

# Liquid Junction Potential in Potentiometric Titrations. 5. Deduction of the Potential Functions for E.M.F. Cells with Complex Formation and with Liquid Junctions of the Type $AY|AY + BY_{z(B)} + HY + A_yL$

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Equations were derived, in a general form, for the calculation of the total cell e.m.f. for cells containing liquid junctions of constant ionic medium type, where formation of strong complexes takes place. The total cell e.m.f. is:

$$E_j = E_{Oj} + (g/z_j) \log c_j f_{jTS2} + E_D + E_{Df}$$

Here,  $(A^+, Y^-)$  is the ionic medium, J is the potential-determining ion,  $B^{z(B)+}$  is the central metal ion,  $E_D$  is the ideal diffusion potential (Henderson term),  $E_{Df}$  is the contribution of the activity coefficients to the diffusion potential,  $A_yL$  is the ligand.  $f_{jTS2}$  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  $0.5 \leq C \leq 3 \text{ mol dm}^{-3}$ . The charge of the metal ion  $B^{z(B)+}$  should be  $\leq 3$ .

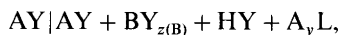
The total potential anomalies in the cells are

$$\Delta E_j = (g/z_j) \log f_{jTS2} + E_D + E_{Df}$$

## 1. Introduction

This work is Part 5 of this series, the earlier parts having been presented in Refs. 1–4. Deduction of the potential functions for e.m.f. cells with liquid junctions of constant ionic medium type and containing mixtures of strong electrolytes was presented in Ref. 1. Definitions and symbols used throughout this series were also given in Ref. 1. Determinations of the ionic molar conductivities in the different e.m.f. cells were presented in Refs. 2–4.

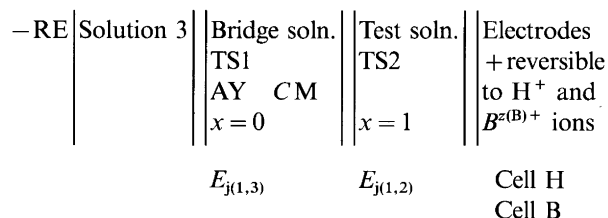
In the present part, potential functions will be derived for the calculation of the total cell e.m.f. of cells with liquid junctions of the type



where formation of strong complexes takes place between the components.

## 2. The composition of e.m.f. cells with complex formation

The cells studied can be described as follows.



Here,  $E_{j(1,3)}$  and  $E_{j(1,2)}$  are the classical liquid junction potential terms, defined by eqn. (8) in Ref. 1 as

$$E_j = -g \int_{TS1}^{TS2} \sum_j \frac{t_j^*}{z_j} d \log(c_j^* f_j) = E_D + E_{Df} \quad (1a)$$

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. Hence, we have

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

The total cell e.m.f. for cells B and H is

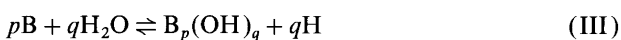
$$E_B = E_{OB} + (g/z_B) \log b f_{BTS2} + E_D + E_{Df} \quad (2)$$

$$E_H = E_{OH} + g \log h f_{HTS2} + E_D + E_{Df} \quad (3)$$

Here,  $E_{OB}$  and  $E_{OH}$  are experimental constants. RE denotes the reference electrode.

We assume that reactions (I)–(III) take place in the

cells, containing the reacting compounds  $\text{BY}_{z(\text{B})} + \text{HY} + \text{A}_y\text{L}$  and the ionic medium  $\text{AY}$ .



Here,  $p, q, r$  are integers. Ionic charges in the chemical formulas are generally omitted for simplicity.

In reactions (II) and (III) the reaction product will be denoted as (i)  $\text{N}_j^{z(\text{N}j)-}$ , if it is a negatively charged metal containing complex ion, (ii)  $\text{P}_i^{z(\text{P}i)+}$ , if it is a positively charged metal containing complex ion. Uncharged species cannot be considered in this theory.

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

$$h = [\text{H}^+]M = H_T^+ - \sum_{p,q,r} q\beta_{p,q,r}b^p h^q l^r \quad (4)$$

the equilibrium concentration of the  $\text{H}^+$  ions, where  $H_T^+$  is the total, analytical concentration of the  $\text{H}^+$  ions in  $M$ ,  $\beta_{p,q,r}$  is the equilibrium constant for the formation reaction of the complexes (conditional, so called concentration constant),

$$l = [\text{L}^{y-}]M = L_T - \sum_{p,q,r} r\beta_{p,q,r}b^p h^q l^r \quad (5)$$

the equilibrium concentration of the ligand, where  $L_T = [\text{A}_y\text{L}]M$ , the total, analytical concentration of the ligand used,

$$\sum_k l_k = \sum_k [\text{L}_k^{z(\text{L}k)-}] = \sum_{q,r} \beta_{q,r} h^q l^r \quad \text{with } k \geq 2 \quad (6)$$

equilibrium concentration of the species of the protolysis of the acid  $\text{H}_y\text{L}$  with  $k \geq 2$ ,

$$b = [\text{B}^{z(\text{B})+}]M = B_T - \sum_{p,q,r} p\beta_{p,q,r}b^p h^q l^r \quad (7)$$

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

$$\begin{aligned} \sum_j n_j &= \sum_j [\text{N}_j^{z(\text{N}j)-}]M \\ &= \sum_{p,q,r} \beta_{p,q,r}b^p h^q l^r, \quad \text{with } j = 1, 2, \dots \end{aligned} \quad (8)$$

equilibrium concentration of the complex ions noted,

$$\begin{aligned} \sum_i p_i \sum_i [\text{P}_i^{z(\text{P}i)+}]M \\ = \sum_{p,q,r} \beta_{p,q,r}b^p h^q l^r, \quad \text{with } i = 1, 2, \dots \end{aligned} \quad (9)$$

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

Potentiometric titrations are generally carried out at three different experimental conditions: (i)  $[\text{A}^+] = \text{CM}$ , is kept constant, (ii)  $[\text{Y}^-] = \text{CM}$ , is kept constant, and (iii)  $l = \text{CM}$ , 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  $\text{A}_y\text{L}$  is used for the increase of the pH of the test solution

$$c_A = [\text{AY}] + yL_T \quad (10)$$

$$c_Y = [\text{AY}] + z_B B_T + \text{HY}_T = c_A - yL_T + z_B B_T + \text{HY}_T \quad (11)$$

If  $[\text{A}^+] = \text{CM}$ , is kept constant,

$$c_Y = C - yL_T + z_B B_T + \text{HY}_T = C + \Delta c_Y \quad (12)$$

If  $[\text{Y}^-] = \text{CM}$ , is kept constant,

$$c_A = C - \text{HY}_T - z_B B_T + yL_T = C + \Delta c_A \quad (13)$$

If  $I = \text{CM}$ , is kept constant, we have for the ionic strength

$$I \equiv C = (1/2)(\text{HY}_T + c_A + c_Y + z_B^2 B_T + y^2 L_T) \quad (14)$$

Inserting  $c_Y$  from the left-hand side of eqn. (11) into eqn. (14), and also  $c_A$  from eqn. (10), we have

$$I \equiv C = \text{HY}_T + [\text{AY}] + \frac{z_B^2 + z_B}{2} B_T + \frac{y^2 + y}{2} L_T \quad (15)$$

From eqn. (15) we can get for the concentration of the ionic medium to be used

$$[\text{AY}] = C - \text{HY}_T - \frac{z_B^2 + z_B}{2} B_T - \frac{y^2 + y}{2} L_T \quad (16)$$

According to eqn. (10) we have

$$\begin{aligned} c_A &= C + yL_T - \frac{y^2 + y}{2} L_T - \text{HY}_T \\ &\quad - \frac{z_B^2 + z_B}{2} B_T = C + \Delta c_A \end{aligned} \quad (17)$$

and from eqn. (11)

$$c_Y = C + z_B B_T - \frac{z_B^2 + z_B}{2} B_T - \frac{y^2 + y}{2} L_T = C + \Delta c_Y \quad (18)$$

In the equations above [cf. eqns. (12)–(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  $\text{HY}_T = [\text{HY}]M$  is the total, analytical concentration for the strong acid used.

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

The equilibrium concentrations depend upon each other through the equilibrium constants  $\beta_{p,q,r}$  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 either be measured, e.g. with the help of an amalgam

electrode (Cell B), or calculated as given in the composition of the cell. The different equilibrium concentrations, such as  $l$ ,  $l_k$ ,  $n_j$ , and  $p_i$  with  $k = 2, 3, 4, \dots$ ,  $j = 1, 2, 3, \dots$ ,  $i = 1, 2, 3, \dots$  can be calculated from the corresponding equilibrium constants determined at the preliminary interpretation of the data, using an incomplete  $\Delta E_j$  function, and from the known, actual total concentrations, as can  $h$  and  $b$ . Preliminary equilibrium constants can be obtained by standard methods<sup>5,6</sup> or by a suitable computer program.<sup>7</sup> The total, analytical concentrations can be calculated on the basis of the mixing rule.

The concentration terms  $\Delta c_Y$  and  $\Delta c_A$  appear due to the changes in the composition of the 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. eqns. (10)–(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,  $c_Y$ ,  $c_A$ , 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,  $\Delta c_Y$ . Hence,  $\Delta E_j$  will be the function of the changes in the composition of the ionic medium,  $\Delta c_Y$ ,  $\Delta c_A$ .

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 will be discussed in chapter 3. 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,  $\Delta E_j$  depends on the experimental conditions chosen and also the type of chemical processes taking place in the test solution.

### 3. Deduction of the potential functions

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,  $CMAY$  (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 eqns. (I)–(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

$$c_j^* = [c_j^*] = xc_{jTS2} + (1-x)c_{jTS1} \quad (19)$$

Hence, we have  $b^* = xb$ ,  $h^* = xh$  and  $l^* = xl$ .

Consequently, the equilibrium concentration of the complexes in the transition layer,  $[cp_x^*]$ , with the general composition  $H_pB_qL_r$ , 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  $\beta_{p,q,r}$  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  $\beta_{p,q,r}$  values found are extrapolated to zero ionic strength.<sup>8</sup> Hence, we can write

$$\begin{aligned} [cp_x^*] &= \beta_{p,q,r} b^{*p} h^{*q} l^{*r} = \beta_{p,q,r} (xb)^p (xh)^q (xl)^r \\ &\equiv \beta_{p,q,r} b^p h^q l^r x^{(p+q+r)} \equiv [cp_x] x^{(p+q+r)} \end{aligned} \quad (20)$$

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

$$\sum_i p_i^* = \sum_i p_i x^{(p+q+r)_i} \equiv \sum_i p_i x^{u_i} \quad (21)$$

$$\sum_j n_j^* = \sum_j n_j x^{(p+q+r)_j} \equiv \sum_j n_j x^{u_j} \quad (22)$$

$$\sum_k l_k^* = \sum_k l_k x^{(p+q+r)_k} \equiv \sum_k l_k x^{u_k} \quad (23)$$

where  $u_i = (p+q+r)_i$  is the sum of the integers in the chemical formula for the species  $P_i^{z_i(p_i)^+}$ ,  $u_j = (p+q+r)_j$  is the same kind of sum for the species  $N_j^{z_j(n_j)^-}$  and  $u_k = (p+q+r)_k$  is the same kind of sum for the species  $L_k^{z_k(l_k)^-}$ .

According to the concentration model suggested above for the transition layer, the mass action law is fulfilled too. Therefore, we can expect very realistic  $\Delta E_j$  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 eqn. (19), again. For example for the experimental condition  $[A^+] = CM$ , constant, we have

$$\begin{aligned} c_A^* &= CM \\ c_Y^* &= C + x(HY_T + z_B B_T - yL_T) \equiv C + x\Delta c_Y \end{aligned} \quad (24)$$

### 4. Calculation of the ideal diffusion potential, $E_D$ , in cells with complex formation

We can rewrite the definition of  $E_D$ , given by eqn. (6) in Ref. 1 as

$$E_D = -g \int_{TS1}^{TS2} \sum_j \frac{t_j^*}{z_j} d \log c_j^* \quad (25a)$$

by making the substitution  $d \log c_j = (1/2.303) d \ln c_j$ . Moreover, we have, for the transport numbers in the

transition layer,  $t_j^*$ , cf. eqn. (12) in Ref. 1

$$t_j^* = \frac{\lambda_j^* c_j^* |z_j|}{\sum_j \lambda_j^* c_j^* |z_j|} \quad (25b)$$

and introducing

$$N = \sum_j \lambda_j c_j^* |z_j| \\ = \sum_j (\lambda_j c_j^* |z_j|)_{\text{cat}} + \sum_j (\lambda_j c_j^* |z_j|)_{\text{an}} \quad (25c)$$

where cat = cation, an = anion.

Considering

$$d \ln c_j^* = dc_j^* / c_j^* \quad (26)$$

the function  $E_D$  can be written as

$$E_D = -(g/2.303) \int_{\text{TS1}}^{\text{TS2}} (1/N) \\ \times \left[ \sum_{\text{cat}} \lambda_{\text{cat}} dc_{\text{cat}}^* - \sum_{\text{an}} \lambda_{\text{an}} dc_{\text{an}}^* \right] \quad (27)$$

Substituting the derivatives of the ion concentrations in the transition layer into eqn. (27), we obtain

$$E_D = -(g/2.303) \int_{\text{TS1},x=0}^{\text{TS2},x=1} (1/N) \\ \times \left[ \lambda_{\text{H}} h + \lambda_{\text{B}} b + \sum_i \lambda_{\text{Pi}} u_i p_i x^{u_i-1} \right. \\ \left. - \lambda_{\text{L}} l - \sum_{k \geq 2} \lambda_{\text{Lk}} u_k c_k x^{u_k-1} \right. \\ \left. - \sum_j \lambda_{\text{Nj}} u_j n_j x^{u_j-1} + \lambda_{\text{A}} dc_{\text{A}}^* - \lambda_{\text{Y}} dc_{\text{Y}}^* \right] dx \quad (28)$$

The last two terms under the integral, in eqn. (28), are concerning the ions of the ionic medium and are different for every experimental condition used out of (i)–(iii). E.g. for  $[A^+] = CM$ , constant,  $\lambda_{\text{A}} dc_{\text{A}}^* = 0$ , and  $-\lambda_{\text{Y}} dc_{\text{Y}}^* = -\lambda \Delta c_{\text{Y}}$ . Similarly, the function  $N$  [cf. eqn. (25c)] should also be expressed in terms of the ion concentrations in the transition layer. This function can always be written in the form

$$N = wx + a + \sum_{k \geq 2} \lambda_{\text{Lk}} |z_{\text{Lk}}| l_k x^{u_k} + \sum_i \lambda_{\text{Pi}} |z_{\text{Pi}}| p_i x^{u_i} \\ + \sum_j \lambda_{\text{Nj}} |z_{\text{Nj}}| n_j x^{u_j} \quad (29a)$$

where for  $[A^+] = CM$  constant, we have

$$w = \lambda_{\text{H}} h + \lambda_{\text{L}} |z_{\text{L}}| l + \lambda_{\text{B}} z_{\text{B}} b + \lambda_{\text{Y}} \Delta c_{\text{Y}} \quad (29b)$$

$$a = C(\lambda_{\text{A}} + \lambda_{\text{Y}}) \quad (29c)$$

Hence, eqn. (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,

$E_{\text{H}}$  (or  $E_{\text{B}}$ )

$$= f \left( h, b, l, \sum_{k \geq 2} l_k, \sum_i p_i, \sum_j n_j, \Delta c_{\text{Y}} \text{ or/and } \Delta c_{\text{A}} \right)$$

4.1. The suggested function for  $E_D$  for the preliminary treatment of e.m.f. 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,  $L^+$ ,  $Y^-$ ,  $A^+$ ,  $B^{z(B)+}$ , and the  $H^+$  ions. Therefore, a simplified version of the function, given by eqn. (28), can be integrated in the following form

$$E_D = -\frac{g}{2.303} \int_{x=0}^{x=1} \frac{\theta_2 dx}{N} \quad (30)$$

where  $N$  can be approximated by

$$N = wx + a \quad (31)$$

The content of the function  $\theta_2$  will be given in forthcoming publications for every special cell studied. Equation (30) can be integrated according to eqn. (18) in Part 2 of Ref. 9:

$$-g \int_{x=0}^{x=1} \frac{\theta dx}{wx + a} = -\frac{g\theta}{w} \ln[(w/a) + 1] \quad (32a)$$

The result is

$$E_D = -\frac{g\theta_2}{2.303w} \ln[(w/a) + 1] \quad (32b)$$

4.2. For small values of  $w/a$  we obtain

$$E_D \cong -g\theta_2/(2.303a) \\ = f_1(h, b, l, \Delta c_{\text{Y}} \text{ or/and } \Delta c_{\text{A}}, C) \quad (33)$$

## 5. Calculation of the contribution of the activity coefficients to the diffusion potential, $E_{\text{Dr}}$ , in cells with complex formation

According to the definition of  $E_{\text{Dr}}$  given by eqn. (23) in Ref. 1, we have

$$E_{\text{Dr}} = -g \int_{\text{TS1}}^{\text{TS2}} \sum_j \frac{t_j^*}{z_j} d \log f_j \quad (34a)$$

$$E_{\text{Dr}} = -g \int_{\text{TS1},x=0}^{\text{TS2},x=1} (1/N) \left\{ xh\lambda_{\text{H}} d \log f_{\text{H}} + xb\lambda_{\text{B}} d \log f_{\text{B}} \right. \\ \left. + c_{\text{A}}^* \lambda_{\text{A}} d \log f_{\text{A}} - xl\lambda_{\text{L}} d \log f_{\text{L}} - c_{\text{Y}}^* \lambda_{\text{Y}} d \log f_{\text{Y}} \right. \\ \left. + \sum_i p_i x^{u_i} \lambda_{\text{Pi}} d \log f_{\text{Pi}} \right. \\ \left. - \sum_{k \geq 2} l_k x^{u_k} \lambda_{\text{Lk}} d \log f_{\text{Lk}} - \sum_j n_j x^{u_j} \lambda_{\text{Nj}} d \log f_{\text{Nj}} \right\} \quad (34b)$$

Here, the functions denoting the ion concentrations  $c_{\text{A}}^*$  and  $c_{\text{Y}}^*$  are different in cells with different experimental conditions. The values of  $\log f_j$  can be estimated, again, with the help of the specific ionic interaction theory.<sup>1</sup> These functions will be given in forthcoming publications for every cell with the chosen experimental condition out of (i)–(iii). Substituting the corresponding  $d \log f_j$  values into eqn. (34b), the integral can be evaluated graphically for every experimental point.

5.1. *The suggested function for  $E_{Dr}$  for the preliminary treatment of e.m.f. data.* We can suggest a simplified function for  $E_{Dr}$ , again, taking only into account the dominating species,  $B^{z(B)+}$ ,  $L^{z-}$ ,  $Y^{-}$ ,  $A^{+}$ , and the  $H^{+}$  ions. In this case the approximate function for  $E_{Dr}$  can always be integrated in the form

$$E_{Dr} \cong \text{corr} - g \int_{x=0}^{x=1} \left( \frac{\phi_3 x dx}{wx+a} + \frac{\theta_3 dx}{wx+a} \right) \quad (35a)$$

where the term 'corr' is defined by eqn. (32) in Ref. 1. The value of the integrals is given by eqn. (31) in Ref. 1. The content of the functions  $\phi_1(x)$  (appearing in corr),  $\phi_3$  and  $\theta_3$  will be given for every experimental cell with the chosen condition out of (i)–(iii), in forthcoming publications.

Hence, we have

$$\text{corr} = -g \int_{x=0}^{x=1} \frac{dD(I^*)}{dx} \frac{\phi_1(x) dx}{wx+a} \quad (35b)$$

$$E_{Dr} = \text{corr} - \frac{g\phi_2}{w} + \frac{g[\phi_2 a - \theta_1 w]}{w^2} \ln \left( \frac{w}{a} + 1 \right). \quad (35c)$$

5.2. *For small values of  $w/a$  we obtain*

$$\begin{aligned} E_{Dr} &\cong \text{corr} - g\theta_3/a \\ &= f_2(h, b, l, \Delta c_A \text{ or/and } \Delta c_Y, C) \end{aligned} \quad (36)$$

## 6. The total cell e.m.f. in cells with complex formation

6.1. *The total e.m.f. of cell B with an amalgam indicator electrode.* The total e.m.f. of cell B can be described by eqn. (2). The total potential anomalies,  $\Delta E_B$ , are

$$\Delta E_B = (g/z_B) \log f_{BTS2} + E_D + E_{Dr} \quad (37)$$

The approximate function of  $E_B$  can always be written in the following form, for the preliminary treatment of e.m.f. data and for small values of  $w/a$ :

$$\begin{aligned} E_B &\cong E_{OB} + (g/z_B) \log b - gz_B[D(I) - D(C)] \\ &\quad + \sum_V Q(B, V)V + \text{corr} \end{aligned} \quad (38a)$$

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  $h, b, l, \Delta c_Y$  or/and  $\Delta c_A$ , the ion concentrations taken into account in the equilibrium solution.  $D(I)$ , the Debye–Hückel term, is given by eqn. (5) in Ref. 1 as

$$D(I) = \frac{0.5115I^{1/2}}{1 + 1.5I^{1/2}} \quad (38b)$$

$D(C)$  is the Debye–Hückel term in CMAY (TS1).

The terms  $\sum_V Q(B, V)V$  give the potential contributions of the ions present in the transition layer, to  $\Delta E_j$ , reduced by the Debye–Hückel terms. They cannot be determined experimentally, in contrast to the slope func-

tions, 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, eqn. (38a) should be extended with a proper term, e.g.  $SL(B, H_yL)[H_yL]$ . The slope function  $SL(B, H_yL)$  denotes the slope of the plot  $E_B - (g/z_B) \log b$  versus  $[H_yL]$ , at constant  $[HY]$ , e.g. 50 mM, and  $[BY_{z(B)}]$ , and varying  $[H_yL]$ .

From eqn. (38a),  $b$  can be calculated by successive approximations, from the constant  $E_{OB}$  and the terms  $\sum_V Q(B, V)V$ . The functions  $Q(B, V)$  will be given in forthcoming publications for every special cell studied.

6.2. *The total e.m.f. of cell H with a  $H^{+}$ -sensitive indicator electrode.* The total e.m.f. of this cell can be described by eqn. (3). The total potential anomaly,  $\Delta E_H$ , is given by

$$\Delta E_H = g \log f_H + E_D + E_{Dr} \quad (39)$$

The approximate function for  $E_H$  can always be written in the following way, for the preliminary treatment of the e.m.f. data and for small values of  $w/a$ :

$$\begin{aligned} E_H &\cong E_{OH} + g \log h - g[D(I) - D(C)] \\ &\quad + \sum_V Q(H, V)V + \text{corr} \end{aligned} \quad (40)$$

where  $Q(H, V)$  is the same type of function as  $Q(B, V)$  and represents a constant.

From eqn. (40),  $h$  can be calculated by successive approximations from the constant  $E_{OH}$  and the terms  $\sum_V Q(H, V)V$ . The functions  $Q(H, V)$  will be given in forthcoming publications for every special cell studied.

If it was found in a separate experiment that the undissociated molecules of  $H_yL$  also influence  $E_H$ , eqn. (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  $E_H - g \log c_H$  versus  $[H_yL]$ , at constant  $[HY]$ , e.g. 50 mM, and  $[BY_{z(B)}]$ , and at varying  $[H_yL]$ .

## 7. 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 e.m.f. assume constant interaction coefficients. These have experimentally been proved to be true in the range  $0.5 \leq I \leq 3 \text{ mol dm}^{-3}$  for cationic charges  $\leq 3$  (cf. the Section 'On the difficulties ...' in Part 1 of Ref. 9). If these interaction coefficients prove to be functions of the ionic strength, new  $\Delta E_j$  functions have to be derived using Pitzer's model (cf. the abovementioned section in Part 1 of Ref. 9) 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 be higher than  $0.5 \text{ mol dm}^{-3}$ .

(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  $\lambda_Y$ ,  $\lambda_A$ ,  $\lambda_B^{tr}$ ,  $\lambda_H^{tr}$  and  $\lambda_L^{tr}$  (here, tr = trace) can be tested by determining the experimental slope functions, e.g.  $SL(H, c_H)$ ,  $SL(H, c_B)$ , presented in Ref. 1 and in forthcoming parts, and  $SL(H, I)$ . 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:

- $E_H - g \log c_H$  versus  $c_H$ , at constant  $c_B$ , defines  $SL(H, c_H)_{1,\beta}$
- $E_H - g \log c_H$  versus  $c_B$ , at constant  $c_H$ , defines  $SL(H, c_B)$
- $E_B - (g/z_B) \log c_B$  versus  $c_B$ , at constant  $c_H$ , defines  $SL(B, c_B)_{1,\beta}$
- $E_B - (g/z_B) \log c_B$  versus  $c_H$ , at constant  $c_B$ , defines  $SL(B, c_H)$
- $E_H - g \log [H^+]$  versus  $I = [Y^-]$ , at constant or very low  $[H^+]$ , defines  $SL(H, I)$ .

The slope functions depend on only 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  $-\log[H^+]$  of the test solution is supposed to be  $\leq 7$ . 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  $\log f_j$  values and in the potential functions:

- $\tilde{\epsilon}(A, OH)[OH^-]$ , in  $\log f_A$
- $\tilde{\epsilon}(A, OH)\Delta c_A$ , in  $\log f_{OH}$ , if  $[Y^-] = CM$ , constant, and  $I = CM$ , constant
- $\tilde{\epsilon}(P_i, OH)[OH^-]$ , in  $\log f_{P_i}$
- $\tilde{\epsilon}(P_i, OH)p_i$  and  $\tilde{\epsilon}(B, OH)b$  in  $\log f_{OH}$ .

If the concentrations  $[OH^-]$ ,  $p_i$  and  $b$  are  $\leq 10^{-3} \text{ mol dm}^{-3}$ , these interaction terms are probably negligible. If the value for the interaction term  $\tilde{\epsilon}(A, OH)\Delta c_A$  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  $\tilde{\epsilon}(H, Y)h$ ,  $\tilde{\epsilon}(H, L)l$  and  $\tilde{\epsilon}(H, N_j)h$ , of course. Moreover,  $\log[H^+]$  should be replaced by

$\log K_w - \log[OH^-]$ . Here,  $K_w$  is the ionic product of water. However, if the composition change of the 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  $\Delta E_j$  is limited by the requirement that  $\lambda_B$  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  $\lambda_L$  should be constant. This can also be tested from the experimental slope function  $SL(H, I)$ , as discussed under point (3). The constancy of  $\lambda_L^{tr}$  can also be investigated by conductivity measurements in the mixtures of  $AY + A_yL$  at the experimental conditions  $[A^+] = CM$ , constant,  $[Y^-] = CM$ , constant, and  $I = CM$ , constant, respectively.

(7) The constancy of the ionic molar conductivities in the test solution ( $\lambda_j$ ), used as approximations for the  $\lambda_j^*$  values in the transition layer, is proved to be true only in junctions of constant ionic medium type, as was shown in Refs. 2–4. 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 Part 6A (to be published) in the protolysis of the acetic acid and in the first step of the protolysis of ascorbic acid.

## References

- Néher-Neumann, E. *Acta Chem. Scand.* 51 (1997) 1141.
- Néher-Neumann, E. *Acta Chem. Scand.* 52 (1998) 873.
- Néher-Neumann, E. *Acta Chem. Scand.* 52 (1998) 1075.
- Néher-Neumann, E. *Acta Chem. Scand.* 53 (1999) 1.
- Rossotti, F. J. C. and Rossotti, H. S. *The Determination of Stability Constants and Other Equilibrium Constants in Solution*, McGraw-Hill, New York 1961.
- Many publications of Sillén, L. G. A list can be obtained from the Department of Chemistry, Inorganic Chemistry, Royal Institute of Technology (KTH), S-100 44 Stockholm, Sweden.
- Meloun, M., Havel, J. and Högföldt, E. *Computation of Solution Equilibria: A Guide to Methods in Potentiometry, Extraction and Spectrophotometry*, Ellis Horwood Limited, Chichester 1988.
- Spáhiu, K. *Carbonate Complex Formation in Lanthanoid and Actinoid Systems*, Dissertation, Royal Institute of Technology (KTH), Stockholm, Sweden 1983.
- Néher-Neumann, E. *The Liquid Junction E.M.F.*, Dissertation, Royal Institute of Technology (KTH), Stockholm, Sweden 1987.

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