equiv \left(\frac{\partial E'_H}{\partial c_H}\right)_{c_B} = gd_4 = gd_2$$

$$\equiv \left(\frac{\partial E'_B}{\partial c_H}\right)_{c_B} \equiv SL(B, c_H) \quad (102)$$

and the intercept is

$$E_{OH\alpha} = E_{OH} + gd_3 c_B \quad (103)$$

(4) For the plot $E'_B \equiv E_B - (g/z_B) \log c_B$ versus c_H, at constant c_B, we have, for the slope

$$SL(B, c_H) \equiv \left(\frac{\partial E'_B}{\partial c_H}\right)_{c_B} = gd_2 \quad (104)$$

and for the intercept

$$E_{OB\alpha} = E_{OB} + gd_1 c_B \quad (105)$$

Experimental details are presented in Part 2 to be published.

Conclusions

The present results clearly show that all ions present in the test solution with concentrations different from those of the bridge solution (C mol dm^{-3} AY) contribute to the potential of every measuring electrode present in the cell.

The composition of the cells shows that the concentrations of the ions of the ionic medium, c_A and c_Y, depend on the concentrations of the potential determining ions, c_B and c_H. This is a unique condition, and is valid only in cells containing the mixtures of strong electrolytes: $HY + BY_{z(B)} + AY$. This condition is not valid in cells with complex formation. This has the result that the different slope functions, determined in cells with strong electrolytes, are not valid in cells with complex formation.

The present results clearly show that the constants of the Nernst equations, E_{OB} and E_{OH}, valid for the total cell emfs, E_B and E_H, are determined in the present practice with systematic errors. The usual plots, used for the determination of the different slope functions, result in conditional constants. From these, the real constants E_{OB} and E_{OH} can be calculated on the basis of conductivity measurements. If we have no equipment for this, the constant E_{OH} should be determined in mixtures of $HY + AY$, in the absence of $B^{z(B)+}$ ions. In the case of E_{OB}, the concentration of the H^+ ions should be only so high that the hydrolysis of the $B^{z(B)+}$ ions is eliminated. The use of conditional constants for E_{OH} and E_{OB} in cells with complex formation may result in the c_B and c_H dependence of the formation constants studied ($\beta_{p,q,r}$), which may be interpreted as formation of polynuclear complexes. The constants E_{OB} and E_{OH} can most easily be determined on the basis of eqns. (40) and (45).

The agreement between the measured and calculated slope functions is good for the different emf cells studied. It means that the chosen conditions for the deduction of the different potential functions are correct. Considering that the upper concentration limit generally used in potentiometric titrations is 0.1 mol dm^{-3} for the metal ions $B^{z(B)+}$, the total potential anomalies ΔE_B can generally be estimated with $\leqslant 0.1$ mV uncertainty. The upper concentration limit for the H^+ ions in potentiometric titrations is ca. 0.05 mol dm^{-3}. This means that the total potential anomalies ΔE_H can in general be estimated with $\leqslant 0.15$ mV uncertainty. The slope functions are linear. It means that the ionic molar conductivities in the transition layer are constant. This was one of the most important conditions for the deduction of the potential functions, valid in cells of constant ionic medium types. The slope functions are valid only in those mixtures where they have been determined. This is the result of the fact that the ionic molar conductivities change very much with the experimental conditions ($[A^+] = C$ M, $[Y^-] = C$ M, $I = C$ M, each of them is kept constant) and they cannot be interchanged.

The experimental slope functions, if they are determined correctly, e.g. $SL(B, c_B)$ at constant level of c_H and at constant $[A^+]$, $[Y^-]$ or I, respectively, are valuable characteristics of the cell. They can be used for checking the theory, developed here, for the calculation of the total potential anomalies. Moreover, the experimental slopes can be used for the estimation of the contributions of the $B^{z(B)+}$ and H^+ ions to E_B and E_H, in cells with complex formation, as it will be shown in Part 6A.

Considering the comparison of the experimental and calculated slope functions, we can see that the cell with the experimental condition that $[Na^+] = 3$ M is kept constant, develops the largest total potential anomalies through the slopes $SL(B, c_B)$ and $SL(H, c_B)$, while the cell with $I = 3$ M kept constant, the smallest one, through the same slopes. Moreover, in cells with $[Na^+] = 3$ M, is kept constant, the slopes $SL(H, c_H)$ and $SL(B, c_H)$ have the smallest values. In cells with the experimental condition $[ClO_4^-] = 3$ M kept constant, the slopes $SL(H, c_H)$ and $SL(B, c_H)$ have the largest value.

The validity of the approximation $\ln[(w/a) + 1] \cong w/a$, for small values of w/a, was checked in solution 1 = 0.1 M $Cd(ClO_4)_2$, 0.025 M $HClO_4$ and X M $NaClO_4$ and in solution 2 = 0.1 M $HClO_4$, 0.050 M $Cd(ClO_4)_2$ and X M $NaClO_4$ at the experimental conditions $[Na^+] =$ 3 M, $[ClO_4^-] = 3$ M and $I = 3$ M kept constant, respectively. The approximation is valid for the solution tested.

For comparison with experimental results, the polarity of the cell should be considered. For cells with poles opposite to those defined here, for cells B and H, the functions E_B and E_H have to be taken with the opposite sign.

If we are to study some complex formation reactions in the cells, at different experimental conditions, the experimental constants E_{OB} and E_{OH} are needed. The constants E^x_{OB} and E^x_{OH} include the contribution of the concentration C to E'_B and E'_H, which is not the case in cells with complex formation. There the potential functions E'_B and E'_H are defined in a different way.

If we use a high (ca. 1 M) and constant concentration for the $B^{z(B)+}$ ions, during both the determination of the constant $E_{OH\alpha}$ and the study of the complex formation, the following approximation is valid: $[B^{z(B)+}]=[BY_{z(B)T}]$. In this case, the conditional constant $E_{OH\alpha}$ is constant and it can be used in a cell with the study of complex formation. This is the so-called self-medium method.[24,25]

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