

The Liquid Junction Potential in Potentiometric Titrations. 6A. The Calculation of Potentials across Liquid Junctions of the Type $AY|AY + BY_{z(B)} + HY + A_yL$ for Cells where Strong Complexes are Formed at $[A^+] = CM$ Constant and $-\log[H^+] \leq 7$

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Equations are derived for the calculation of the total cell e.m.f. of cells where formation of strong complexes takes place at $[A^+] = CM$ constant. This can be defined at 25 °C as

$$E_j = E_{0j} + (59.16/z_j) \log c_j f_{jTS2} + E_D + E_{Df}$$

Here, c_j is the concentration and z_j is the charge of the potential determining ion J, TS2 denotes the terminal solution 2 (i.e. the test solution), f_j is the activity coefficient of ion J around the measuring electrode, E_D is the ideal diffusion potential, E_{Df} is the contribution to the activity factors to E_D . The cells have liquid junctions of constant ionic medium type: $AY|AY + HY + BY_{z(B)} + A_yL$. They are assumed to contain equilibrium solutions which exist in the system $HY - BY_{z(B)} - A_yL$ in the ionic medium (A^+ , Y^-). Here, L^- denotes the ligand. E_{0j} is an experimental constant. The cells have indicator electrodes reversible for the $B^{z(B)+}$ (cell B') and H^+ ions (cell H), respectively; $B^{z(B)+}$ is the central metal ion.

The dissociation of the complexing agent HL and H_2L has been studied. The usefulness of the derived potential functions is proved on the $H^+ - H$ ascorbate⁻ and $H^+ - \text{acetate}^-$ systems as some examples.

This work is Part 6A of this series. The earlier parts can be found in Refs. 1–6. Symbols and definitions used throughout this series are defined in Ref. 1. Symbols and definitions used in equilibrium systems are given in Ref. 5 (Part 5).

In the following parts of this series, we shall consider cells in which complex formation takes place under different experimental conditions. Considering the concentration conditions generally used in potentiometric titrations, the concentration of the ionic medium chosen is much larger than the concentration of the other components. The ligand is also generally present in large excess. Thus, the reacting species are often present only in trace concentrations and it is generally believed that the total potential anomalies, in such cells, can be neglected. This hypothesis will be tested in the present paper.

In Refs. 1–4 cells containing mixtures of strong electrolytes have been studied realizing different experimental

conditions: $[A^+] = CM$, constant, $[Y^-] = CM$, constant, and $I = CM$, constant, respectively. The total potential anomalies, ΔE_j , have been calculated and compared with the measured ones for these cells containing different mixtures of $HClO_4 + Cd(ClO_4)_2 + NaClO_4$. The agreement was good between the calculated and measured ΔE_j values. It means that the calculation method used describes quite well the total potential anomalies appearing in e.m.f. cells with liquid junctions of constant ionic medium type. On the basis of these results, it is assumed that the same method can be used for the calculation of ΔE_j in cells where complex formation takes place as well.

It is assumed that strong complexes of any kind can be formed in the test solution with a ligand which may be the anion of a weak or strong acid, as defined in Ref. 5. The deduction of the potential functions E_D , E_{Df} , ΔE_B , ΔE_H , in a general form, for cells with complex formation, is presented in Ref. 5. Here, we shall follow this general treatment.

Approximate potential functions will be suggested for

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the preliminary treatment of e.m.f. data, taking into account, first, only the potential contributions of the H^+ , $B^{z(B)+}$, L^{y-} , A^+ and Y^- ions to ΔE_j . Then a procedure will be suggested for the refinement of the preliminary chemical model and equilibrium constants.

The definition of the complex formation reactions and the cells studied is given in Ref. 5. The composition of the test solution and of the transition layer is also given there.

The titrations can be carried out in different ways. Some possibilities are summarized in the Appendix of this paper. It is important to realize that the different ways of making the titration will result in quite different data sets. The point is that the equilibrium concentration of the undissociated acid H_yL is different in the 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 different magnitude. This effect has not been recognized previously. The proof of this hypothesis will be given in a forthcoming chapter.

The determination of the constants E_{OB} and E_{OH} should be done as described in Ref. 1.

We derive the equations for the case when A_yL was used as a complexing agent at constant or varied 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 the function c_Y .

The ionic strength in the test solution is

$$I = C + (1/2) \left(h + \Delta c_Y + \sum_k l_k z_{Lk}^2 + \sum_j n_j z_{Nj}^2 + \sum_i p_i z_{Pi}^2 + b z_B^2 + l z_L^2 \right) \quad (1)$$

The necessary functions for the calculation of the potential terms E_D and E_{Df} , moreover, for the total cell e.m.f. E_B and E_H , considering the functions derived in Parts 1¹ and 5,⁵ are presented below.

Survey of the potential functions for the HY-BY_{z(B)}-A_yL-AY system

1. *The calculation of the ideal diffusion potential term, E_D .* The complete function for the description of the potential contribution E_D is given by eqn. (28) in Ref. 5.

$$E_D = -(g/2.303) \int_{TS1}^{TS2} (1/N) \times \left\{ \left[\lambda_H h + \lambda_B b + \sum_i (\lambda_{Pi} u_i p_i x^{u_i-1}) - \lambda_L l \right] - \sum_{k \geq 2} (\lambda_{Lk} u_k c_k x^{u_k-1}) - \sum_j (\lambda_{Nj} u_j n_j x^{u_j-1}) \right\} dx + \lambda_A dc_A^* - \lambda_Y dc_Y^* \quad (2a)$$

where the potential contributions of the ions of the ionic medium is

$$\lambda_A dc_A^* = 0, \quad -\lambda_Y dc_Y^* = -\lambda_Y \Delta c_Y dx \quad (2b)$$

In the function N , given by eqn. (29a) in Ref. 5, the coefficient w and the term a appear. In the present cell, they have the following values

$$a = C(\lambda_A + \lambda_Y) \quad (3)$$

$$w = \lambda_H h + \lambda_B z_B b + \lambda_L y l + \lambda_Y \Delta c_Y \quad (4)$$

Substituting the values of a and w for the eqn. (28) and (29a) in Ref. 5, the integral defined by eqn. (2a), here, can be obtained graphically.

1.1. *The approximated function for E_D , suggested for the preliminary treatment of the data.* For the establishment of the preliminary chemical model and equilibrium constants, an approximate function can be used for E_D , supposing only the species L^{y-} , Y^- , A^+ , $B^{z(B)+}$ and H^+ to be present in the test solution. This function is given by eqn. (30) in Ref. 5. In this equation, the coefficient θ_2 has the following value

$$\theta_2 = \lambda_H h + \lambda_B b - \lambda_L l - \lambda_Y \Delta c_Y \quad (5)$$

After the integration, eqn. (32b) describes the function E_D in Ref. 5.

1.1.1. *For small values of w/a we obtain, using the approximation $\ln[(w/a) + 1] \approx w/a$, according to eqn. (33) in Ref. 5*

$$E_D \approx -gF_0(\lambda_H h + \lambda_B b - \lambda_L l - \lambda_Y \Delta c_Y) \quad (6)$$

where

$$F_0 = 1/[2.303C(\lambda_A + \lambda_Y)] \quad (7)$$

1.2.2. As the considered ions represent a mixture of strong electrolytes, the function E_D can also be integrated in the same way as was already discussed for this case in Ref. 1. Hence, E_D can also be calculated on the basis of the potential functions given below.

$$U_{TS2} - U_{TS1} = \theta_2 \quad (8)$$

[cf. eqn. (16) in Ref. 1]

$$S_{TS2} - S_{TS1} = h\lambda_H + b z_B \lambda_B + \lambda_Y \Delta c_Y + |z_L| l \lambda_L = w \quad (9)$$

[cf. eqn. (17) in Ref. 1]

$$S_{TS2} = h\lambda_H + b z_B \lambda_B + C(\lambda_A + \lambda_Y) + \lambda_Y \Delta c_Y + |z_L| l \lambda_L \equiv w + a \quad (10)$$

$$S_{TS1} = C(\lambda_A + \lambda_Y) \equiv a \quad (11)$$

2. *The calculation of the contribution of the activity coefficients to the diffusion potential, E_{Df} .* The complete function which describes the potential contribution E_{Df} , in this cell, is given by eqn. (34b) in Ref. 5. The ion concentrations c_A and c_Y , given there, moreover, the $d \log f_j$ values for the different ions should be substituted into this equation.

We define $\log f_j$ in general, according to the specific

ionic interaction theory, SIT,⁷⁻¹⁵ cf. eqns. (25)–(28) in Ref. 1. The reference state is chosen in such a way that the trace activity coefficients $f_j^T \rightarrow 1$ as $c_j \rightarrow 0$ in C M A Y as solvent. Hence, we can write for some intermediate plane in the transition layer

$$\begin{aligned} \log f_j = & -z_j^2 [D(I^*) - D(C)] \\ & + \left[\sum_k \tilde{\epsilon}(J, L_k) l_k^* + \sum_j \tilde{\epsilon}(J, N_j) n_j^* + \tilde{\epsilon}(J, Y) (c_Y^* - C) \right]_{ca} \\ & + \left[\tilde{\epsilon}(J, H) h^* + \tilde{\epsilon}(J, B) b^* + \sum_i \tilde{\epsilon}(J, P_i) p_i^* \right]_{an} \end{aligned} \quad (12)$$

Here, $[\dots]_{ca}$ = the terms to be used if J is a cation
 $[\dots]_{an}$ = the terms to be used if J is an anion.

The other symbols have the same meaning as in Ref. 5.

Considering eqn. (12) and the actual ion concentrations in the transition layer, given in Ref. 5 and here, the individual $\log f_j$ values can be formed. At this procedure, the interactions with the ions of minor concentrations can probably be neglected, such as

$$\begin{aligned} & \tilde{\epsilon}(H, N_j) n_j^*, \quad \tilde{\epsilon}(B, N_j) n_j^*, \quad \tilde{\epsilon}(A, N_j) n_j^*, \quad \tilde{\epsilon}(P_i, N_j) n_j^*, \\ & \tilde{\epsilon}(P_i, Y) p_i^*, \quad \tilde{\epsilon}(L_k, H) h^*, \quad \tilde{\epsilon}(P_i, L_k) p_i^*, \quad \tilde{\epsilon}(H, N_j) h^*, \\ & \tilde{\epsilon}(P_i, N_j) p_i^*, \quad \tilde{\epsilon}(H, Y) h^*. \end{aligned}$$

Therefore, we obtain e.g. for the H^+ and $B^{z(B)+}$ ions, assuming that the ion interactions mentioned above are negligible

$$\begin{aligned} \log f_H \simeq & -[D(I^*) - D(C)] \\ & + \sum_k \tilde{\epsilon}(H, L_k) l_k x^{u_k} + \tilde{\epsilon}(H, Y) x \Delta c_Y \end{aligned} \quad (13a)$$

$$\begin{aligned} d \log f_H \simeq & \left[-\frac{dD(I^*)}{dx} + \sum_k \tilde{\epsilon}(H, L_k) u_k l_k x^{(u_k-1)} \right. \\ & \left. + \tilde{\epsilon}(H, Y) \Delta c_Y \right] dx \end{aligned} \quad (13b)$$

$$\begin{aligned} \log f_B \simeq & -z_B^2 [D(I^*) - D(C)] \\ & + \sum_k \tilde{\epsilon}(B, L_k) x^{u_k} l_k + \tilde{\epsilon}(B, Y) x \Delta c_Y \end{aligned} \quad (14a)$$

$$\begin{aligned} d \log f_B \simeq & \left[-z_B^2 \frac{dD(I^*)}{dx} + \sum_k \tilde{\epsilon}(B, L_k) l_k u_k x^{(u_k-1)} \right. \\ & \left. + \tilde{\epsilon}(B, Y) \Delta c_Y \right] dx \end{aligned} \quad (14b)$$

Here, $D(I^*)$ is the Debye–Hückel term expressed with the ion concentrations in the transition layer. The $d \log f_j$ values, for the other ions involved, can be obtained in the same way. Substituting these values into eqn. (34b) in Ref. 5, the function E_{Df} can be integrated graphically.

2.1. *The suggested approximate function for E_{Df} , for the preliminary treatment of the data.* For the preliminary treatment of e.m.f. data we can suppose, again, that only the ions H^+ , $B^{z(B)+}$, L^{y-} , Y^- and A^+ should be considered when we calculate the potential contributions to E_{Df} . The approximated function can be obtained by the

integration of eqn. (35a) in Ref. 5. The functions $\phi_1(x)$,⁵ ϕ_3 and θ_3 are included in this equation. These have the content given below in this cell.

$$\begin{aligned} \phi_1(x) \simeq & x(-h\lambda_H - z_B^2 b\lambda_B + \Delta c_Y \lambda_Y + y^2 l\lambda_L) \\ & + C(\lambda_Y - \lambda_A) \end{aligned} \quad (15)$$

$$\begin{aligned} \phi_3 \simeq & h\lambda_H[\tilde{\epsilon}(H, L)l + \tilde{\epsilon}(H, Y)\Delta c_Y] \\ & + b\lambda_B[\tilde{\epsilon}(B, L)l + \tilde{\epsilon}(B, Y)\Delta c_Y] \\ & - \Delta c_Y \lambda_Y [\tilde{\epsilon}(B, Y)b + \tilde{\epsilon}(H, Y)h] \\ & - l\lambda_L [\tilde{\epsilon}(H, L)h + \tilde{\epsilon}(B, L)b] \end{aligned} \quad (16)$$

$$\begin{aligned} \theta_3 \simeq & C\lambda_A[\tilde{\epsilon}(A, L)l + \tilde{\epsilon}(A, Y)\Delta c_Y] \\ & - C\lambda_Y[\tilde{\epsilon}(B, Y)b + \tilde{\epsilon}(H, Y)h] \end{aligned} \quad (17)$$

After the integration of eqn. (35a),⁵ the function E_{Df} is given by eqn. (31) in Ref. 1.

2.1.1. *For small values of w/a ,* we can use the form given by eqn. (36) in Ref. 5. Hence, we have

$$\begin{aligned} E_{Df} \simeq & \text{corr} - gt_A[\tilde{\epsilon}(A, L)l + \tilde{\epsilon}(A, Y)\Delta c_Y] \\ & + gt_Y[\tilde{\epsilon}(B, Y)b + \tilde{\epsilon}(H, Y)h] \end{aligned} \quad (18)$$

where

$$t_A = \lambda_A/(\lambda_A + \lambda_Y) \quad \text{and} \quad t_Y = \lambda_Y/(\lambda_A + \lambda_Y) \quad (19)$$

and corr is given by eqn. (32) in Ref. 1.

3. *The total e.m.f. of cell B with an amalgam indicator electrode and for small values of w/a .* For the preliminary treatment of e.m.f. data, we can use the approximated functions obtained for E_D and E_{Df} for small values of w/a , given by eqns. (6) and (18), respectively. Hence, we can write, considering only the species H^+ , $B^{z(B)+}$, L^{y-} , A^+ and Y^- to be important in the test solution

$$\begin{aligned} E_B \simeq & E_{OB} + (g/z_B) \log b - gz_B [D(I) - D(C)] \\ & + \sum_V Q(B, V) V + \text{corr} \end{aligned} \quad (20)$$

where V denotes all the changing concentration terms appearing in eqn. (20) ($b, h, l, \Delta c_Y$). $Q(B, V)$ is a function with constant value, in terms of some interaction coefficients and ionic molar conductivities measured in TS2 in equilibrium.

In the present cells studied, the different $Q(B, V)$ functions in eqn. (20) have the following values

$$Q(B, h) = -g\lambda_H F_0 + gt_Y \tilde{\epsilon}(H, Y) \quad (21)$$

$$Q(B, b) = -g\lambda_B F_0 + gt_Y \tilde{\epsilon}(B, Y) \quad (22)$$

$$Q(B, l) = (g/z_B) \tilde{\epsilon}(B, L) + g\lambda_L F_0 - gt_A \tilde{\epsilon}(A, L) \quad (23)$$

$$Q(B, \Delta c_Y) = (g/z_B) \tilde{\epsilon}(B, Y) + g\lambda_Y F_0 - gt_A \tilde{\epsilon}(A, Y) \quad (24)$$

The function F_0 is defined by eqn. (7). Moreover, we have

$$\Delta E_B = -gz_B [D(I) - D(C)] + \sum_V Q(B, V) V + \text{corr} \quad (25)$$

According to the treatment presented above, eqn. (20) 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 approximation in the knowledge of E_{0B} and the functions $Q(B, V)$. The determination of the constant E_{0B} is discussed in Ref. 1. It is important to remember that a conditional constant, denoted either $E_{0B\alpha}$ or $E_{0B\beta}$ and E_{0B}^* in Ref. 1, cannot be used here. The estimation of the functions $Q(B, V)$ will be used in a following section.

As is seen, the term ΔE_B depends on the ion concentration and the deviation of the anion concentration of the ionic medium from the composition of the ionic medium, and not on total concentrations.

In eqn. (20), 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, e.g. in the cell containing mixtures of strong electrolytes with the experimental condition $[A^+] = C M$, constant (cf. Ref. 1). 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^+ , λ_H^+ and λ_L^+ , is necessary. We can try to get this information in the ways as to be discussed in the following section. The estimation of the term *corr* has to be made for a titration where C and the maximum values for B_T and L_T are used during the study of complex formation.

The equations derived above are valid also for the case where the ligand is an anion of a strong acid. 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 ones defined here, for cells B and H, the function E_B must be taken with the opposite sign.

4. *The total e.m.f. of cell H with a H^+ ion-sensitive indicator electrode and for small values of w/a .* For the preliminary treatment of e.m.f. data we can derive an approximate function for E_H , using the same reasoning and conditions as under Section 3. Hence, we obtain

$$E_H \simeq E_{0H} + g \log h - g[D(I) - D(C)] + \sum_V Q(H, V)V + \text{corr} \quad (26)$$

Here, V denotes the variables we have defined in Section 3 and $Q(H, V)$ denotes a function with constant value, again, in terms of some interaction coefficients and ionic molar conductivities measured in the equilibrium solution. The functions $Q(H, V)$ cannot be determined experimentally, but they can be calculated. Those ones valid for the present cell are presented below.

$$Q(H, h) = -g\lambda_H F_0 + g t_Y \tilde{\epsilon}(H, Y) \quad (27)$$

$$Q(H, b) = -g\lambda_B F_0 + g t_Y \tilde{\epsilon}(B, Y) \quad (28)$$

$$Q(H, l) = g\tilde{\epsilon}(H, L) + g\lambda_L F_0 - g t_A \tilde{\epsilon}(A, L) \quad (29)$$

$$Q(H, \Delta c_Y) = g\tilde{\epsilon}(H, Y) + g\lambda_Y F_0 - g t_A \tilde{\epsilon}(A, Y) \quad (30)$$

Moreover, we have

$$\Delta E_H = -g[D(I) - D(C)] + \sum_V Q(H, V)V + \text{corr} \quad (31)$$

If it was found in some separate experiments that the cell e.m.f. is influenced by the presence of the $H_Y L$ molecules as well, eqn. (26) should be extended as follows

$$E_H = E_{0H} + g \log h - g[D(I) - D(C)] + \sum_V Q(H, V)V + \text{SL}(H, \text{acid})[H_Y L] + \text{corr} \quad (32)$$

where $[H_Y L]$ denotes equilibrium and not total concentration. The slope function $\text{SL}(H, \text{acid})$ stands for the slope of the plot $E_H - g \log[H^+] + g[D(I) - D(C)]$ versus $[H_Y L]$, at constant $[HY]$ and $[A^+] = C M$, constant. It should be noted that the magnitude of this slope depends on the way the titration is carried out.

According to the treatment presented above, eqn. (26) or (32) 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 $Q(H, V)$. The determination of the constant E_{0H} is discussed in Ref. 1.

We should remember that a conditional constant, denoted either $E_{0H\alpha}$ or $E_{0H\beta}$ and E_{0H}^* in Ref. 1, cannot be used here. The functions $Q(H, V)$ can be estimated in the same way as the functions $Q(B, V)$, as it will be discussed in the next section.

The equations presented under Section 4 are valid also in cases when the ligand is an anion of a strong acid and strong complexes are formed.

For cells with polarity opposite to that one defined here, for cell H, the function E_H must be taken with the opposite sign.

The use of the derived equations

The purpose of the e.m.f. studies on equilibrium systems is to determine the composition of the species present in equilibrium solutions and to determine the equilibrium constants for the formation reactions of these species. The necessary calculations are based upon the knowledge of some of the free, equilibrium concentrations of the reacting species H^+ , L^{y-} and $B^{z(B)+}$: h , l and b , respectively. As it was shown above, some of these equilibrium concentrations h and b can be determined by the use of e.m.f. cells, through successive approximations.

1. *The calculation of the free, equilibrium concentrations h and b from e.m.f. measurements.* As was suggested above, first we should do a preliminary data treatment based on potential functions for which only the presence of the species H^+ , $B^{z(B)+}$, L^{y-} , A^+ and Y^- was taken into account. It means that we should consider only the potential contributions of these ions described by the corresponding terms $Q(B, V)V$ or $Q(H, V)V$. For the calculation of the preliminary values h_1 and b_1 , the knowledge of these functions is necessary.

2. *The estimation of the preliminary functions $Q(B, V)$ and $Q(H, V)$ for $V = h, b, l$ and Δc_Y .* These functions are presented above. As is seen, they depend on the ionic

molar conductivities $\lambda_{\text{H}}^{\text{tr}}$, $\lambda_{\text{B}}^{\text{tr}}$, $\lambda_{\text{L}}^{\text{tr}}$, λ_{A} , λ_{Y} , to be determined in the equilibrium solution studied, and some molar interaction coefficients. However, the measurement of the conductivity in equilibrium solutions cannot be interpreted in terms of the ionic molar conductivities without knowing the equilibrium concentrations and compositions for, at least, the main species. Therefore, the preliminary equilibrium concentrations h_1 and b_1 can only be calculated by using preliminary values for the $Q(\text{H}, V)$ and $Q(\text{B}, V)$ functions in question, calculated with preliminary values for $\lambda_{\text{H}}^{\text{tr}}$, $\lambda_{\text{B}}^{\text{tr}}$, $\lambda_{\text{L}}^{\text{tr}}$, λ_{A} and λ_{Y} , determined in mixtures of strong electrolytes. This can be done as follows.

2.1. *The estimation of $\lambda_{\text{B}}^{\text{tr}}$, $\lambda_{\text{H}}^{\text{tr}}$, λ_{A} and λ_{Y} in mixtures of strong electrolytes.* For the estimation of the λ_{J} values given in the title or of $Q(\text{H}, b)$ respective $Q(\text{B}, b)$, we have two possibilities.

2.1.1. The conductivity of the electrolyte mixture given below should be measured by accurate conductivity measurements:

$0 \leq c_{\text{B}} \leq B_{\text{Tmax}}$
 $1 \leq c_{\text{H}} \leq \sim 5 \text{ mM}$, constant, or a level should be used which prevents the hydrolysis and complex formation of the $\text{B}^{z(\text{B})+}$ ions

$[\text{H}_y\text{L}] \text{ M}$ undissociated acid, constant
 $C \text{ M AY}$, keeping $[\text{A}^+] = C \text{ M}$, constant.

Here, B_{Tmax} denotes the maximum level of the total, analytical concentration used for $\text{BY}_{z(\text{B})}$ 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 under the study of the 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. ML AB ,¹⁶ minimizing least-square sums and using the unknown λ_{J} values as parameters. This treatment has already been described in Ref. 2.

2.1.2. Another possibility is to estimate the function $Q(\text{H}, b)$ or $Q(\text{B}, b)$. For this purpose, we should measure, e.g., the experimental slope function $\text{SL}(\text{H}, c_{\text{B}})_{\alpha \text{exptl}}$ in the mixture in question, which is the slope of the plot¹ $E_{\text{H}} - g \log c_{\text{H}} + g[D(I) - D(C)] - \text{corr}$ vs. c_{B} at constant c_{H} . Hence, we have

$$\text{SL}(\text{H}, c_{\text{B}})_{\alpha} = g d_3 \quad (33a)$$

where d_3 is given by eqn. (46) in Ref. 1. Then we should form and calculate the difference function $Q(\text{H}, b) - \text{SL}(\text{H}, c_{\text{B}})_{\alpha}$. Hence, we obtain

$$Q(\text{H}, b) = \text{SL}(\text{H}, c_{\text{B}})_{\alpha \text{exptl}} + \text{the difference function} \quad (33b)$$

where the difference function is

$$-g z_{\text{B}} \tilde{\epsilon}(\text{H}, Y) - g z_{\text{B}} \lambda_{\text{Y}} F_0 + g z_{\text{B}} t_{\text{A}} \tilde{\epsilon}(\text{A}, Y) \quad (33c)$$

and exptl denotes experimental.

The function $Q(\text{B}, b)$ can be estimated similarly, through the slope function $\text{SL}(\text{B}, c_{\text{B}})_{\alpha}$, cf. eqns. (41) and (44) in Ref. 1.

2.2. *The estimation of $\lambda_{\text{L}}^{\text{tr}}$, λ_{A} and λ_{Y} in mixtures of strong electrolytes.* The value of $\lambda_{\text{L}}^{\text{tr}}$ can be estimated in two ways.

2.2.1. By measuring the conductivity, $10^3 \kappa$, in the mixtures of

$0 \leq [\text{A}_y\text{L}] \leq L_{\text{Tmax}}$
 $[\text{H}_y\text{L}] \text{ M}$ undissociated acid, constant
 AY , keeping $[\text{A}^+] = C \text{ M}$, constant

we can make the estimation in question. From these data, $\lambda_{\text{L}}^{\text{tr}}$ can be estimated in a similar way as was used for the estimation of $\lambda_{\text{Cd}}^{\text{tr}}$, discussed in Ref. 2. We can assume that λ_{Y} has the same value as in $C \text{ M AY}$ solution. λ_{A} should be calculated in terms of the ionic strength fractions.

The ionic strength in this mixture is

$$I = [\text{AY}] + L_{\text{T}}(y + y^2)/2 \quad (34a)$$

Hence, we have

$$\lambda_{\text{A}}^{\text{Mix}} = \lambda_{\text{A}}(C \text{ M AY})[\text{AY}]/I + \lambda_{\text{A}}(C/y \text{ M A}_y\text{L})L_{\text{T}}(y + y^2)/2I \quad (34b)$$

According to the additivity we have

$$10^3 \kappa_{\text{add}} = C \lambda_{\text{A}}^{\text{Mix}} + [\text{AY}] \lambda_{\text{Y}}(C \text{ M AY}) + y L_{\text{T}} \lambda_{\text{L}}(C/y \text{ M A}_y\text{L}) \quad (35)$$

We assume that the deviations from additivity are due to the deviation of $\lambda_{\text{L}}^{\text{tr}}$ from its value in $C/y \text{ M A}_y\text{L}$ solution, denoted as

$$\Delta(\lambda_{\text{L}}^{\text{tr}}) = \pm y L_{\text{T}} r_1 \quad (36)$$

This deviation is described by the following function

$$\begin{aligned} \Delta(\lambda_{\text{L}}^{\text{tr}}) &= 10^3 \kappa - C \lambda_{\text{A}}^{\text{Mix}} - [\text{AY}] \lambda_{\text{Y}}(C \text{ M AY}) \\ &\quad - y L_{\text{T}} \lambda_{\text{L}}(C/y \text{ M A}_y\text{L}) \\ &= \pm y L_{\text{T}} r_1 \end{aligned} \quad (37)$$

Here, $10^3 \kappa$ denotes the measured conductivity of the mixture studied. Plotting $\Delta(\lambda_{\text{L}}^{\text{tr}})$ vs. L_{T}, r_1 can be calculated from the slope. Then we have

$$\lambda_{\text{L}}^{\text{tr}} = \lambda_{\text{L}}(C/y \text{ M A}_y\text{L}) - r_1 \quad (38)$$

where

$$\lambda_{\text{L}}(C/y \text{ M A}_y\text{L}) = t_{\text{L}}(C/y \text{ M A}_y\text{L}) \Lambda(C/y \text{ M A}_y\text{L}) \quad (39)$$

The transport numbers in $C/y \text{ M}$ solution of the pure electrolyte A_yL , t_{L} and t_{A} , can be determined with the help of an e.m.f. cell (cf. Ref. 17), if the $\text{p}K_{\text{a}}$ values of the corresponding acid are well separated.

2.2.2. The estimation of an approximate value for $\lambda_{\text{L}}^{\text{tr}}$ or $Q(\text{H}, l)$ can be done, for the ligand HL and HL^- , from the experimental (exptl) value of the slope function $\text{SL}(\text{H}, l)$, defined by eqn. (61), determined by e.m.f. measurements as suggested in a later section. Having the experimental slope function, we can act in two ways.

2.2.2.1. Using the definition of the slope function, the value of $\lambda_{\text{E}}^{\text{f}}$ can directly be calculated from the known function.

2.2.2.2. We form and calculate the difference function $Q(H, I) - SL(H, I)$ on the basis of the definitions. Then

$$Q(H, I) = SL(H, I)_{\text{exptl}} + \text{the difference function} \quad (40)$$

This estimation requires the assumption that the ionic molar conductivities have the same values in both functions. Therefore, the experiments, done for obtaining $SL(H, I)$ and to study the complex formation, must be done practically in the same way. In these calculations, for the values of λ_{A} and λ_{Y} we can use those which were either determined under Section 2.1 or valid in C M ionic medium AY .

During the study of the equilibrium system, the equilibrium concentration of the ligand, $I = [L^-]$, is changed while $[A^+] C$ M, is kept constant, and $10^{-7} < [H^+] < 10^{-3}$ M. During the determination of the slope function $SL(H, I)$, the $[H^+]$ is kept at a constant or negligible level by using the buffer system $HL - L^-$, and $[A^+] = C$ M, is kept constant, while $[L^-]$ is changed in the range $0 - L_T$ M. Therefore, we can hope that λ_{L} has the same value in both systems.

It is important to emphasize that $Q(H, I)$ and $SL(H, I)$ are two different functions and they cannot be interchanged.

3. *Refinement of the equilibrium constants.* For the preliminary treatment of e.m.f. data, we have suggested preliminary functions for ΔE_{J} , e.g. $Q(H, h)$, $Q(H, I)$, $Q(H, b)$ and $Q(H, \Delta c_{\text{Y}})$. This treatment will result in preliminary values for h_1 and b_1 ; moreover, it gives chemical model and equilibrium constants. As a second step, we can refine the results by using the complete functions for E_{D} and E_{Dr} , for the treatment of the e.m.f. data. For this purpose we must know the ionic molar conductivities in the equilibrium solution. These can be estimated by carrying out two identical titrations. One of the titrations should be an e.m.f. titration, and the other a conductivity titration. We can calculate the equilibrium concentrations from the e.m.f. titration. Then the data from the conductivity titration can be treated with a curve-fitting computer program, where the unknown λ_{j} values are parameters. In these calculations, λ_{ClO_4} and λ_{Na} can be calculated in terms of the ionic strength fractions, as was shown earlier. Having the composition and the ionic molar conductivities in the equilibrium system, we can check the validity of the approximation $\ln[(w/a) + 1] \approx w/a$.

4. *The effect of the composition changes of the ionic medium on E_{B} , in mV and in $\log \beta_{\text{pqr}}$ units.* As it was already pointed out, potentiometric titrations can be carried out in different ways. Hence, the change of the composition of the ionic medium, Δc_{Y} , can have different magnitudes in the different titrations. The corresponding potential contribution to ΔE_{J} , e.g. in cell B the term

$Q(B, \Delta c_{\text{Y}}) \Delta c_{\text{Y}}$, seems to be a dominating one, and it can be useful to see how it develops in different titrations. Therefore, this term will be estimated in this section for four representative titrations (T1–T4). On the basis of these estimations, the concentration limits to be used for the reacting species in potentiometric titrations can be established, in order to obtain a favourable magnitude of ΔE_{J} .

We assume that cell B contains the equilibrium system $H^+ - BY_{z(\text{B})} - L^y^-$ in the ionic medium (A^+, Y^-) where reactions I–III can take place.⁵ The composition of the solutions to be used for titrations T1–T4 is listed in Table 1. The titrations are supposed to be carried out as follows: to a 50 ml solution S , obtained at the end of the titration where the constants E_{OB} and E_{OH} had been determined, $v_1 = v_2 = 30$ ml solutions S_1 and S_2 are added. The value of the potential function $Q(B, \Delta c_{\text{Y}})$ is calculated according to the definition [cf. eqn. (24)]. Here $B = \text{Cd}^{2+}$, $Y^- = \text{ClO}_4^-$, $A^+ = \text{Na}^+$. For the NaClO_4 ionic medium, the following approximations are introduced:

$$t_{\text{Y}} = \lambda_{\text{Y}} / (\lambda_{\text{A}} + \lambda_{\text{Y}}) \approx t_{\text{Y}}(3 \text{ M NaClO}_4) = 0.57$$

and

$$t_{\text{A}} = \lambda_{\text{A}} / (\lambda_{\text{A}} + \lambda_{\text{Y}}) \approx t_{\text{A}}(3 \text{ M NaClO}_4) = 0.43$$

These transport numbers were taken from Ref. 1.

The interaction coefficients are taken from Ref. 1 and the approximation $\tilde{\epsilon}(\text{Na, ClO}_4) \approx \epsilon(\text{Na, ClO}_4) = 0.03$ kg solvent $(\text{mol})^{-1}$ has been used. The value of the function $Q(B, \Delta c_{\text{Y}})$ is, for the titrations T1–T4,

$$Q(B, \Delta c_{\text{Y}}) = 11.83 + 4.88 - 0.76 = 15.95 \text{ mV/M } \Delta c_{\text{Y}}$$

This value is the sum of the following terms

$$(g/z_{\text{B}})\tilde{\epsilon}(\text{B, Y}) = 11.83 \text{ mV/M } \Delta c_{\text{Y}}$$

$$g\lambda_{\text{Y}}/2.303C(\lambda_{\text{A}} + \lambda_{\text{Y}}) = 4.88 \text{ mV/M } \Delta c_{\text{Y}}$$

$$-gt_{\text{A}}\tilde{\epsilon}(\text{A, Y}) = -0.76 \text{ mV/M } \Delta c_{\text{Y}}$$

As is seen, the activity factor change of the potential-determining ion is a dominating term. The ideal diffusion potential change (4.88 mV M^{-1}) cannot be neglected either. The calculated potential contributions for titrations T1–T4 are summarized in Table 2. Here, we show the potential contributions in the first and last titration points. As is seen, we shall obtain $\log \beta_{\text{pqr}}$ values which will increase monotonously in one direction. Consequently, this effect will be interpreted as formation of polynuclear complexes, as

$$\Delta c_{\text{Y}} \equiv c_{\text{Y}} - C = HY_{\text{T}} + z_{\text{B}}B_{\text{T}} - yL_{\text{T}},^5$$

namely depends on B_{T} and L_{T} .

As is seen, these potential contributions show the magnitude of the uncertainty of the equilibrium constants $\log \beta_{\text{pqr}}$, if we do not make correction for the contribution $Q(B, \Delta c_{\text{Y}}) \Delta c_{\text{Y}}$. However, the real uncertainty of the constants determined can be even higher, as the potential contributions $Q(B, b)b$ and $Q(B, I)I$ can also be significant.

Table 1. Survey of the composition of the solutions to be used in titrations T1-T4 ($[Na^+] = 3 M$, constant).

Titration	Solution S	Solution S ₁	Solution S ₂
T1	The system 0.01 M Cd(ClO ₄) ₂ -0.2 M H ₂ L _T -H ⁺ -3 M Na(ClO ₄) 0.01 M Cd(ClO ₄) ₂ ~0.001 M HClO ₄ 0.2 M H ₂ L _T 3 M NaClO ₄ 3.021 M [ClO ₄ ⁻]	0.02 M Cd(ClO ₄) ₂ ~0.005 M HClO ₄ 0.4 M H ₂ L _T 3 M NaClO ₄ 3.045 M [ClO ₄ ⁻]	0.050 M NaOH 2.950 M NaClO ₄
T2	The system 0.1 M Cd(ClO ₄) ₂ -0.5 M H ₂ L _T -H ⁺ -3 M Na(ClO ₄) 0.1 M Cd(ClO ₄) ₂ ~0.001 M HClO ₄ 0.5 M H ₂ L _T 3 M NaClO ₄ 3.201 M [ClO ₄ ⁻]	0.2 M Cd(ClO ₄) ₂ ~0.001 M HClO ₄ 1 M H ₂ L _T 3 M NaClO ₄ 3.401 M [ClO ₄ ⁻]	0.1 M NaOH 2.9 M NaClO ₄
T3	The system 0.1 M Cd(ClO ₄) ₂ -0.5 M Na ₂ L _T -H ⁺ -3 M Na(ClO ₄) 0.1 M Cd(ClO ₄) ₂ 0.5 M Na ₂ L _T 1.001 M HClO ₄ 2 M NaClO ₄ 3.201 M [ClO ₄ ⁻]	0.1 M Cd(ClO ₄) ₂ 0.5 M Na ₂ L _T ~0.001 M HClO ₄ 2 M NaClO ₄ 2.201 M [ClO ₄ ⁻]	
T4	The system 0.01 M Cd(ClO ₄) ₂ -H ⁺ -NaL varied-3 M Na(ClO ₄) 0.01 M Cd(ClO ₄) ₂ ~0.001 M HClO ₄ 3 M NaClO ₄ 3.021 M [ClO ₄ ⁻]	0.01 M Cd(ClO ₄) ₂ 3 M NaL 0.02 M [ClO ₄ ⁻]	

Table 2. The effect of the change of the composition of the ionic medium on E_B , in mV and in $\log \beta_{p,q,r}$ units [$Q(B, \Delta c_Y) = 15.95 \text{ mV/M } \Delta c$].

Effects	Titrations			
	T1	T2	T3	T4
Burette additions/ml	$v_1 = 1, v_2 = 1$	$v_1 = 1, v_2 = 1$	$v_1 = 1$	$v_1 = 1$
c_Y/M	3.0201	3.199 058	3.181 39	2.962 157
$\Delta c_Y/M$	0.0201	0.199 058	0.181 39	-0.037 843
$Q(B, \Delta c_Y) \Delta c_Y/mV$	0.32	3.17	2.89	-0.60
$-(1/g)Q(B, \Delta c_Y) \Delta c_Y$ in $\log \beta_{p,q,r}$ units	-0.005	-0.054	-0.049	0.010
Burette additions/ml	$v_1 = 30, v_2 = 30$	$v_1 = 30, v_2 = 30$	$v_1 = 30$	$v_1 = 30$
c_Y/M	3.008 18	3.173 454	2.826	1.895 625
$\Delta c_Y/M$	0.008 18	0.173 454	-0.174	-1.104 375
$Q(B, \Delta c_Y) \Delta c_Y/mV$	0.13	2.77	-2.77	-17.61
$-(1/g)Q(B, \Delta c_Y) \Delta c_Y$ in $\log \beta_{p,q,r}$ units	-0.002	-0.047	0.047	0.298

The following fundamental equations were used for these calculations: $\log \beta_{p,q,r} = \log [\text{complex}] - q \log h - r \log l - p \log b$, $\log h = (E - E_{OH})/g + D(I) - D(C) - (1/g) \sum_v Q(B, V) V - \text{corr}/g$

Survey of the potential functions for the protolysis of the weak acids HL and H₂L

We shall use the same cell as before, with a glass or H₂(g) indicator electrode. The test solution can be prepared by titrating v ml solution S (being the result of the determination of the constant E_{OH}) with $v_1 = v_2$ ml solution S₁ and S₂. The composition of the solutions used can be:

$$S: \text{HY}_S = [H^+] \approx 10^{-3} M$$

$$c_{HL} = [HL]$$

$$c_{AYS} = [AY] = C - \text{AOH}_{TS}$$

The E_{OH} determination should be evaluated with the help of a Gran plot,¹⁸ in order to check the acid level HY_S .

S₁: $\text{HY}_1 = [\text{H}^+]$, is present in trace amounts

$$2c_{\text{HL}} = [\text{HL}]$$

$$c_{\text{AY}1} = [\text{AY}]$$

S₂: $c_{\text{AOH}2} = [\text{AOH}]$

$$c_{\text{AY}2} = [\text{AY}] = C - c_{\text{AOH}2}$$

We assume that the following chemical reaction takes place in the cell



The composition of the test solution is essentially the same as that one described in Ref. 5. Only for the concentration of the ions in the ionic medium have we different values.

$$c_{\text{A}} = [\text{A}^+] = C M \equiv c_{\text{AY}} + \text{AOH}_{\text{T}}$$

$$c_{\text{Y}} = [\text{Y}^-] = C + \text{HY}_{\text{T}} - \text{AOH}_{\text{T}} = C + \Delta c_{\text{Y}}$$

where

$$\Delta c_{\text{Y}} = \text{HY}_{\text{T}} - \text{AOH}_{\text{T}}$$

The necessary equations for the calculations of ΔE_{H} , valid in this system, can be obtained from those ones presented in Ref. 1 and in this paper. Here, we give only the final results for some important functions

$$I = C + (1/2)(h + \Delta c_{\text{Y}} + lz_{\text{L}}^2) \quad (41)$$

1. *The calculation of the ideal diffusion potential term E_{D} .* The test solution is essentially a mixture of the strong electrolytes AL and AY. Therefore, we shall integrate the function E_{D} with the help of the formulas used in mixtures of strong electrolytes.¹ According to this treatment, we must know the following functions

$$U_{\text{TS}2} - U_{\text{TS}1} = h\lambda_{\text{H}} - \lambda_{\text{Y}}\Delta c_{\text{Y}} - l\lambda_{\text{L}} \quad (42)$$

$$S_{\text{TS}2} - S_{\text{TS}1} = h\lambda_{\text{H}} + \lambda_{\text{Y}}\Delta c_{\text{Y}} + |z_{\text{L}}|l\lambda_{\text{L}} \equiv w \quad (43)$$

$$S_{\text{TS}2} = h\lambda_{\text{H}} + C(\lambda_{\text{A}} + \lambda_{\text{Y}}) + \lambda_{\text{Y}}\Delta c_{\text{Y}} + |z_{\text{L}}|l\lambda_{\text{L}} \equiv w + a \quad (44)$$

Hence, we obtain for small values of w/a

$$E_{\text{D}} = -gF_0(h\lambda_{\text{H}} - \lambda_{\text{Y}}\Delta c_{\text{Y}} - l\lambda_{\text{L}}) \quad (45)$$

2. *The calculation of the contribution of the activity factors to E_{D} , E_{Df} .* We shall follow the same treatment as given in Ref. 5 for the preliminary treatment of equilibrium data. The value of some important functions is

$$\phi_1(x) = x[-h\lambda_{\text{H}} + \lambda_{\text{Y}}\Delta c_{\text{Y}} + l\lambda_{\text{L}}z_{\text{L}}^2] + C(\lambda_{\text{Y}} - \lambda_{\text{A}}) \quad (46)$$

$$\phi_3 = h\lambda_{\text{H}}[\tilde{\epsilon}(\text{H},\text{L})l + \tilde{\epsilon}(\text{H},\text{Y})\Delta c_{\text{Y}}] \quad (47)$$

$$\theta_3 = C\lambda_{\text{A}}[\tilde{\epsilon}(\text{A},\text{L})l + \tilde{\epsilon}(\text{A},\text{Y})\Delta c_{\text{Y}}] - C\lambda_{\text{Y}}\tilde{\epsilon}(\text{H},\text{Y})h \quad (48)$$

$$N \approx wx + a \quad (49)$$

$$\log f_{\text{H}} = -[D(I) - D(C)] + \tilde{\epsilon}(\text{H},\text{L})l + \tilde{\epsilon}(\text{H},\text{Y})\Delta c_{\text{Y}} \quad (50)$$

We obtain for small values of w/a .

$$E_{\text{Df}} \approx \text{corr} - gt_{\text{A}}[\tilde{\epsilon}(\text{A},\text{L})l + \tilde{\epsilon}(\text{A},\text{Y})\Delta c_{\text{Y}}] + gt_{\text{Y}}\tilde{\epsilon}(\text{H},\text{Y})h \quad (51)$$

3. *The total cell e.m.f. for small values of w/a .* For the total e.m.f. of cell H we have, considering $h \sim 0$

$$E_{\text{H}} \approx E_{\text{OH}} + g \log h + \Delta E_{\text{H}} \quad (52a)$$

where

$$\begin{aligned} \Delta E_{\text{H}} &= g \log f_{\text{H}} + E_{\text{D}} + E_{\text{Df}} \\ &\approx -g[D(I) - D(C)] + Q(\text{H},l)l \\ &\quad + Q(\text{H},\Delta c_{\text{Y}})\Delta c_{\text{Y}} + \text{corr} \end{aligned} \quad (52b)$$

If it was found in a separate experiment that the total cell e.m.f. is influenced by the presence of the uncharged molecules HL too, then we can write

$$\begin{aligned} E_{\text{H}} &= E_{\text{OH}} + g \log h - g[D(I) - D(C)] + Q(\text{H},l)l \\ &\quad + Q(\text{H},\Delta c_{\text{Y}})\Delta c_{\text{Y}} + \text{SL}(\text{H},\text{acid})[\text{HL}] + \text{corr} \end{aligned} \quad (53)$$

h can be calculated from eqn. (53) by successive approximations knowing E_{OH} and the potential functions involved. These functions can be estimated in the same way as it was discussed before. It should be noted that [HL] means equilibrium and not total concentration.

The constant E_{OH} can be determined at the beginning of the titration when we can use solution S₀ containing $\text{HY}_{\text{S}0} \approx 25$ mM strong acid. The other components of S₀ can be those ones as used in solution S. Solution S₀ can be titrated with $v_1 = v_2$ ml solution of S₁ and S₂.

During this so called E_0 titration, the hydrogen ion concentration of the test solution can be given as

$$[\text{H}^+] = \text{HY}_{\text{T}} - \text{AOH}_{\text{T}}$$

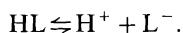
$[\text{H}^+]$ is formally identical with c_{H} in Ref. 1. Thus, the cell can be treated in the same way as it has been done for cell H in the mixture of strong electrolytes, considering $c_{\text{B}} = 0$. This case was discussed in Ref. 1. Therefore, the following potential function is valid

$$\begin{aligned} E_{\text{H}} &= E_{\text{OH}} + g \log [\text{H}^+] - g[D(I) - D(C)] \\ &\quad + \text{SL}(\text{H},c_{\text{H}})[\text{H}^+] + \text{SL}(\text{H},\text{acid})[\text{HL}] + \text{corr} \end{aligned} \quad (54)$$

The intercept of the plot $E_{\text{H}} - g \log [\text{H}^+] + g[D(I) - D(C)] - \text{SL}(\text{H},\text{acid})[\text{HL}] - \text{corr}$ vs. $[\text{H}^+]$ will result in E_{OH} . The slope of this plot is $\text{SL}(\text{H},c_{\text{H}})$.

4. *EMF titration suggested for the determination of the experimental slope function $\text{SL}(\text{H},l)_{\text{exptl}}$ and the proof of the usefulness of the derived equations.* The knowledge of the experimental slope function $\text{SL}(\text{H},l)_{\text{exptl}}$ is very useful for the estimation of the function $Q(\text{H},l)$, moreover, for the calculation of an approximate starting value of λ_{L} in the interpretation of the conductivity data of an equilibrium system. Moreover, as the experimental slope functions are the result of the changes of the ion concentrations going on and the ionic molar conductivities, we have in the transition layer of the junction studied, they can be used for checking the theory presented here.

We shall study the protolysis



We shall titrate with a solution containing the buffer system HL-AL in the determination of the slope function $\text{SL}(\text{H}, l)$ in order to assure a stable and negligible level for the concentration of the H^+ ions. The concentration of the acid component HL, in the solutions used, has to be chosen in such a way that $3 \leq -\log[\text{H}^+] \leq 10$ in the test solution. Hence, neither the H^+ nor the OH^- ions are present in a 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. We use the same cell as before. If the $-\log[\text{H}^+]$ of the test solution studied is less than 9, then a glass electrode can be used. Otherwise a hydrogen gas electrode is necessary. First, the constant of the Nernst equation, E_{OH} , should be determined as discussed under Section 3. This can be done either in the presence or in the absence of HL. When we reached the acidity level $-\log[\text{H}^+] = 3$, the E_0 titration should be considered as fulfilled. It should be evaluated with the help of a Gran plot.¹⁸

Then we can decrease the volume of the test solution to v_0^* , if it is necessary, by sucking out a known volume of the solution with a pipette calibrated to inlet. We assume that the constant E_{OH} was determined in the absence of HL. Then totally v_2 ml solution S_2 should be added to v_0^* ml test solution, in several steps. Solution S_2 can have the composition S_2 , 0.1 M HL; 1.8 M AL $\equiv L_{\text{T}}$ and $C - L_{\text{T}}$ M AY = 1.2 M AY.

Now, we have the following species in the test solution: H^+ , L^- , HL, A^+ and Y^- . It is obvious that the protolysis of the HL molecules will be strongly pressed back by the high concentration of the salt component used, in the test solution. Therefore, we can use the following approximations:

$$[\text{HL}] \simeq [\text{acid}]_{\text{F}}$$

$$[\text{L}^-] = l \simeq [\text{salt}]_{\text{F}} \equiv L_{\text{T}}$$

Consequently, the acidity of the test solution can be calculated as

$$\log[\text{H}^+] \cong \log K_1 - \log([\text{salt}]_{\text{F}}/[\text{acid}]_{\text{F}}) \quad (55)$$

Here, F denotes formal concentration and K_1 is the protolysis constant. During this titration, the $\log[\text{H}^+]$ of the test solution will be constant, because the ratio $[\text{salt}]_{\text{F}}/[\text{acid}]_{\text{F}}$ is constant. For the ion concentration of the ionic medium in the test solution we have

$$c_{\text{A}} = C M, \text{ constant} = c_{\text{AY}} + \text{AOH}_{\text{T}} + L_{\text{T}}$$

$$c_{\text{Y}} = C - \text{AOH}_{\text{T}} - L_{\text{T}} + \text{HY}_{\text{T}}$$

$$\Delta c_{\text{Y}} = c_{\text{Y}} - C = \text{HY}_{\text{T}} - \text{AOH}_{\text{T}} - L_{\text{T}} = -L_{\text{T}} \quad (56a)$$

as $\text{HY}_{\text{T}} - \text{AOH}_{\text{T}} \simeq 0$ at the end of the E_0 titration.

4.1. *The presentation of the theoretical and experimental slope function for the system studied, if $-\log[\text{H}^+] \leq 7$ in*

the test solution. The necessary equations for the deduction of the value ΔE_{H} , in the present system, can be obtained from those ones presented in Sections 3 and 4. Here, we give only the final results for some important functions. Considering the composition of the test solution, we have, now

$$I = C + (1/2)(h \simeq 0) \quad (56b)$$

$$w = h\lambda_{\text{H}} + (\lambda_{\text{L}} - \lambda_{\text{Y}})L_{\text{T}} \quad (57)$$

a has the same meaning as before [cf. eqn. (3)]

$$\log f_{\text{H}} = -[D(I) - D(C)] + \tilde{\epsilon}(\text{H}, \text{L})L_{\text{T}} - \tilde{\epsilon}(\text{H}, \text{Y})L_{\text{T}} \quad (58)$$

$$\phi_1(x) = x[-h\lambda_{\text{H}} + (\lambda_{\text{L}} - \lambda_{\text{Y}})L_{\text{T}}] + C(\lambda_{\text{Y}} - \lambda_{\text{A}}) \quad (59)$$

According to the earlier treatment of the problem, presented in Ref. 1 and here, we obtain eqn. (53) for the total cell e.m.f. E_{H} and for small values of w/a . Moreover, we can also write

$$E_{\text{H}} = E_{\text{OH}} + g \log h + \text{SL}(\text{H}, \text{acid})[\text{HL}] + \text{SL}(\text{H}, l) - g[D(I) - D(C)] + \text{corr} \quad (60a)$$

and

$$\begin{aligned} \Delta E_{\text{H}} &\equiv g \log f_{\text{H}} + E_{\text{D}} + E_{\text{Df}} \\ &= -g[D(I) - D(C)] + \text{SL}(\text{H}, \text{acid})[\text{HL}]_{\text{F}} \\ &\quad + \text{SL}(\text{H}, l) + \text{corr} \end{aligned} \quad (60b)$$

$\text{SL}(\text{H}, l)$ is the slope of the plot E_{H}'' versus $l = L_{\text{T}}$. Considering eqns. (52a) and (52b), we have

$$\begin{aligned} E_{\text{H}}'' &\equiv E_{\text{H}} - g \log h + g[D(I) - D(C)] \\ &\quad - \text{SL}(\text{H}, \text{acid})[\text{HL}]_{\text{F}} - \text{corr} \\ &= E_{\text{OH}} + Q(\text{H}, l)l + Q(\text{H}, \Delta c_{\text{Y}})\Delta c_{\text{Y}} \end{aligned} \quad (60c)$$

Considering eqns. (29), (30) and Δc_{Y} , for the calculated slope function we obtain

$$\begin{aligned} \text{SL}(\text{H}, l) &\equiv \frac{dE_{\text{H}}''}{dl} = g[\tilde{\epsilon}(\text{H}, \text{L}) - \tilde{\epsilon}(\text{H}, \text{Y})] - gF_0(\lambda_{\text{Y}} - \lambda_{\text{L}}) \\ &\quad - gt_{\text{A}}[\tilde{\epsilon}(\text{A}, \text{L}) - \tilde{\epsilon}(\text{A}, \text{Y})] \end{aligned} \quad (61)$$

It is important to emphasize that this slope function is valid only in the case when a buffer solution of suitable concentration was used as a titrating solution and the approximations $[\text{HL}] \simeq [\text{acid}]_{\text{F}}$ and $l \simeq [\text{salt}]_{\text{F}}$ is valid. This is not the case when we titrate with dilute NaOH and a solution containing HL. In this case the function $Q(\text{H}, l)$ describes the potential contribution of the ligand in the preliminary data treatment. Therefore, the function $\text{SL}(\text{H}, l)$ must be recalculated to $Q(\text{H}, l)$.

In order to get the experimental slope function $\text{SL}(\text{H}, l)$, eqn. (55) should be inserted into eqn. (60a). Then we obtain

$$\begin{aligned} E_{\text{H}}'' &\equiv E_{\text{H}} + g[D(I) - D(C)] - \text{SL}(\text{H}, \text{acid})[\text{HL}]_{\text{F}} - \text{corr} \\ &\quad + g \log([\text{salt}]_{\text{F}}/[\text{acid}]_{\text{F}}) \\ &= \text{constant} + \text{SL}(\text{H}, l)L_{\text{T}} \end{aligned} \quad (62)$$

where

$$\text{constant} = E_{OH} + g \log K_1 \quad (63)$$

As is seen, the slope of the plot E_H'' vs. L_T gives $SL(H,l)$ and from the intercept = constant the protolysis constant $\log K_1$ can be obtained with high accuracy in a broad concentration range. This graphical method is the correct way for the determination of $\log K_1$ and this treatment does not result in the suggestion of non-existing dimer, trimer and so on 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.

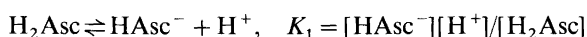
If we want to recalculate $SL(H,l)$ into $Q(H,l)$, first, the difference function given below should be formed

$$\begin{aligned} Q(H,l) - SL(H,l)_{\text{exptl}} \\ \equiv \text{eqn. (29)} - \text{eqn. (61)} \\ = g\tilde{\epsilon}(H,Y) + g\lambda_Y F_0 - gt_A \tilde{\epsilon}(A,Y) \end{aligned} \quad (64)$$

Using the known value for the experimental slope function $SL(H,l)_{\text{exptl}}$, $Q(H,l)$ can be calculated from eqn. (64).

4.2. *The study of the H^+ -Ascorbate⁻ and H^+ -acetate⁻ systems, as a proof of the theory.* The protolysis of the systems given in the title was studied by potentiometric titrations at different experimental conditions. The cell was the same as defined in the introduction. We used a glass electrode as measuring electrode. $NaClO_4$ ionic medium was used in all experiments at $[Na^+] = 3$ M kept constant.

4.2.1. *The H^+ -Ascorbate⁻ system.* After the determination of E_{OH} , this system was studied by potentiometric titrations, as described in Section 4.1, at the experimental conditions given below. The equilibrium studied is



4.2.1.1. We chose $[H_2Asc]_F = 0.29749$ M kept constant. Here, H_2Asc denotes ascorbic acid. 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. 1, based upon eqn. (62). Here, we obtained from the slope of this plot the slope function

$$SL(H,HAsc) = -7.6 \text{ mV/M } HAsc^-$$

valid in the buffer system. From the intercept of the plot given in Fig. 1, the following value was obtained for the protolysis constant

$$\log K_1 = -4.348 \pm 0.002$$

This slope function was recalculated to the function $Q(H,l)$, according to eqn. (64).

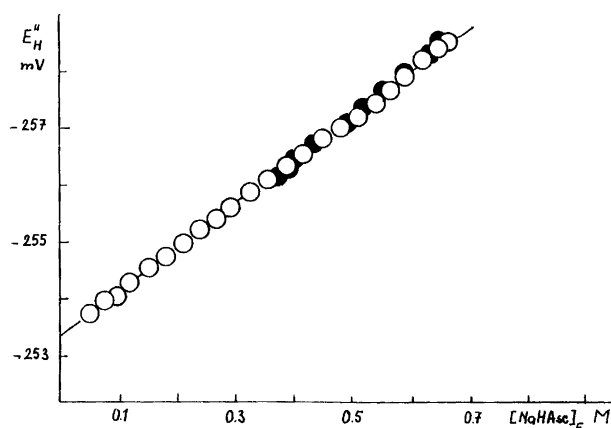


Fig. 1. The determination of the slope function $SL(H, HAsc)$ and the first protolysis constant of the ascorbic acid, $\log K_1$, at $[H_2Asc]_F = 0.29749$ M, is kept constant, and $[Na^+] = 3$ M, is kept constant. The plot of E_H'' vs. $[NaHAsc]_F$ is based upon eqn. (62). Filled symbols denote back titration.

$$\begin{aligned} Q(H,l) &= SL(H,l)_{\text{exptl}} + \text{difference function} \\ &= -7.6 + 14.8 = 7.2 \text{ mV/M } HAsc^- \end{aligned}$$

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 3. Hence, the total systematic error at $[NaHAsc] = 1$ M is -8.7 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.

4.2.1.2. Now 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. 2. The graphical treatment of the data resulted in the following results

$$SL(H,HAsc) = -8.1 \text{ mV/M } NaHAsc$$

$$\log K_1 = -4.359 \pm 0.002$$

As we can see, 0.009 unit difference appears between the protolysis constants obtained until now. This can be the

Table 3. Survey of the potential contributions to the total potential anomalies in the H^+ - $HAsc^-$ system, when dilute $NaOH$ and H_2Asc 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	$\longleftarrow 13^{19} [H_2Asc]$	0 mV
(b) The effect of the ligand $HAsc^-$:		
at $[NaHAsc] = 0$ M		$[NaHAsc] = 1$ M
0 mV	$\longrightarrow Q(H,HAsc)[HAsc^-]$	7.2 mV
(c) The effect of the composition change of the ionic medium:		
0 mV	$\longrightarrow Q(H,\Delta c_Y)\Delta c_Y$	-15.9 mV

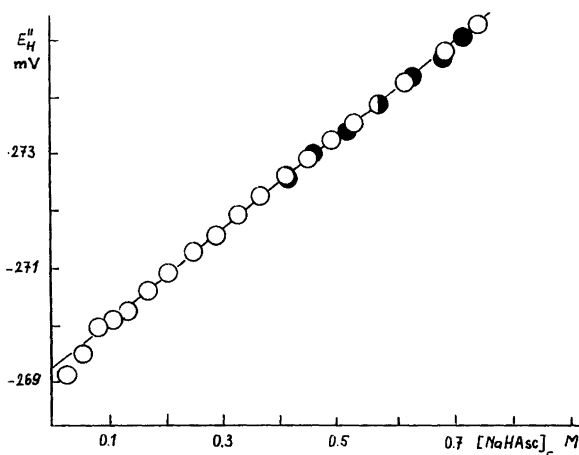


Fig. 2. The determination of the slope function $SL(H, HAsc)$ and the first protolysis constant of the ascorbic acid, $\log K_1$, at $[H_2Asc]_F = 0.100$ M, is kept constant, and $[Na^+] = 3$ M, is kept constant. The plot of E_H'' vs. $[NaHAsc]_F$ is based upon eqn. (62). Filled symbols denote back titration.

result of some changes in the contribution of the H_2Asc molecules and/or the change of the value of E_{OH} .

4.2.1.3. A titration was carried out at constant $[acid]_F/[salt]_F$ ratio, too, which was equal to 0.186 20. The constant E_{OH} was determined in the absence of H_2Asc . During the main titration we used the following solution in the burette: 0.299 41 M H_2Asc , 1.607 99 M $NaHAsc$ and 1.392 01 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. 3. The graphical treatment of the data resulted in the following results

$$SL(H, HAsc) = -9.6 \text{ mV/M } HAsc^-$$

$$\log K_1 = -4.359 \pm 0.002$$

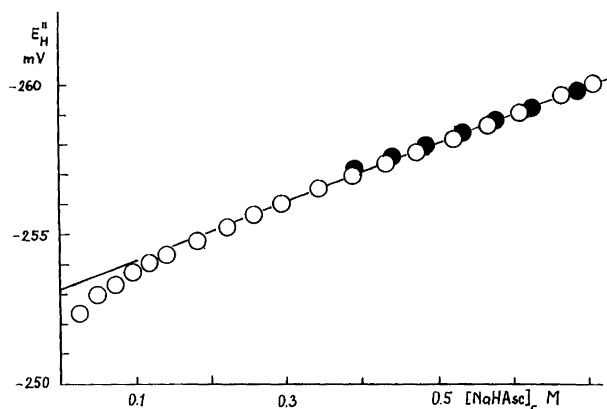
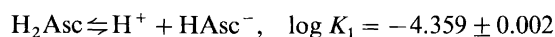


Fig. 3. The determination of the slope function $SL(H, HAsc)$ and the first protolysis constant of the ascorbic acid, $\log K_1$, at constant $[acid]_F/[salt]_F$ ratio, which was equal to 0.186 20, and $[Na^+] = 3$ M, is kept constant. The plot of E_H'' vs. $[NaHAsc]_F$ is based upon eqn. (62). Filled symbols denote back titration.

As is seen, all data could be explained by the equilibrium



which could be obtained in a broad concentration range without the suggestion of dimer, trimer, etc. species.

These titration data were also treated by linear regression analysis. Equation (62) was fitted to the data. We obtained very similar results to those discussed above,

For the forward titration:

$$SL(H, HAsc^-) = -9.8 \text{ mV/M } HAsc^-$$

$$\log K_1 = -4.356$$

For the back titration we obtained:

$$SL(H, HAsc^-) = -8.8 \text{ mV/M } HAsc^-$$

$$\log K_1 = -4.366$$

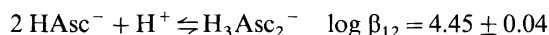
The average of $\log K_1 = -4.361 \pm 0.005$.

This system was also studied by Wahlberg and Ulmgren¹⁹ in the concentration range $0 \leq [H_2Asc]_T \leq 1$ M. The data were explained by assuming the following equilibrium processes

(i) for $[H_2Asc]_T \leq 0.1$ M



(ii) for $[H_2Asc]_T \geq 0.25$ M



As is seen, our result for $\log K_1$ is exactly the same as that obtained in Ref. 19 at a low concentration of H_2Asc , namely ≤ 0.1 M. Hence, we can conclude that the species $H_3Asc_2^-$ and H_4Asc_2 are artifacts. They appear due to the neglect of important potential contributions at the explanation of the data. The $\log K_1$ value in this system should be correctly calculated as given below [cf. eqn. (62)].

$$\log K_1 = (1/g)\{E_H - E_{OH} - SL(H, HL)[HL]_F$$

$$- SL(H, L)[AL]_F - \text{corr}\}$$

$$+ [D(I) - D(C)] - \log[HL]_F/[AL]_F \quad (65)$$

By the neglect of the effect of the ligand ions on $\log K_1$, $SL(H, L)[AL]_F$, the caused systematic error in $\log K_1$ will be for the acid H_qL

$$\Delta \log K_1 \equiv q \Delta \log h = q(1/g) SL(HL)[AL]_F \quad (66)$$

This will result in monotonously increasing equilibrium constant, as seen from Table 4. This effect will be interpreted as the formation of dimer, trimer etc. species, which are artifacts.

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 $SL(H, I)$ and the study of metal complex formation must be carried out in the same way.

Table 4. The estimation of the systematic error in the first dissociation constant of the ascorbic acid ($\log K_1$) caused by the neglect of the potential contribution of the HAscorbate⁻ ions to ΔE_H : $SL(H, HAsc^-)$ [HAsc⁻]_F in mV, using NaClO₄ ionic medium at [Na⁺]=3 M, constant, and the cell $-RE \parallel 3 M NaClO_4 \parallel Test\ soln | GE +$. The slope $SL(H, HAsc^-) = -8.1$ mV/M was used.

[NaHAsc] _F /M	Neglected effect/mV	$\Delta \log K_1$ [cf. eqn. (66)]
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 found¹⁹ at low concentrations: -4.359 ± 0.006 .

4.2.1.4. The slope function $SL(H, H_2Asc) = 13$ mV/M H₂Asc was determined in Ref. 19, on the basis of the change of E_{OH} with [H₂Asc]_T. This slope function was checked by the author in the following mixture: 10 mM HClO₄, 0.100 M Cd(ClO₄)₂ and 3 M NaClO₄. All of these concentrations were kept constant and H₂Asc was varied in the range 0.15–0.3 M. Here, we obtained

$$SL(H, H_2Asc) = 22.9 \text{ mV/M H}_2\text{Asc}$$

As is seen, the value of this slope function changes with the experimental conditions.

4.2.2. *The H⁺-acetate⁻ system.* This system was also studied by potentiometric titrations at different experimental conditions, in a similar way as described in the previous section for the H⁺-Ascorbate⁻ system.

4.2.2.1. A potentiometric titration was carried out at constant ratio of [acid]_F/[salt]_F which was equal to 0.1000. 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 eqn. (62). For the slope function $SL(H, HAc)$ the value $6.7 \text{ mV M}^{-1} \text{ HAc}$ was used, determined by the author in a cell free from liquid junctions and at [HClO₄]=50 mM kept constant. The plot is shown in Fig. 4. The results given in Table 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 the burettes. From the intercept of the plot in question [cf. eqn. (62)], the following constant was obtained for the protolysis of acetic acid in 3 M NaClO₄:

$$\log K_1 = -5.026 \pm 0.002$$

In the 'Stability Constants'²⁰ the following values can be

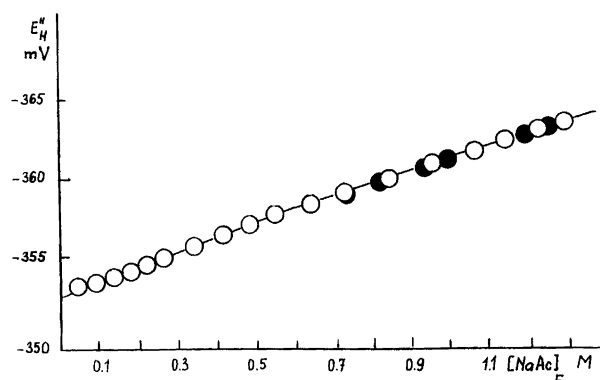


Fig. 4. The determination of the slope function $SL(H, Ac)$ and the protolysis constant of the acetic acid, $\log K_1$, at constant ratio of [acid]_F/[salt]_F which was equal to 0.1000, and [Na⁺]=3 M, is kept constant. The plot of E_H'' vs. [NaAc]_F is based upon eqn. (62). Filled symbols denote back titration.

Table 5. The determination of the slope function $SL(H, Ac)$ and the function $Q(H, Ac)$, using the plot defined by eqn. (62) for the cell Ref. half-cell $\parallel 3 M NaClO_4 \parallel Test\ solution | glass\ electrode$.

[NaAc] _F /M	$SL(H, Ac)$ /mV M ⁻¹ NaAc	$Q(H, Ac)$ /mV M ⁻¹ NaAc
0–0.58	-9.1	5.6
0.58–1.3	-7.7	7.1

found:

$$\log K_1 = -5.017 \quad (\text{Ref. 21})$$

$$= -5.02 \pm 0.01 \quad (\text{Ref. 22})$$

$$= -5.01 \quad (\text{Ref. 23})$$

This titration data were also treated by linear regression analysis. Equation (62) was fitted to the data. The following results were obtained.

For the forward titration:

$$0 \leq [NaAc] \leq 0.58 \text{ M}$$

$$SL(H, Ac^-) = -9.3 \text{ mV M}^{-1} \text{ Ac}^-$$

$$\log K_1 = -5.024$$

$$0.58 \leq [NaAc] \leq 1.3 \text{ M}$$

$$SL(H, Ac^-) = -7.8 \text{ mV/M Ac}^-$$

$$\log K_1 = -5.039$$

For the back titration:

$$SL(H, Ac^-) = -8.0 \text{ mV/M Ac}^-$$

$$\log K_1 = -5.035$$

For the average value we obtained: $\log K_1 = -5.033 \pm 0.006$. We can see that this value of $\log K_1$ agrees well with that one obtained above.

As is seen, the same $\log K_1$ value was obtained as it was published by other scientists for low concentrations of HAc_T. No dimers or trimers were found, even though

Table 6. The estimation of the systematic error in the dissociation constant of the acetic acid ($\log K_1$) caused by the neglect of the potential contribution of the acetate⁻ ions to ΔE_H : SL(H,Ac) [Ac⁻]_F in mV, using NaClO₄ ionic medium at [Na⁺]=3 M, constant, and the cell -RE||3 M NaClO₄||Test soln|GE+.

[NaAc] _F /M	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 .

such species were reported in the 'Stability Constants'. The neglect of the effect of the acetate ions on $\log K_1$ will result in monotonically increasing equilibrium constant, as seen from Table 6. This can be interpreted as the formation of dimer species, which are artifacts.

Persson has investigated²³ this system in NaClO₄ ionic medium at $I=3$ M, constant, in an e.m.f. cell with poles opposite 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 liquid junction and with liquid junction. In both cases, the author could describe the measurements by assuming the presence of the species HAc, Ac⁻, HAc₂⁻ and (HAc)₂. However, he pointed out that the formation of the 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

$$SL(H,HAc) = -6.7 \text{ mV M}^{-1} \text{ HAc}$$

$$SL(H,Ac) = 7.7 \text{ mV M}^{-1} \text{ NaAc}$$

As is seen, the maximum value of the systematic error, at [NaAc]_F=1 M, was 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.

$$E_H = E_{OH} - g \log[H^+] - g \log f_H - g \log[Cl^-] - g \log f_{Cl} - 6.7[HAc] \quad (67)$$

We can write according to the specific ionic interaction theory

$$\log f_H = -[D(I) - D(3)] + \tilde{\epsilon}(H,ClO_4)(c_Y - 3) + \tilde{\epsilon}(H,Ac)[NaAc]_F \quad (68)$$

$$\log f_{Cl} = -[D(I) - D(3)] + \tilde{\epsilon}(Na,Cl)(c_{Na} - 3) + \tilde{\epsilon}(H,Cl)[H^+] \quad (69)$$

As is seen, these activity factors are not constant.

The change of $\log f_H$ is especially significant. Here, $\tilde{\epsilon}(H,ClO_4)=0.18^1$ litre solution mol⁻¹, $\tilde{\epsilon}(H,Ac)=0.12$ litre solution mol⁻¹ determined¹⁷ by the author and $\tilde{\epsilon}(Na,Cl)\approx 0.03$ litre solution mol⁻¹.¹

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.

4.2.2.2. Some titrations were carried out at constant level of acetic acid too. The purpose of these experiments was to show how the magnitude of the slope function SL(H,Ac) changes with the experimental conditions.

In one case we chose [HAc]_F=0.010 M, is kept constant. Here, we obtained the following slope functions

$$0 \leq [Na,Ac]_F \leq 90 \text{ mM,}$$

$$SL(H,Ac) = -28.2 \text{ mV/M Ac}^-$$

$$90 \leq [Na,Ac]_F \leq 215 \text{ mM,}$$

$$SL(H,Ac) = -11.2 \text{ mV/M Ac}^-$$

$$215 \leq [Na,Ac]_F \leq 450 \text{ mM,}$$

$$SL(H,Ac) = -8.3 \text{ mV/M Ac}^-$$

In another titration, we chose [HAc]_F=1.000 M, is kept constant. The slope function

$$SL(H,Ac) = -9.5 \text{ mV/M Ac}^-$$

was obtained in the concentration range $0 \leq [NaAc]_F \leq 250$ mM. These changes correspond to the change of the ionic molar conductivities. The change of the slope function with the experimental conditions cannot be explained on the basis of the present theory. 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 studied²⁴ the appearance of the liquid junction potential in the H⁺-acetate⁻ system, using buffer solutions, at different [acid]_F/[salt]_F ratios, which were kept constant during one titration. 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 [acid]_F/[salt]_F ratios studied. Moreover, Olin and Svanström have modelled the influence of varying liquid junction potentials and activity coefficients on calculated stability constants of the Pb²⁺-benzoate, Cd²⁺-benzoate and Pb²⁺-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 e.m.f. measurements of central ion concentrations. Realistic estimates of the uncertainties in these constants can therefore be obtained only by a study of these influences.'

4.2.2.3. The value of the slope function SL(H,HAc)_F was also checked in two different cells.

4.2.2.3.1. In a cell with liquid junction the test solution contained [HClO₄]=50 mM, kept constant, 3 M NaClO₄, kept constant and [HAc]_F was varied in the

range 0–0.45 M. Here, we obtained

$$0 \leq [\text{HAc}]_F \leq 180 \text{ mM},$$

$$\text{SL}(\text{H}, \text{HAc}) = 2.2 \text{ mV/M HAc}$$

$$180 \leq [\text{HAc}]_F \leq 45 \text{ mM},$$

$$\text{SL}(\text{H}, \text{HAc}) = 3.0 \text{ mV/M HAc}$$

4.2.2.3.2. In the cell given below, free from liquid junctions,

Ag, AgCl | Test solution | glass electrode

at $[\text{HClO}_4] = 50 \text{ mM}$, kept constant, and $[\text{Cl}^-] = 10 \text{ mM}$, kept constant, the following results were obtained

$$0 \leq [\text{HAc}]_F \leq 90 \text{ mM},$$

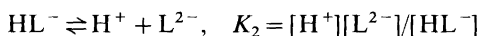
$$\text{SL}(\text{H}, \text{HAc}) = 7.4 \text{ mV/M HAc}$$

$$90 \leq [\text{HAc}]_F \leq 390 \text{ mM},$$

$$\text{SL}(\text{H}, \text{HAc}) = 8.4 \text{ mV/M HAc}$$

As is seen, the potential contribution of the undissociated molecules HL to the 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 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.

5. The calculation of the second protolysis constant of the acid H_2L . We shall study the equilibrium



in the ionic medium AY during the experimental condition that $[\text{A}^+] = C \text{ M}$ is kept constant. The values of $\log K_1$ and $\log K_2$ should be well separated. First we determine the constant E_{OH} in the absence of the ligand as it was described earlier. During the main titration we can add a solution with the composition 0.2 M AHL + 1 M A_2L + 0.8 M AY. In our equilibrium solution, the following ions are present: H^+ , $[\text{HL}^-] = [\text{acid}]_F$, $l = [\text{L}^{2-}] \equiv [\text{salt}]_F \equiv L_T$, Y^- and $[\text{A}^+] = C \text{ M}$. The acidity of the test solution can be calculated as

$$\log[\text{H}^+] = \log K_2 - \log([\text{salt}]_F/[\text{acid}]_F) \quad (70)$$

The composition of the test solution is also described in Ref. 5.

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.

For the calculation of the ideal diffusion potential term, E_D , we have [cf. eqn. (28) in Ref. 5]

$$E_D = -(g/2.303) \int_{\text{TS1}, x=0}^{\text{TS2}, x=1} (1/N) \times [\lambda_{\text{H}}h - \lambda_{\text{L}}l - \lambda_{\text{HL}}2[\text{acid}]_F x - \lambda_{\text{Y}}\Delta c_{\text{Y}}] dx \quad (71)$$

where

$$c_{\text{A}} = C \text{ M constant} = c_{\text{AY}} + \text{AOH}_T + yL_T + \text{HL}_T^- \text{ M} \quad (72)$$

$$c_{\text{Y}} = C - \text{AOH}_T - yL_T - \text{HL}_T^- + \text{HY}_T = C + \Delta c_{\text{Y}} \text{ M} \quad (73)$$

$$\Delta c_{\text{Y}} = c_{\text{Y}} - C = -yL_T - \text{HL}_T^- \text{ M} \quad (74)$$

$$N = [\lambda_{\text{H}}h + \lambda_{\text{L}}2l - \lambda_{\text{Y}}(L_T y + \text{HL}_T^-)]x + C(\lambda_{\text{A}} + \lambda_{\text{Y}}) + \lambda_{\text{HL}}[\text{acid}]_F x^2 \quad (75)$$

as given in eqns. (29a–c) of Ref. 5. Then E_D can be obtained by graphical integration of eqn. (71). Here, HL_T^- denotes the total concentration of AHL.

For the calculation of the contribution of the activity coefficients to the diffusion potential, E_{Df} , we have [cf. eqn. (34b) in Ref. 5]

$$E_{\text{Df}} = -g \int_{\text{TS1}, x=0}^{\text{TS2}, x=1} (1/N) \times \left\{ -\frac{dD(I^*)}{dx} [xh\lambda_{\text{H}} + C\lambda_{\text{A}} - xl\lambda_{\text{L}}z_{\text{L}}^2 - (C + x\Delta c_{\text{Y}})\lambda_{\text{Y}} - [\text{acid}]_F x^2 \lambda_{\text{HL}}] + xh\lambda_{\text{H}} - (C + x\Delta c_{\text{Y}})\lambda_{\text{Y}} - [\text{acid}]_F x^2 \lambda_{\text{HL}} + xh\lambda_{\text{H}} \times \{ \tilde{\epsilon}(\text{H}, \text{L})l + \tilde{\epsilon}(\text{H}, \text{HL})2[\text{acid}]_F x + \tilde{\epsilon}(\text{H}, \text{Y})\Delta c_{\text{Y}} \} + C\lambda_{\text{A}} \{ \tilde{\epsilon}(\text{A}, \text{L})l + \tilde{\epsilon}(\text{A}, \text{HL})2[\text{acid}]_F x + \tilde{\epsilon}(\text{A}, \text{Y})\Delta c_{\text{Y}} \} \right\} dx \quad (76)$$

E_{Df} can be obtained by graphical integration of eqn. (76).

Moreover, $\log f_{\text{HTS2}}$ is needed for the calculation of the total cell e.m.f., E_{H} .

$$\log f_{\text{HTS2}} = -[D(I) - D(C)] + \tilde{\epsilon}(\text{H}, \text{L})l + \tilde{\epsilon}(\text{H}, \text{HL})[\text{acid}]_F + \tilde{\epsilon}(\text{H}, \text{Y})\Delta c_{\text{Y}} \quad (77)$$

The term $dD(I^*)/dx$ is given by eqn. (34) and I^* by eqn. (29), both in Ref. 1.

For the total cell e.m.f., E_{H} , we have

$$E_{\text{H}} = E_{\text{OH}} + g \log[\text{H}^+] + g \log f_{\text{HTS2}} + E_D + E_{\text{Df}} \quad (78)$$

inserting $\log[\text{H}^+]$, given by eqn. (70), into eqn. (78), we have for $\log K_2$

$$1/g \left\{ E_{\text{H}} - g \log \frac{[\text{acid}]_F}{[\text{salt}]_F} - g \log f_{\text{HTS2}} - E_D - E_{\text{Df}} - E_{\text{OH}} \right\} = \log K_2 \quad (79)$$

The determination of some interaction coefficients, $\tilde{\epsilon}_j$, will be discussed in Part 7, to be published.

We can use a simpler alternative method too for the determination of $\log K_2$ utilizing the fact that the buffer system AHL– A_2L is a mixture of strong electrolytes.

Determination of $\log K_2$ with the help of the slope functions $\text{SL}(\text{H}, \text{HL}^-)$ and $\text{SL}(\text{H}, \text{L})$. $\log K_2$ can also be determined in the buffer system AHL– A_2L given above, from the known slope function $\text{SL}(\text{H}, \text{HL}^-)$ and $\text{SL}(\text{H}, \text{L})$ which should be determined. The potentiometric titration

can be carried out at the constant ratio of $[AHL^-]_F/[A_2L]_F$. 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 above. The total cell e.m.f. in this system is

$$E_H = E_{OH} + g \log h - g[D(I) - D(C)] + SL(H,HL^-)[HL^-]_F + SL(H,L)[L]_F + \text{corr} \quad (80)$$

Inserting $\log h$ from eqn. (70) into eqn. (80), we can form the function E'' and neglect 'corr'

$$E'' \equiv E_H + g \log \frac{[\text{salt}]_F}{[\text{acid}]_F} + g[D(I) - D(C)] - SL(H,HL^-)[HL^-]_F = E_{OH} + g \log K_2 + SL(H,L)[L]_F \quad (81)$$

The slope $SL(H,HL^-)$ can be determined as in the $H_2Asc-NaHAsc$ buffer system, described in Chapter 4 according to eqn. (62). Plotting the function E'' vs. $[L]_F$, $\log K_2$ can be calculated from the intercept

$$\log K_2 = (\text{Intercept} - E_{OH})/g \quad (82)$$

The slope of this plot is $SL(H,L)$.

If we use the same ratio of $[\text{salt}]_F/[\text{acid}]_F$ as above, the pH of the test solution will be around 12. Therefore, the use of $H_2(g)$ electrode is necessary in both cases.

The theoretical potential functions, defined in Parts 1 and 5 and valid in the mixtures of $AHL + A_2L + AY$, can be obtained by repeating the deduction for this system. The deduction is based on the following ion concentrations at some intermediate plane of the transition layer:

$$h^* = xh, \quad [HL^-]^* = xHL_T^-, \quad [L]^* \equiv xL_T,$$

$$c_A^* = C, \quad c_Y^* = C + x\Delta c_Y$$

The results given below can be obtained.

$$\theta_2 = U_{TS2} - U_{TS1} \quad [\text{cf. eqn. (16) in Part 1}] = h\lambda_H - \lambda_Y\Delta c_Y - HL_T^- \lambda_{HL} - L_T \lambda_L \quad (83)$$

$$w \equiv S_{TS2} - S_{TS1} \quad [\text{cf. eqn. (17) in Part 1}] = h\lambda_H + \lambda_Y\Delta c_Y + HL_T^- |z_{HL}| \lambda_{HL} + L_T |z_L| \lambda_L \quad (84)$$

For small values of w/a , we have

$$E_D \approx -g[h\lambda_H - \lambda_Y\Delta c_Y - HL_T^- \lambda_{HL} - L_T \lambda_L] / \{2.303C(\lambda_A + \lambda_Y)\} \quad (85)$$

$$\log f_{HTS2} = -[D(I) - D(C)] + \tilde{\epsilon}(H,L)L_T + \tilde{\epsilon}(H,HL)HL_T^- + \tilde{\epsilon}(H,Y)\Delta c_Y \quad (86)$$

$$F_1(x) = x[-h\lambda_H + HL_T^- \lambda_{HL} + L_T \lambda_L z_L^2 + \lambda_Y\Delta c_Y] + C(\lambda_Y - \lambda_A) \quad (87)$$

$$\phi_3 = h\lambda_H[\tilde{\epsilon}(H,L)L_T + \tilde{\epsilon}(H,HL)HL_T^- + \tilde{\epsilon}(H,Y)\Delta c_Y] - HL_T^- \lambda_{HL} \tilde{\epsilon}(H,HL)h - L_T \lambda_L \tilde{\epsilon}(H,L)h - \Delta c_Y \lambda \tilde{\epsilon}(H,Y)h \quad (88)$$

$$\theta_3 = C\lambda_A[\tilde{\epsilon}(A,L)L_T + \tilde{\epsilon}(A,HL)HL_T^- + \tilde{\epsilon}(A,Y)\Delta c_Y] - C\lambda_Y \tilde{\epsilon}(H,Y)h \quad (89)$$

For small values of w/a , we obtain

$$E_{Df} \approx \text{corr} - gt_A[\tilde{\epsilon}(A,L)L_T + \tilde{\epsilon}(A,HL)HL_T^- + \tilde{\epsilon}(A,Y)\Delta c_Y] + gt_Y \tilde{\epsilon}(H,Y)h \quad (90)$$

t_A and t_Y are given by eqn. (19).

For the total cell e.m.f. in cell H, we obtain eqn. (80), where the function $SL(H,HL^-)$ is given by eqn. (61) and $SL(H,L)$ is

$$SL(H,L) = g[\tilde{\epsilon}(H,L) - y\tilde{\epsilon}(H,Y)] + g(\lambda_L - y\lambda_Y)/\{2.303C(\lambda_A + \lambda_Y)\} - gt_A[\tilde{\epsilon}(A,L) - y\tilde{\epsilon}(A,Y)] \quad (91)$$

These equations are valid for the buffer systems studied. If we use $AOH + H_2L$ or A_2L as titrating solution, we must recalculate $SL(H,L)$ into $Q(H,l)$. We form the difference function $Q(H,l) - SL(H,L) = \text{eqn. (29)} - \text{eqn. (91)}$. From here, we obtain

$$Q(H,l) = SL(H,L)_{\text{exptl}} + gy\tilde{\epsilon}(H,Y) + gy\lambda_Y F_0 - gy t_A \tilde{\epsilon}(A,Y) \quad (92)$$

Discussion

Potential functions have been derived for liquid junctions of constant ionic medium type: $AY|AY + HY + BY_{z(B)} + A_YL$, for the preliminary treatment of e.m.f. data [cf. eqns. (20)–(31)]. The potential contributions given below have been estimated.

1. The potential contribution of the change of the concentration of the ionic medium to the total cell e.m.f. E_B , $Q(B,\Delta c_Y)\Delta c_Y$, have been estimated for four representative titrations (cf. Table 2). It is seen that the neglect of this potential contribution causes the change of the equilibrium constants $\log \beta_{p,q,r}$ with Δc_Y . This effect will be interpreted as the formation of polynuclear complexes, as Δc_Y is the function of B_T , L_T and HY_T .

2. The potential contribution $Q(H,l)$ [$l=L_T$] to E_H has been estimated for cells containing the ions H^+ , $B^{z(B)+}$, L^- , A^+ and Y^- [cf. eqns. (40) and (64)]. Here, L^- denotes Hascorbate⁻ and acetate⁻ ions. The neglect of the term $Q(H,l)$ [$l=L_T$] will cause the change of the protolysis constant $\log K_1$ with $[AL]$, M (cf. Tables 4–6). This effect may be interpreted as the formation of dimer, trimer, etc. species. It was shown in this study that species dimer, trimer, etc. do not exist in the H^+ -acetate⁻ and H^+ -Hascorbate⁻ systems, if we take into account the potential contributions of the ligand to the total potential anomalies.

3. Similarly, the potential contribution of $Q(H,b)b$ can also be estimated according to eqns. (33a)–(33c). Here $SL(H,c_B)_{\alpha,\text{exptl}} = 42.4 \text{ mV M}^{-1}$ [Cd^{2+}] (cf. Table 1 in Ref. 1 and Table 5 in Ref. 2).

At $[Cd^{2+}] = 0.040 \text{ M}$, the difference function is

-29.43 mV M⁻¹ [Cd²⁺]. The result is $Q(H,b) = 12.97$ mV M⁻¹ [Cd²⁺].

At changing [Cd²⁺] we have:

$b = [Cd^{2+}]/M$	0.020	0.050
$Q(H,b)b/mV$	0.26	0.65

As is seen, the potential contributions $Q(H,b)b$ are larger than the uncertainty of the potential readings (0.01 mV). This term cannot be neglected.

4. The potential contribution of $Q(H,h)h$ to E_H has also been estimated.

$$Q(H,h) = SL(H,c_H)_{\alpha, \text{exptl}} + \text{the difference function} \quad (93)$$

where

$$SL(H,c_H)_{\alpha, \text{exptl}} = -2.6 \text{ mV/M } [H^+] = gd_4 \quad (94)$$

The function d_4 is given by eqn. (47) in Ref. 1. The difference function is equal to

$$\begin{aligned} Q(H,h) - SL(H,c_H)_{\alpha} \\ = -g\tilde{\epsilon}(H,Y) - g\lambda_Y F_0 + gt_A \tilde{\epsilon}(A,Y) \\ = -14.72 \text{ mV M}^{-1} [H^+] \end{aligned} \quad (95)$$

Hence, we have

$$Q(H,h) = -17.33 \text{ mV M}^{-1} [H^+]$$

In this calculation, the ionic molar conductivities were taken from Table 6 in Ref. 2. In e.m.f. cells with complex formation, the concentration of the H⁺ ions $\leq 1 \times 10^{-3}$ M. At this H⁺ level, $Q(H,h)h = -0.02$ mV. This potential contribution is the same order of magnitude as the uncertainty of the potential readings. Therefore, it can be neglected.

5. The potential contribution $SL(H,HL)[HL^-]$ mV/M [HL⁻] has also been measured for the Hascorbate⁻ and acetic acid species. In these experiments, $c_H = 0.050$ M, constant, was used and the concentration of the acid, [HL], was changed. The slope functions of the plot $E_H - g \log c_H + g[D(I) - D(C)] = SL(H, \text{acid}) [\text{acid}]$ vs. [acid], at constant c_H , were determined. This potential contribution must also be taken into account.

Experimental

Sodium perchlorate and dilute perchloric acid solutions were prepared and analyzed as usually in this laboratory.²⁵ Sodium hydroxide stock solution was prepared from Merck tritol ampulles and was standardized before every use against KH(IO₃)₂, Merck p.a. quality. Dilute sodium hydroxide solutions were prepared freshly, by dilution, from a more concentrated stock solution. Acetic acid stock solution was prepared from a Merck product, p.a. quality. The ascorbic acid-sodium ascorbate buffer solutions were prepared freshly, from solid ascorbic acid, Merck p.a. quality, and NaOH stock solution. The acetic acid-sodium acetate buffer solutions were prepared freshly, from an acetic acid stock solution which was standardized before use against NaOH solu-

Table 7. Primary titration data (cf. Fig. 3) for the determination of the constant E_{0H} and the first dissociation constant of the ascorbic acid, $\log K_1$, in addition to the slope function $SL(H, HAsc^-)$ [cf. eqn. (62)].

The determination of E_{0H}			
Vessel: 50.05 ml 0.024 804 M HClO ₄ , 3.00 M NaClO ₄			
Burette: 0.102 599 M NaOH, 2.897 401 M NaClO ₄			
[v _B (ml), E _H (mV)]: (0.00, -90.41), (0.98, -93.12), (2.02, -96.13), (3.04, -99.37), (4.04, -102.84), (5.03, -106.66), (6.03, -111.00), (7.09, -116.41), (8.05, -122.31), (9.08, -130.47), (10.08, -141.57), (11.05, -159.87).			
The intercept of the plot $E_H - 59.16 \log[H^+]$ vs. $[H^+]$ is $E_{0H} = 4.69$ mV.			
Main titration			
Vessel: 62.33 ml solution containing 0.2964×10^{-3} M OH ⁻ , 3.00 M NaClO ₄			
Burette: 0.299 408 M H ₂ Asc, 1.607 995 M NaHAsc, 1.392 01 M NaClO ₄			
v _B /ml	[HAsc ⁻] _F /M	[H ₂ Asc] _F /M	E _H /mV
1.00	0.025 683	0.004 4357	-297.41
2.00	0.050 279	0.009 0215	-296.99
3.00	0.074 123	0.013 466	-296.96
3.97	0.096 565	0.017 649	-297.14
4.98	0.119 243	0.021 878	-297.32
5.98	0.141 037	0.025 941	-297.48
7.96	0.182 360	0.033 643	-297.78
9.94	0.221 418	0.040 925	-298.08
11.96	0.259 121	0.047 953	-298.35
13.98	0.294 827	0.054 609	-298.60
16.98	0.344 499	0.063 869	-298.95
19.97	0.390 402	0.072 427	-299.27
22.97	0.433 226	0.080 409	-299.56
25.98	0.473 266	0.087 874	-299.83
29.96	0.522 201	0.096 996	-300.16
34.00	0.567 739	0.105 485	-300.48
38.00	0.609 212	0.113 217	-300.77
44.00	0.665 572	0.123 723	-301.17
49.00	0.707 897	0.131 613	-301.46
Back titration			
Vessel: 61.28 ml solution containing 43.3799 mmol NaHAsc, 8.065 24 mmol H ₂ Asc, 2.292 103 M NaClO ₄			
Burette: 3.00 M NaClO ₄			
2.00	0.685 523	0.127 453	-301.27
4.00	0.664 521	0.123 548	-301.12
8.02	0.625 973	0.116 381	-300.86
14.00	0.576 248	0.107 136	-300.52
20.00	0.533 71	0.099 228	-300.27
28.00	0.485 886	0.090 336	-299.96
38.00	0.436 945	0.081 237	-299.66

tion of known concentration. For the salt component of the buffer, a waterfree, solid sodium acetate was used, Merck p.a. quality.

The experimental details of the e.m.f. measurements are presented in Ref. 26. Glass electrodes were of the type 6.0102.000 from the Metrohm Co. The e.m.f. of the cells was measured with a digital multimeter, type Fluke 8840 A.

The primary data of the titrations presented in Fig. 3 are given in Table 7, as one example. In this table v_B

denotes the additions from burette in ml, E_H/mV stands for the measured e.m.f. of the glass electrode.

Appendix

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_{OB} and E_{OH} should be determined by titrating v_0 ml solution S_0 with v_0 ml solution T_0 with the compositions given here.

$$S_0 = 2B_T M B^{z(B)+}$$

$$25 \times 10^{-3} M HY$$

$$AYS_0 = C M AY$$

$$T_0 = 20 \times 10^{-3} M AOH_T$$

$$AYT_0 = (C - 20 \times 10^{-3} M AOH_T) M AY$$

At the end of the E_0 titration, we have the composition of solution S:

$$S = B_T, HYS = 2.5 \times 10^{-3} M HY, AOH_T,$$

$$AYS = C - AOH_T M AY$$

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.

$$\text{Solution } T_1: 2B_T, HY_1, AY_1 = C M$$

$$\text{Solution } T_2: L_{T2}, AY_2 = C - yL_{T2}.$$

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_{OB} and E_{OH} can be determined as shown in Ref. 1.

(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

$$S_0: 2B_T M B^{z(B)+}$$

$$25 \times 10^{-3} M HY$$

$$AYS_0 = C M AY$$

$$2c_{H_yL} M H_yL$$

T_0 has the same composition as before. Moreover,

$$S: B_T, HYS, c_{H_yL}, AYS = C - AOH_T M AY$$

$$T_1: 2B_T, HY_1, 2c_{H_yL}, AY_1 = C M$$

$$T_2: AOH_2, AY_2 = C - AOH_2 M AY$$

(3) If the total concentration $[A^+]$, $[BY_{z(B)}]$ 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

$$S_0: 2B_T M B^{z(B)+}$$

$$HY = 25 \times 10^{-3} + y2L_T M$$

$$AYS_0 = C - y2L_T M AY$$

$$2L_T M A_yL$$

T_0 has the same composition as before.

$$S: B_T, L_T, HYS = 1 \times 10^{-3} + yL_T M,$$

$$AYS = C - AOH_T - yL_T M AY$$

$$T_1: B_T, L_T, HY_1 = x \times 10^{-3} M, AY_1 = C - yL_T M$$

(4) The main titration can be carried out by the addition of a buffer solution containing $[acid]_F = [HL^{-y+1}]_F M$, $[salt]_F = [L^y]_F = L_T$ and $C - y[salt]_F M AY$ to solution S.

The composition of the solution S_0 , T_0 , S and T_1 has the same values as given under point (1). Here, F denotes formal concentration.

$$T_2: c_{HL}, L_{T2}, AY_2 = C - yL_{T2}$$

This titration can be carried out in different ways:

(4a) either we can keep the formal concentration of the acid constant, when the ratio $[acid]_F/[salt]_F$ is changing,

(4b) or we can keep the ratio $[acid]_F/[salt]_F$ constant, and titrations are made at different ratios.

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.
- Néher-Neumann, E. *Acta Chem. Scand.* 53 (1999) 314.
- Néher-Neumann, E. The Liquid Junction E.M.F., *Dissertation*, The Royal Institute of Technology (KTH), Stockholm, Sweden 1987.
- Ciavatta, L., Ferri, D., Grenthe, I., Salvatore, F. and Spahiu, K. *Acta Chem. Scand., Ser. A* 35 (1981) 403.
- Brönsted, J. N. N. *J. Am. Chem. Soc.* 44 (1922) 938 and 877.
- Guggenheim, E. A. *Applications of Statistical Mechanics*, Clarendon Press, Oxford 1966.
- Scatchard, G. *Chem. Rev.* 19 (1936) 309.
- Guggenheim, E. A. and Turgeon, J. C. *Trans. Faraday Soc.* 51 (1955) 747.
- Biedermann, G. In: Goldberg, E. D., Ed., *On the Nature of Sea Water*, Dahlem Konferenzen, Berlin 1975.
- Ciavatta, L. *Ann. Chim. (Rome)* 70 (1980) 551.
- Biedermann, G. In: Lutze, W., Ed., *Scientific Basis for Radioactive Waste Management - V.*, Elsevier, Amsterdam, 1982.
- Spahiu, K. *Carbonate Complex Formation in Lanthanoid and Actinoid Systems*, *Dissertation*, The Royal Institute of Technology (KTH), Stockholm 1983.
- MLAB An on-line modelling laboratory*, 1st Edn., Beginner's Guide, Division of Computer Research and Technology, National Institutes of Health, Bethesda, MD 1979.
- Néher-Neumann, E. The Liquid Junction Potential in Potentiometric Titrations. 7. *To be published*.
- Gran, G. *Analyst* 77 (1952) 661.
- Wahlberg, O. and Ulmgren, P. *Acta Chem. Scand.* 21 (1967) 2759.

20. Perrin, D. D. *Stability Constants of Metal Ion Complexes, Part B, Organic Ligands*, IUPAC Chemical Data Series No. 22, Pergamon Press, Exeter 1979.
21. Ciavatta, L. and Nunziata, G. *Ric. Sci.* 38 (1968) 318.
22. Ciavatta, L., Nunziata, G. and Sillén, L. G. *Acta Chem. Scand.* 23 (1969) 1637.
23. Persson, H. *Acta Chem. Scand.* 25 (1971) 1775.
24. Olin, Å. and Svanström, P. *Acta Chem. Scand., Ser. A* 32 (1978) 283.
25. Biedermann, G. *Ark. Kem.* 9 (1956) 277.
26. Néher-Neumann, E. *Acta Chem. Scand., Ser. A* 33 (1979) 421.

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