Evaluation of the Concentration Changes near the Electrodes in Electrolysis with Natural Convection*

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Dedicated to Professor August Guyer

Summary

In electrolytic processes the composition of the solution is not the same in the bulk of the cell and at the electrode-electrolyte interface. The concentration changes near the electrodes are of importance in many applications of electrochemistry. The mass transport to or from the electrode determines the concentration differences which build up at a given current density. The methods for the evaluation of interfacial concentrations are discussed for solutions containing one or several electrolytes. The case of steady state natural convection at plane vertical electrodes is considered in detail. The problem is treated for the boundary condition of a uniform current density distribution over the electrode surface. Von Kármán's approximation is used to calculate the interfacial concentrations of H^+-ions and Cu^{2+}-ions in the electrolysis of a solution of $CuSO_4 + H_2SO_4$. The results of the computation are in good agreement with experimental data taken from the literature.

For the case of a great excess of indifferent electrolyte the results of the theoretical derivation are presented in generalized form.

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1. General Aspects of the Problem

In heterogeneous processes there is, in general, close to the phase boundary, a zone with changed concentration, called the diffusion layer. At the interface, the composition of a mixture is different from its value in the bulk of the phase. This applies also to electrolysis, which is the case considered in this paper.

The existence of the diffusion layer is closely linked with the mass transport to or from the interface which, in electrolysis, takes place in general by diffusion, convection and electric migration. The concentration changes near the electrodes and the mass transport phenomena play an important role in electrochemistry. They can, for instance, strongly affect the structure of an electrodeposited metal.*

This paper deals with the evaluation of the concentration differences which are built up between bulk and interface at a given current density. Attention will be focussed on the electrolysis of solutions containing two electrolytes. In the case of a mixture of electrolytes there are, in principle, as many diffusion layers as there are ionic species in the solution (with the restriction, however, that the various diffusion layers are not entirely independent of each other since the electroneutrality condition must be fulfilled). We will consider the system $CuSO_4 + H_2SO_4$, which is widely used in industrial electrolysis (copper refining, electroplating). Usually, the cathode potential is such that copper is deposited virtually without concomitant hydrogen evolution. The cathodic diffusion layer obtained in this case is shown schematically in Fig. 1. There is electric migration of the

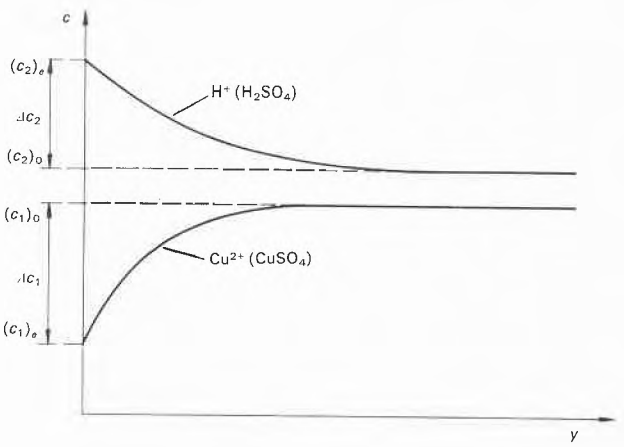

Fig. 1. Diffusion layers in copper deposition from $CuSO_4 + H_2SO_4$ without hydrogen evolution; plot of concentration vs. electrode distance (schematic)

Cu^{2+}-ions toward the cathode, but the number of moles of cations thus transported toward the interface per unit time is smaller than that of the cations which are discharged. Close to the electrode, where convection vanishes because of the friction forces at the solid interface, the transport by electric migration must therefore be complemented by transport through diffusion, i.e. a concentration gradient toward the cathode is set up. The result is that the concentration of Cu^{2+}-ions is smaller in the diffusion layer than in the bulk. On the other hand, the H^+-ions too migrate toward the cathode under the influence of the electric field, but they are not discharged there; therefore, they accumulate at the interface until a steady state is reached in which the concentration gradient of the H^+-ions is such that the electric force pulling the H^+-ions toward the cathode is compensated by the "diffusion" (or "osmotic") force acting in the opposite direction. The diffusion layer is thus enriched with respect to H^+-ions. The pH is different from its value in the bulk. This can substantially change the properties and the structure of an electrodeposited metal.[1,2]

The calculation of electrolytic mass transport has received much attention in recent years.* Usually, the simplification has been made that either there is only one electrolyte or at least that only one ionic species reacts at the electrode and that this species is a minor constituent, i.e. is present in a small amount as compared to the other ionic species of the solution (great excess of an indifferent electrolyte). Under these conditions the electric migration of the reacting species can be taken care of in a very simple manner, or entirely neglected. The problem can then be treated in the same way as non-electrolytic mass transport and one can also make full use of the analogy between mass and heat transfer. However, this does not apply to calculations such as that of the interfacial concentration of H^+-ions in our example of the electrolysis of a mixture of $CuSO_4$ and H_2SO_4. In this case, the electric migration is the cause of the concentration differences in the diffusion layer and its influence is essential. A complete integration of the fundamental differential equations of convective mass transport is then extremely difficult and has not been achieved so far.** In this paper approximate procedures will be used which yield the quantities of practical interest in a relatively simple manner.

As a concrete example we will consider steady state natural convection at a plane, vertical cathode. Even in a solution which is not artificially stirred there is, along a vertical cathode, an ascending flow of liquid due to the buoyancy force resulting from the density differences between bulk solution and diffusion layer. It is called natural or free convection. This type of hydrodynamic flow is of considerable technical interest. In copper refining, for instance, the stirring is essentially ensured by natural convection.

2. The Boundary Condition at the Interface

The integration of the fundamental differential equations depends on the boundary conditions of the problem. The boundary condition most commonly considered in the theory of electrolytic mass transport is that of a constant interfacial concentration c_e along the whole electrode surface. This situation is realized (at least for the

* For a recent review see ref. [1,2].

* For a review of the subject see [3,4,5].

** Since the presentation of this paper at the IUPAC-Congress NEWMAN and TOBIAS have quite recently given a rigorous treatment of the contribution of migration in a mixture for the case of the limiting current.[31,32]

reacting species) at the limiting current ($c_e = 0$). In electrochemical engineering the case of the limiting current is of importance, among others, in connection with optimization.[6] In general, however, electrolysis is carried out at current densities below the limiting value, i.e. the interfacial concentration of the reacting species is different from zero. Obviously the interfacial concentration of the H^+-ions in cases such as that of Fig. 1 is always different from zero. The problem of practical interest is then the computation of the interfacial composition of the solution which establishes itself at a given current density i. This is the object of this paper.

In the following we thus consider the case that the current density i is well below the limiting value i_g ($c_e \neq 0$). As boundary condition we will then assume that the local current density is the same everywhere along the whole electrode surface. This is, below the limiting current, a more realistic condition than $c_e = \text{const}$. It has been shown by WAGNER that ist is realized with a good approximation for $i < 0.3$ to $0.5\, i_g$ at plane symmetrically arranged electrodes of a not too small size, so that edge effects can be neglected.[7,8] The computation of interfacial concentrations at a given, uniformly distributed current density has received much less attention than the problem of the calculation of the current density for a constant interfacial concentration. A few cases, however, have been considered in the literature. Relationships for the interfacial concentrations at a given current have been indicated by WAGNER[7] and by WRANGLÉN[24, 25] for natural convection and for forced laminar flow along a plate.

3. Interfacial Concentration in the Case of a Single Electrolyte

The following equation has been given by WAGNER[7] for the concentration difference Δc between bulk and interface in steady state natural convection at a vertical plane electrode with the boundary condition of a uniform current distribution ($i = \text{const}$)**

$$\Delta c = 1.62 \frac{j^* x}{D} \left(\frac{0.8 + Sc}{Sc^2 Gr_x^*} \right)^{1/5} . \qquad [1]$$

This relationship is based on a nearly rigorous treatment of the corresponding heat transfer problem by SPARROW and GREGG.[9,10] Eq. [1] was derived from the results of these authors by making use of the analogy between heat and mass transfer.

In aqueous solutions the Schmidt number Sc is of the order of 1000. Eq. [1] then reduces to

$$\Delta c = 1.62 \frac{j^* x (Sc\, Gr_x^*)^{-1/5}}{D} = 1.62 \left(\frac{x \nu \varrho_0 j^{*4} \Delta c}{g(\varrho_0 - \varrho_e) D^3} \right)^{1/5} . \qquad [2]$$

** A key of the notation is given at the end of the paper.

For a cathodic metal deposition this can also be written as

$$\Delta c = 1.62 \left(\frac{i(1-t)}{zF} \right)^{4/5} \left(\frac{x \nu \varrho_0 \Delta c}{g(\varrho_0 - \varrho_e) D^3} \right)^{1/5} \qquad [3]$$

or

$$\Delta c = 1.62 \left(\frac{i(1-t)}{zF} \right)^{4/5} \left(\frac{x \nu}{g \alpha D^3} \right)^{1/5} \qquad [3']$$

where the mass transfer rate excluding migration j^* has been expressed in terms of the current density i according to the equation

$$j^* = \frac{i(1-t)}{zF} . \qquad [4]$$

In relation [4] the contribution of electric migration to the mass transport is taken care of in the following manner. For any ionic species k of a solution we write for the total mass transport rate (or flux) at the interface, i.e. at the point $y = 0$ (where there is no mass transport by convection)

$$j_k = D_k \left(\frac{dc_k}{dy} \right)_e + \frac{i t_k}{z_k F} = j_k^* + \frac{i t_k}{z_k F} . \qquad [5]$$

The term $D_k \left(\frac{dc_k}{dy} \right)_e$ stands for mass transport by diffusion; the term $i t_k / z_k F$ represents transport by electric migration; t_k is the transference number of the considered species in the bulk solution, i.e. the fraction of the total current which is transported, in the bulk solution, by that species.

The current density i flowing through the electrode is connected with the flux at the interface j_k by

$$i = F j_k / s_k \qquad [6]$$

where s_k is the number of moles of the considered species k which react at the electrode when one Faraday flows through the cell. In the case of a metal deposition with 100% current efficiency, $1/s = z$, and the combination of equations [5] and [6] yields eq. [4]. In our example of copper deposition $1/s = z = 2$.

A more general relationship for the flux than eq. [5] is the following:

$$j_k = D_k \left(\frac{dc_k}{dy} \right)_e + \frac{z_k F D_k c_k}{RT} \left(\frac{dE}{dy} \right)_e . \qquad [7]$$

It can be shown[3] that this equation reduces to eq. [4] for a single electrolyte or for a minor ionic constituent of a mixture of electrolytes (in which case t_k is virtually zero). This is not true, however, for a species of intermediate concentration. The validity of eq. [2] is therefore restricted to the case of a single electrolyte.**

** In principle, eq. [2] is also valid for a minor constituent of a mixture. However, in the case of natural convection, the hydrodynamic conditions depend on the Δc for all constituents, because $\varrho_0 - \varrho_e$ is influenced by the concentration changes of all constituents. The evaluation of $\varrho_0 - \varrho_e$ thus implies the application of eq. [4] or [5] to at least one major constituent and this also holds true whenever eq. [3] is used to actually calculate Δc for a given current i (because any numerical application of eq. [3] requires that $\varrho_0 - \varrho_e$ be expressed in terms of concentrations, see section 4).

As has been pointed out earlier, this is one of the two cases in which mass transport in electrolysis can be treated in the same manner as non electrolytic mass transport and the analogy between heat and mass transport can be made use of.

4. Interfacial Concentrations in the Case of a Mixture; Approximation of a Constant Transference Number

Eq. [4] has been repeatedly used in the literature in a general way, i.e. including mixtures of intermediate composition. However, it is in this case only an approximation, the accuracy of which is not well known.

If eq. [4] is assumed to be generally valid at least as a first approximation, the same applies to eq. [3]. This relationship can then be used to calculate approximately the interfacial concentration of the reacting species in the case of a mixture of any composition.

We can evaluate along similar lines the interfacial concentration of a non reacting species, such as H^+ in our example of the electrolysis of $CuSO_4 + H_2SO_4$. The following procedure has been first developed by WILKE, TOBIAS and EISENBERG for natural convection[11, 12]; it has been later used by several authors for various types of flow.[1, 13, 24]

For the H^+-ions of our example, which do not react at the electrode, the flux at the interface j_2 must be zero. If we further solve eq. [2] for j^* and assume that the same relationship holds for the Cu^{2+} and the H^+-ions we obtain from [5]:

$$j_2 = 0 = \frac{i t_2}{F} + j_2^* = \frac{i t_2}{F} + \\ + (1.62)^{-5/4} \Delta c_2 \left(\frac{g (\varrho_0 - \varrho_e) D_2^3}{x \varrho_0 \nu} \right)^{1/4} \qquad [8]$$

or

$$\Delta c_2 = -1.83 \frac{i t_2}{F} \left(\frac{x \varrho_0 \nu}{g (\varrho_0 - \varrho_e) D_2^3} \right)^{1/4} \qquad [9]$$

where the subscript 2 refers to the H^+-ions.

We can now also combine equations [9] and [3] (the latter equation being written for the Cu^{2+}-ions which we denote with the subscript 1); this yields

$$\frac{\Delta c_2}{\Delta c_1} = -\frac{2 t_2}{1 - t_1} \left(\frac{D_1}{D_2} \right)^{3/4}. \qquad [10]$$

According to eq. [10] the ratio of the interfacial increase in H^+-ion concentration to the decrease in Cu^{2+}-ion concentration is related in a simple manner with the transference numbers and the diffusion coefficients.

When eq. [3] is used to actually calculate Δc for a given current i the density difference $\varrho_0 - \varrho_e$ must be expressed in terms of concentrations. This can be done by using as a first approximation a linear relationship between the density and the concentration of the components of the mixture:

$$\frac{1}{\varrho_0} \frac{\partial \varrho}{\partial c} = \alpha.$$

However, the densification coefficients of the individual ions are not known and one has to use instead the densification coefficient α of the electrically neutral electrolytes of the mixture (in our example, $CuSO_4$ and H_2SO_4),** α being then defined as the change in density per mole of the neutral electrolyte. The molar concentrations of the ions are related to the molar concentrations of the neutral electrolyte by the factor z/n where n is the number of g equiv. per mole of neutral electrolyte ($n = 2$ for both $CuSO_4$ and H_2SO_4). Therefore, since we are denoting with c the molar concentrations of the *ions*, we have to multiply c with z/n when we use the densification coefficient of the neutral electrolyte to calculate $\varrho_0 - \varrho_e$. The contributions of the various components of the mixture to the overall density change are usually taken as additive, which is regarded as a sufficient approximation in problems of natural convection. However, in adding the contributions of the individual terms, only the cathodic (or the anionic) species are to be considered because the contribution of the ions of opposite charge is automatically taken care of when using the α values for the neutral electrolyte. For the system $CuSO_4 + H_2SO_4$ we thus have (α_1 and α_2 being the densification coefficients of $CUSO_4$ and H_2SO_4, respectively:

$$\frac{\varrho_0 - \varrho_e}{\varrho_0} = \alpha_1 \Delta c_1 + \frac{\alpha_2}{2} \Delta c_2 = \alpha^* \Delta c_1 \qquad [11]$$

with

$$\alpha^* = \alpha_1 - \alpha_2 \frac{t_2}{1 - t_1} \left(\frac{D_1}{D_2} \right)^{3/4}.$$

Equations [8] to [11] are restricted to copper deposition from $CuSO_4 + H_2SO_4$ without H_2-evolution. However, they can easily be generalized, to apply to a mixture of any number of ions of any valence. The derivation is quite similar to that of equations [8] to [11]. If s, z, i and n are regarded as algebraic quantities*** we obtain instead of equations [11], [10] and [3'], respectively°

$$\frac{\varrho_0 - \varrho_e}{\varrho_0} = \Sigma z_k \alpha_k \Delta c_k / n_k = \alpha^* \Delta c_i \qquad [11']$$

$$\frac{\Delta c_k}{\Delta c_i} = \left(\frac{s_k - t_k/z_k}{s_i - t_i/z_i} \right) \left(\frac{D_i}{D_k} \right)^{3/4} \qquad [10']$$

with

$$\alpha^* = \Sigma \frac{\alpha_k (z_k s_k - t_k) D_i^{3/4}}{n_k (s_i - t_i/z_i) D_k^{3/4}}$$

and

$$\Delta c_i = 1.62 \left[\frac{i (s_i - t_i/z_i)}{F} \right]^{4/5} \left(\frac{\nu x}{\alpha^* g D_i^3} \right)^{1/5}. \qquad [3'']$$

** A similar remark applies to the diffusion coefficients D_1 and D_2 entering eq. [10]. In the literature, one has usually taken for D_1 and D_2 the diffusion coefficients of $CuSO_4$ and H_2SO_4, respectively (rather than those of the individual ions, which are not known anyhow).

*** See key to notation.

° In the case of a single electrolyte eq. [11'] reduces to $\frac{\varrho_0 - \varrho_e}{\varrho_0} = \alpha \Delta c$. We have made use of this relationship in writing eq. [3'].

These equations hold for cathodic as well as anodic processes, including redox reactions. Δc_i represents the concentration difference between bulk and interface for any selected component. The summation Σ has to be extended *only* over all cationic *or* all anionic species when using the densification coefficients for the neutral electrolytes.**

With the help of equations [3″], [10′] and [11′] (or [3′], [10] and [11] for $CuSO_4 + H_2SO_4$) we are now able to make a complete calculation of the interfacial concentrations of all species of the mixture.

The simple method outlined above implies the following assumptions: a) An equation of the form of eq. [2] can be applied to both the reacting and the non reacting ions. b) The flux of the mass transport by migration is the same at the interface as in the bulk, in spite of the changed concentration and the presence of a concentration gradient at the interface. It is very difficult to estimate the extent of the error involved. The approximation might be rather poor in certain cases.

In the next section a more involved treatment, in which the above assumptions are not needed, will be given. It is based on the integral method of VON KÁRMÁN[14, 15], which has been successfully applied to problems of natural convection by various authors[12, 15, 16, 17].

5. Interfacial Concentrations in the Case of a Mixture; Application of the Method of von Kármán to Electrolysis

We will first apply VON KÁRMÁN's method to a somewhat more general case than our example of $CuSO_4$ and H_2SO_4. We will consider metal deposition*** from a mixture of two electrolytes with a common anion; cation 1 is discharged at the cathode but cation 2 does not react at the electrode. We will return later to our particular example of copper deposition from a solution of $CuSO_4 + H_2SO_4$.

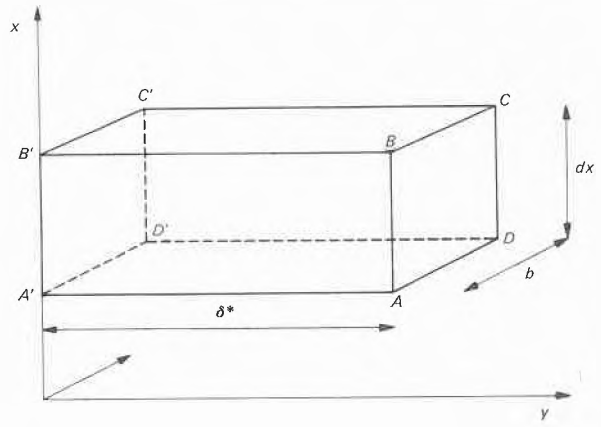

Fig. 2. Control volume for theoretical derivation

We consider a control volume of height dx and breadth b (Fig. 2). The width δ^* is such that the volume includes the whole hydrodynamic boundary layer and the whole diffusion layer (i.e. the whole region where the flow velocity or the concentration is different from its value in the bulk). The balance of forces and momentum yields the known relationship [16]

$$\nu\left(\frac{du}{dy}\right)_e = g\int_0^{\delta^*}\left(\frac{\varrho_0-\varrho}{\varrho_0}\right)dy =$$

$$= -g\int_0^{\delta^*}\left[\frac{z_1\alpha_1}{n_1}\left(c_1-(c_1)_0\right)+\frac{z_2\alpha_2}{n_2}\left(c_2-(c_2)_0\right)\right]dy. \quad [12]$$

It expresses that the shearing stress at the wall is balanced by the buoyancy force acting on the solution contained in the control volume. This buoyancy force is given by the density difference between bulk solution and diffusion layer which can be expressed in terms of concentrations by a relationship of the form of eq. [11′]. This yields the term with the densification coefficients α on the right of eq. [12]. The flow of momentum through the boundary planes $AA'DD'$ and $BB'CC'$ needs not be considered because the corresponding additional term $\frac{d}{dx}\int_0^{\delta^*} u^2 dy$ is negligible at the high Schmidt numbers prevailing in aqueous solutions.

Two further basic equations are obtained by making a mass balance for the cations entering and leaving the control volume. The number of moles entering the control volume through the boundary plane $ABCD$ is $(it/zF)bdx$ for the transport by migration and v_0c_0bdx for the transport by convection. The horizontal velocity component v_0 can be eliminated with the help of the continuity equation

$$\frac{\partial u}{\partial x}+\frac{\partial v}{\partial y}=0$$

which yields

$$v_0 = -\int_0^{\delta^*}\frac{\partial u}{dx}\,dy. \quad [13]$$

The difference between the number of moles entering and leaving per unit time the control volume through the horizontal boundary planes $AA'DD'$ and $BB'CC'$ is $\left(\frac{d}{dx}\int cudy\right)bdx$.

Since we have assumed that cation 2 does not react at the cathode no such cations leave the control volume through plane $A'B'C'D'$. The mass balance for cation 2 ($z = z_2$) thus yields

$$\frac{it_2}{z_2F} = \frac{d}{dx}\int_0^{\delta_2}\left(c_2-(c_2)_0\right)udy. \quad [14]$$

** A choice must therefore be made. Unfortunately, the result can depend upon this choice.

*** For the case of metal dissolution, which is not considered here, quite similar relationships will hold.

On the other hand, cations 1 are discharged at the cathode and is_1bdx/F moles of cations 1 leave, per unit time, the control volume through plane $ABCD$. The mass balance for this cation ($z = z_1$) thus yields

$$\frac{i\,(s_1 - t_1/z_1)}{F} = -\frac{d}{dx}\int_0^{\delta_1} (c_1 - (c_1)_0)\, u dy. \qquad [15]$$

We need not make a mass balance for the anions in common since their concentration is given by that of the cations 1 and 2 because of the electroneutrality of the solution.

δ_1 and δ_2 are the thicknesses of the diffusion layer for cation 1 and 2, respectively. In principle, the integration in equations [14] and [15] should extend from $y = 0$ to $y = \delta^*$, i.e. over the whole width of the control volume. However, since $c_1 = (c_1)_0$ for $y \geqslant \delta_1$ the value of the integral [15] between δ_1 and δ^* is zero and we can take δ_1 as the upper limit of the integral in eq. [15]. In a similar way we can take δ_2 as the upper limit of the integral in eq. [14]. The thickness δ^* of the hydrodynamic boundary layer (i.e. of the region where the upward flow velocity u is different from zero) is certainly not smaller than δ_1 or δ_2, because in aqueous solutions the viscosity ν (which can be regarded as the diffusion coefficient of momentum) is much larger than the diffusion coefficient for the mass ($\nu > D$). We have therefore taken δ^* for the width of our control volume (Fig. 2) and the integration of eq. [12] has to be carried out between the limits 0 and δ^*.

Equations [12], [14] and [15] are our basic relationships. In order to solve them we will introduce later certain functions for the flow velocities and concentrations. Even then equations [12], [14] and [15] do not suffice to solve the problem entirely. We need further relationships. These are obtained by establishing the equations which connect the current with the concentration gradients at the interface. We can eliminate the potential from eq. [7] by multiplying all terms of this equation with z_k/D_k, by applying the equation to all ionic species of the solution and adding all these equations. If we remember the electroneutrality condition $\Sigma z_k c_k = 0$ and if we take into account eq. [6] we then obtain

$$\left(\frac{dE}{dy}\right)_e = \frac{iRT}{F^2}\,\frac{\Sigma z_k s_k/D_k}{\Sigma z_k^2 (c_k)_e}. \qquad [16]$$

Introducing this value of the field $(dE/dy)_e$ into eq. [7] we get

$$\left(\frac{dc_k}{dy}\right)_e = \frac{i}{F}\left[\frac{s_k}{D_k} - z_k c_k \frac{\Sigma z_k s_k/D_k}{\Sigma z_k^2 (c_k)_e}\right]. \qquad [17]$$

Eq. [17] can now be combined with equations [12], [14] and [15]. In order to carry out the integration of equations [12], [14] and [15] we assume arbitrary but plausible profiles for the upward flow velocity u and for the concentrations. We take

$$u = U\frac{y}{\delta^*}\left(1 - \frac{y}{\delta^*}\right)^2 \qquad [20]$$

$$c_1 - (c_1)_0 = \left[(c_1)_e - (c_1)_0\right](1 - y/\delta_1)^2 = \\ = -\Delta c_1\,(1 - y/\delta_1)^2 \qquad [21]$$

$$c_2 - (c_2)_0 = \left[(c_2)_e - (c_2)_0\right](1 - y/\delta_2)^2 = \\ = -\Delta c_2\,(1 - y/\delta_2)^2 \qquad [22]$$

These profiles fulfill the conditions: $u = 0$ for $y = \delta^*$, $c_1 = (c_1)_0$ for $y = \delta_1$, $c_2 = (c_2)_0$ for $y = \delta_2$. Furthermore, $u = 0$ for $y = 0$ which must be the case because of the friction forces at a solid wall. The velocity goes through a maximum located at $y = \delta^*/3$. The maximum velocity is equal to $4U/27$. The maximum flow velocities in natural convection have been measured by IBL and MÜLLER for the case of a single electrolyte.[18]

With the help of the above profiles we have now to calculate from equations [12], [14], [15] and from two equations of the form [17] (for $k = 1,2$) the following quantities: Δc_1 and Δc_2 (which are the quantities of primary practical interest), the parameter U (which is related in a simple manner with the maximum flow velocity) and the parameters δ^*, δ_1 and δ_2 (which represent the thicknesses of the hydrodynamic boundary layer and of the two diffusion layers). We have thus 6 unknowns but only 5 equations. We must therefore make a further assumption regarding one of the parameters involved, as it is usually the case in VON KÁRMÁN's method. Since in our problem the hydrodynamic flow is due only to the concentration differences in the solution we will assimilate the hydrodynamic boundary layer to the thicker of the two diffusion layers. We have then the two possibilities: $\delta_2 > \delta_1$ or $\delta_2 < \delta_1$, i.e. the diffusion layer for the non reacting cations is the larger of the two, or inversely. Depending on the circumstances we will therefore put $\delta^* = \delta_2$ or $\delta^* = \delta_1$. We will start by treating the first case. This is the one to be considered in our example of an acidified $CuSO_4$ solution. The diffusion coefficient of the H^+-ions is considerably larger than that of the Cu^{2+}-ions ($D_2 > D_1$); it is thus to be expected that the diffusion layer for the H^+-ions is larger than for the Cu^{2+}-ions ($\delta_2 > \delta_1$)**, because in general, in mass, heat and momentum transport the thickness of the boundary layer increases with increasing value of the corresponding transport coefficient. We will deal with the second case ($\delta_2 < \delta_1$) later on and for the moment we will carry on our computation setting $\delta^* = \delta_2$. In reality, δ^* is probably somewhat larger than δ_2. However, by varying

** The greater thickness of the diffusion layer for the H^+-ions was observed experimentally by IBL and MÜLLER[19]. The anodic dissolution of copper was studied by an interferometric method which gives a curve showing the refractivity vs. electrode distance.[20] When the solution contained H_2SO_4 the curve exhibited a sharp minimum which was absent when there was only $CuSO_4$ without H_2SO_4 in the solution. This indicates that in presence of H_2SO_4 there is a depleted layer of H^+ which extends over a greater distance than the layer enriched with Cu^{2+} ($\delta_2 > \delta_1$).

the form of the assumed profiles it has been shown in an earlier work[18] that the results obtained by VON KÁRMÁN's approximation depend very little on the assumed shape of the velocity profile in the outer parts of the boundary layer (i.e. beyond the maximum, toward the interior of the solution). This has been confirmed later by experiments in which a counter wall was brought successively nearer to the working electrode.[21] The mass transfer rate was substantially affected only when the counter wall was closer than a distance corresponding roughly to the thickness of the diffusion layer.

Profiles of the same form as those of equations [20] to [22] (with the assumption of an equal thickness for the hydrodynamic and for the diffusion, or temperature boundary layer) have been used by WILKE *et al.*[11] and ECKERT[15] in their treatment of natural convection at a vertical plate with the boundary condition of a constant concentration c_e (or a constant density ϱ_e) along the interface. The mass transfer rates thus calculated were in close agreement[22] with those obtained by OSTRACH[23] from a much more rigorous integration of the fundamental differential equations of the problem. In our case, the boundary condition is a different one, namely a constant local current density along the interface (see section 2). However, for this boundary condition too, the velocity and concentration profiles [20] to [22] have already been used to calculate the concentration difference Δc in the case of a single electrolyte**; the relationship thus obtained was identical with eq. [2] which has been derived by a more rigorous method (the numerical coefficient is 1.26 both for the VON KÁRMÁN approximation and for the nearly rigorous procedure). It appears reasonable to use the same profiles*** also in the case of a mixture such as that considered in the present paper.

By differentiating equations [20] to [22] with respect to y we obtain (with $y = 0$) simple relationships connecting the concentration gradients at the interface with Δc_1, Δc_2 and U. On the other hand, the interfacial concentration gradients are linked (by eq. [17]) with the current density which is the directly measurable quantity and is regarded as given in our problem. We apply this equation to both cations and remember that $s_2 = s_3 = 0$. We thus obtain:

$$\left(\frac{dc_1}{dy}\right)_e = \frac{2\Delta c_1}{\delta_1} = \frac{is_1}{D_1 F}\left[1 - \frac{z_1^2 (c_1)_e}{z_1^2 (c_1)_e + z_2^2 (c_2)_e + z_3^2 (c_3)_e}\right] \quad [23]$$

$$\left(\frac{dc_2}{dy}\right)_e = \frac{2\Delta c_2}{\delta_2} = -\frac{is_1}{D_1 F}\left[\frac{z_1 z_2 (c_2)_e}{z_1^2 (c_1)_e + z_2^2 (c_2)_e + z_3^2 (c_3)_e}\right] \quad [24]$$

$$\left(\frac{du}{dy}\right)_e = \frac{U}{\delta_2} \quad [25]$$

** Unpublished calculation of N. IBL.

*** A somewhat better accuracy could probably be achieved by using the profiles suggested earlier for the calculation of the hydrodynamic flow velocities.[18] However, the computation would then become much more involved. The resulting complication would be hardly justified in the present case where we are primarily interested in the concentrations rather than in the flow velocities.

To simplify the calculation we will first consider the case $(c_2)_0 \gg (c_1)_0$, i.e. that the concentration of the non reacting species is much larger than that of the reacting species. This is the situation commonly encountered in polarography, for instance. We will drop later the restriction of a large excess of non reacting electrolyte.

With $(c_2)_0 \gg (c_1)_0$ we have $(c_1)_e \ll (c_2)_e$ and $z_2 (c_2)_e \cong -z_3 (c_3)_e$, because the diffusion layer is enriched with respect to the non reacting cation and therefore $(c_2)_e > (c_2)_0$. Furthermore, the transference number of the reacting species is then very small, so that $t_1 \ll 1$. Equations [23], [24] and [15] thus reduce to

$$\frac{\Delta c_1}{\delta_1} = \frac{is_1}{2 D_1 F} \quad [23']$$

$$\frac{\Delta c_2}{\delta_2} = \frac{-is_1 z_1}{2 D_1 F (z_2 - z_3)} \quad [24']$$

$$\frac{is_1}{F} = -\frac{d}{dx}\int_0^{\delta_1} (c_1 - (c_1)_0)\, u\, dy. \quad [26]$$

Our next step is to introduce the values of u, $c_1 - (c_1)_0$ and $c_2 - (c_2)_0$ as given by the profiles of equations [20], [21] and [22] into the basic relationships [12], [14] and [26] and to perform the integration. We denote by ε the ratio of the thicknesses of the diffusion layers for the reacting and the non reacting cation: $\delta_1 = \varepsilon \delta_2$. From equations [20], [21] and [26] we obtain**

$$\frac{is_1}{F} = \frac{d}{dx}\int_0^{\delta_1} \Delta c_1 U \frac{y}{\delta_2}\left(1 - \frac{y}{\delta_1}\right)^2 \left(1 - \frac{y}{\delta_2}\right)^2 dy =$$

$$= \varepsilon\left(\frac{1}{12} - \frac{\varepsilon}{15} + \frac{\varepsilon^2}{60}\right)\frac{d}{dx}(\Delta c_1 U \delta_1). \quad [27]$$

Combining eq. [27] with eq. [23'] and remembering our boundary condition of a uniform current density distribution (i independent of x) we get

$$\frac{\varepsilon}{2 D_1}\left(\frac{1}{12} - \frac{\varepsilon}{15} + \frac{\varepsilon^2}{60}\right)\frac{d}{dx}(U\delta_1^2) = 1. \quad [28]$$

In a similar manner we obtain from equations [14], [20], [22] and [24']

$$\frac{it_2}{z_2 F} = -\frac{d}{dx}\int_0^{\delta_2} \Delta c_2 U \frac{y}{\delta_2}\left(1 - \frac{y}{\delta_2}\right)^4 dy =$$

$$= -\frac{1}{30}\frac{d}{dx}(\Delta c_2 U \delta_2) = \frac{s_1 z_1 i}{60 D_1 F (z_2 - z_3)}\frac{d}{dx}(U\delta_2^2). \quad [29]$$

** ε is regarded as independent of x, which is expected to be a sufficient approximation for our purposes.

Combination of equations [28] and [29] yields (remembering that ε stands for δ_1/δ_2)

$$\frac{2}{\varepsilon^3(\varepsilon^2-4\varepsilon+5)} = \frac{(z_2-z_3)t_2}{s_1 z_1 z_2} = mt_2. \qquad [30]$$

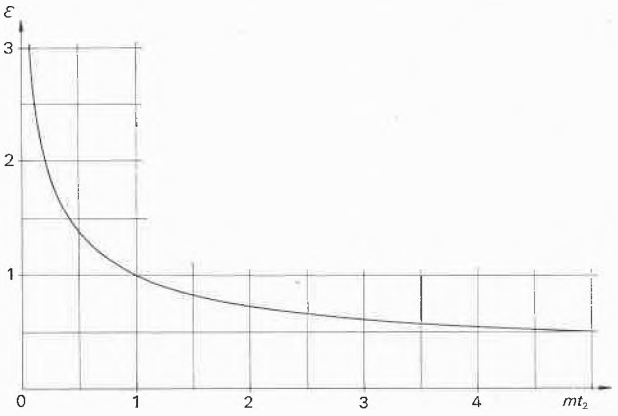

Fig. 3. Ratios of the thicknesses of the diffusion layers for the reacting and the non reacting species; dependence on the transference number of the non reacting species

The solution of eq. [30] is shown graphically on Fig. 3. On the abscisse is plotted the quantity mt_2 which is proportional to the transference number t_2 of the non reacting cation. This proportionality factor m is

$$m = \frac{z_2 - z_3}{s_1 z_1 z_2} \qquad [31]$$

or

$$m = 1 - z_3/z_2 \qquad [31']$$

since $s_1 z_1 = 1$ in the case of metal deposition. For $mt_2 < 1$ the ratio ε is larger than 1, i.e. our premice $\delta_1 < \delta_2$ is no longer fulfilled. Therefore, we cannot use eq. [30] to calculate the upper part of the curve (above $\varepsilon = 1$). In this case we have to start from the premice $\delta_1/\delta_2 > 1$, i.e. we have to set $\delta^* = \delta_1$. If we carry out the same calculation as before with the condition $\delta^* = \delta_1$ (instead of $\delta^* = \delta_2$) we obtain instead of eq. [30]

$$\frac{1-4\varepsilon+5\varepsilon^2}{2\varepsilon^5} = mt_2. \qquad [30']$$

The upper part of the curve of Fig. 3 (above $\varepsilon = 1$) was computed from this equation. The whole curve now allows to predict ε from t_2 without knowing *a priori* which one of the two diffusion layers is the thicker one. The curve is valid for any metal deposition from a mixture of two electrolytes with a common anion, one reacting and one non reacting cation, the non reacting cation being in great excess.

The ratio ε is related in a simple manner to the ratio of the interfacial increase of the concentration of cation 2 to the decrease of the concentration of cation 1. From equations [23'] and [24'] we obtain:

$$\frac{\Delta c_2}{\Delta c_1} = -\frac{z_1}{(z_2-z_3)\varepsilon}. \qquad [32]$$

The absolute value of Δc_1 can be obtained by integrating the momentum equation [12]. From equations [12], [21], [22] and [25] follows

$$\frac{\nu}{g}\left(\frac{du}{dy}\right)_e = \frac{\nu U}{g\delta_2} = \int_0^{\delta_1} \frac{z_1}{n_1}\alpha_1 \Delta c_1 \left(1-\frac{y}{\delta_1}\right)^2 dy + \int_0^{\delta_2} \frac{z_2}{n_2}\alpha_2 \Delta c_2 \left(1-\frac{y}{\delta_2}\right)^2 dy = \frac{z_1\alpha_1\Delta c_1\delta_1}{3n_1} + \frac{z_2\alpha_2\Delta c_2\delta_2}{3n_2}. \qquad [33]$$

Combination of eq. [33] with equations [23'] and [24'] yields (with $s_1 z_1 = 1$)

$$U = \frac{ig\delta_1^3}{6\nu D_1 F\varepsilon}\left(\frac{\alpha_1}{n_1} - \frac{z_2\alpha_2}{n_2\varepsilon^2(z_2-z_3)}\right). \qquad [34]$$

We insert this value of U into eq. [28] and take into account that δ_1 is a function of the height x, δ_1 being 0 at $x = 0$, i.e. at the lower end of the cathode. After separating the variables we integrate from the lower end of the cathode until the height x. We obtain

$$\delta_1 = \left(\frac{720\, x\nu D_1^2 F}{Agi(\varepsilon^2-4\varepsilon+5)}\right)^{1/5} \qquad [35]$$

$$\Delta c_1 = 1.864\, s_1 \left(\frac{i}{F}\right)^{4/5}\left(\frac{x\nu}{AD_1^3 g(\varepsilon^2-4\varepsilon+5)}\right)^{1/5} \qquad [36]$$

with

$$A = \frac{\alpha_1}{n_1} - \frac{z_2\alpha_2}{n_2\varepsilon^2(z_2-z_3)}. \qquad [37]$$

The concentration difference between interface and bulk is proportional to the current density i raised to the power 4/5 and is inversely proportional to the diffusion coefficient raised to a power of 3/5. The concentration difference also slightly increases with the height x and the viscosity ν but it varies only as the fifth root of these two quantities. The dependence of Δc_1 upon i, x, ν and D is the same as in the case of a single electrolyte (eq. [3]).

From equations [36] and [32] we obtain Δc_1 and Δc_2 and therefore the interfacial concentrations of both electrolytes of the mixture. The validity of equations [32] and [36] is restricted to the case of a great excess of the non reacting electrolyte. However, when this condition is not fulfilled we can use the values calculated from these equations as a first approximation and obtain the final values by iteration (inasmuch as the con-

centration of the non reacting ions is not too small). The procedure is as follows. If $(c_2)_0$ is not much larger than $(c_1)_0$ equations [23'] [24'] and [26] are not valid and equations [23], [24] and [15] must be used instead. Therefore, we calculate first $(c_1)_e$ and $(c_2)_e$ from equations [36] and [32] and introduce the numerical values thus obtained into equations [23] and [24]. We then start from equations [23], [24] and [15] (instead of equations [23'], [24'] and [26]) to derive the analogous equations of [36] and [32], the whole calculation being exactly the same as that we have done previously. We thus obtain new values of the interfacial concentrations which are again introduced into equations [23] and [24] and the whole procedure is repeated until interfacial concentrations are obtained which are the same as those of the preceding iteration. A numerical illustration of the iteration procedure will be given in the next section.

It is interesting to note that for a great excess of non reacting electrolyte ε, i. e. the ratio of the thicknesses of the two diffusion layers, depends only on the transference number t_2 of the *non* reacting cation and not on the diffusion coefficient of the reacting cation. However, this is no longer the case for intermediate compositions because we are using for the iteration the values of $(c_1)_e$ and $(c_2)_e$ which are obtained from equations [36] and [32] and which therefore depend on D_1.

6. Numerical Illustration; Comparison with Experiment

For a numerical application let us now return to our system $CuSO_4 + H_2SO_4$ which we have selected as example partly because of its technical importance and partly because it is one of the few cases for which experimental data are available. BRENNER[26] has frozen quickly the diffusion layer around a cylindrical electrode by pouring suddenly a freezing mixture into the cylinder. The frozen layer was turned off on a lathe and slices of about 0.1 mm thickness were obtained which were analyzed for H^+ and Cu^{2+}. The concentration could thus be determined at a few points of the diffusion layer and the interfacial composition was obtained by extrapolation. We will carry out the numerical evaluation of the interfacial concentrations for the conditions of BRENNER's experiments. These conditions, as well as the physical properties of the system used in the computation are given in the appendix.

For $CuSO_4 + H_2SO_4$ $s_1 = \frac{1}{2}$, $z_1 = 2$, $z_2 = 1$, $z_3 = -2$, $n_1 = n_2 = 2$. The value of m (eq. [31]) is therefore 3 and eq. [32] takes the form

$$\Delta c_2/\Delta c_1 = -\frac{2}{3\varepsilon}. \qquad [32']$$

The transference number of H^+ in H_2SO_4 is 0.81 which gives, according to Fig. 3, for ε a value of 0.665. The diffusion layer for the H_2SO_4 is therefore 1.5 times thicker than for the $CuSO_4$. The ratio $\Delta c_2/\Delta c_1$, calculated from eq. [32] is equal to 1.00, the concentration differences between bulk and interface, $\overline{\Delta c_1}$ and $\overline{\Delta c_2}$, obtained from [36] and [32'], are -0.335 and $+0.336$, respectively.**

These values apply to a great excess of H_2SO_4. However, in BRENNER's experiments the ratio of $H_2SO_4 : CuSO_4$ was 1:1, the solution being 2N. In order to find the interfacial concentrations we have to use the iteration procedure outlined in section 4. From the above mentioned values of $\overline{\Delta c_1}$ and $\overline{\Delta c_2}$ we get as first approximation for the interfacial concentrations (great excess of H_2SO_4): $(c_1)_e = 0.66$ moles/l, $(c_2)_e = 2.34$ moles/l, $(c_3)_e = 1.83$ moles/l. Introducing these values into equations [23] and [24] we get (remembering the values of z and s for $CuSO_4 + H_2SO_4$)

$$\frac{2\Delta c_1}{\delta_1} = \frac{i}{D_1 F}\left[\frac{1}{2} - \frac{1.33}{12.3}\right] = \frac{0.392\, i}{D_1 F} \qquad [23'']$$

$$\frac{2\Delta c_2}{\delta_2} = -\frac{i}{D_1 F}\left[\frac{2.34}{12.3}\right] = -\frac{0.189\, i}{F D_1}. \qquad [24'']$$

Since the transference number of Cu^{2+} is not negligible we use instead of eq. [26]

$$-\frac{i}{F}\left(\frac{1}{2} - \frac{0.096}{2}\right) = -0.452\,\frac{i}{F} = \frac{d}{dx}\int_0^{\delta_1} (c_1 - (c_1)_0)\, u\, dy. \qquad [26']$$

Starting form these equations, we get, by the same procedure as that outlined in section 5, the following equations instead of [30] and [37]

$$0.704 = \varepsilon^3(\varepsilon^2 - 4\varepsilon + 5); \quad \varepsilon = 0.624 \qquad [30']$$

$$\frac{\Delta c_2}{\Delta c_1} = -\frac{0.483}{\varepsilon} \qquad [32']$$

$$A = 0.392\,(\alpha_1 - 0.62\,\alpha_2) \qquad [37']$$

which yields for $\Delta c_2/\Delta c_1 - 0.77$, for $(c_2)_e$ 2.22 moles/l and for $(c_1)_e$ 0.72 moles/l. Introducing these values into equations [23] and [24] we get for $\Delta c_2/\Delta c_1$: -0.76. A further iteration does not modify the results. Experimentally BRENNER has found for the above ratio -0.81. The agreement is very good.***

** BRENNER used in his experiments a 10 cm high cylindrical cathode; his experimental results for Δc represent a mean Δc. For this reason, in the above computation the average value $\overline{\Delta c}$ between $x = 0$ and $x = 10$ cm was calculated:

$$\overline{\Delta c} = \frac{1}{10}\int_0^{10\,\mathrm{cm}} \Delta c\, dx = \frac{5}{6}\,\Delta c_{x=10\,\mathrm{cm}}.$$

*** The good agreement between the theoretical values of $\Delta c_2/\Delta c_1$ and BRENNER's measurements was already noted in an earlier paper of N. IBL.[20] However, profiles different from those of this paper were used in applying von KÁRMÁN's method (the details of the calculation were not published at that time and only the main results were mentioned).

On the other hand, if we calculate $\Delta c_2/\Delta c_1$ from eq. [10] (approximation of a constant transference number discussed in section 4) we obtain for $\Delta c_2/\Delta c_1 = -0.56$ which is further away from the experimental value.

Although the agreement between experiment and VON KÁRMÁN's approximation is very good indeed the available experimental data are too few to allow a well founded conclusion about the reliability of the application of VON KÁRMÁN's method to electrolytic mixtures. In our laboratory we are presently engaged in a study of the diffusion layer by a refined version of the freezing method. The layer is frozen within about 1 second and slices of 10μ thickness are obtained by using a microtome. It is intended to compare the results of the measurements with the theory.

Notation

A = coefficient defined by eq. [37]
c = concentration of ions at given point y [moles/cm³]
c_e, c_0 = concentration at interface and in bulk solution, respectively [moles/cm³]
Δc = $c_0 - c_e$ = concentration difference between bulk and interface [moles/cm³]
D = diffusion coefficient [cm² s⁻¹]
F = Faraday's constant [Cb/g equiv.]
g = gravitational acceleration [cm s⁻²]
Gr_x^* = modified Grashof number = $\frac{g(\varrho_0 - \varrho_e) j^* x^4}{\varrho_0 D \nu^2 \Delta c}$
i = current density (positive for cathode, negative for anode) [A/cm²]
j = mass transport rate (flux) at interface ($y = 0$) [mole cm⁻² s⁻¹]
j^* = mass transport rate (flux) at interface, *excluding* migration [mole cm⁻² s⁻¹]
m = transference coefficient, defined by eq. [31]
n = number of gequiv. per mole of neutral electrolyte, positive when applied to a cation, negative for an anion [gequiv./mole]
R = ideal gas constant [cal degree⁻¹ mole⁻¹]
s = number of moles reacting at electrode when one Faraday flows through cell (positive when the considered species is consumed in a cathodic process or evolved in an anodic process, otherwise negative) [mole (g equiv.)⁻¹]
Sc = Schmidt number = ν/D
t = transference number
T = absolute temperature [degree]
u = upward flow velocity (x-component of velocity vector) [cm s⁻¹]
U = parameter of velocity profile (eq. [20]) [cm s⁻¹]
v = velocity of flow perpendicular to electrode (y-component of velocity vector) [cm s⁻¹]
x = vertical coordinate (parallel to gravity force), height distance from leading edge of electrode) [cm]
y = horizontal coordinate (perpendicular to electrode); distance from electrode [cm]
z = ionic charge (positive for cations, negative for anions) [gequiv. mole⁻¹]
α = densification coefficient for neutral electrolyte [cm³/mole]
δ = thickness of diffusion layer [cm]
δ^* = thickness of hydrodynamic boundary layer [cm]
ε = δ_1/δ_2 = ratio of the thicknesses of the diffusion layers for the reacting and the non reacting cations, respectively
ν = kinematic viscosity [cm² s⁻¹]
ϱ = density [g cm⁻³]

Subscripts

e denotes the interface, 0 the bulk of the solution, k any species of the solution. In the equations of the 5th section: 1: reacting cation; 2: non reacting cation; 3: common anion. In the equations for the system $CuSO_4 + H_2SO_4$ 1, 2, and 3 denote Cu^{2+}, H^+ and SO_4^{--}, respectively.

Appendix

Experimental conditions and physical properties for numerical calculations. Solution: $CuSO_4$ 2N + H_2SO_4 2N, $i = 0.02$ A/cm²; $x = 10$ cm; $a_1 = 144$ mole/cm³ ($CuSO_4$); $a_2 = 52$ mole/cm³ (H_2SO_4);[12] $g = 981$ cm s⁻²; $\nu = 1.72 \times 10^{-2}$ cm² s⁻¹;[30] $D_1 = 5.3 \times 10^{-6}$ cm² s⁻¹; $D_2 = 1.74 \times 10^{-5}$ cm² s⁻¹;[29] $t_2 = 0.81$ (for H_2SO_4); $t_2 = 0.62$ (for $CuSO_4$ 2N + H_2SO_4 2N); $t_1 = 0.096$ (for $CuSO_4 + H_2SO_4$). The transference numbers t were calculated from the mobilities λ[28] by means of the relation[27]

$$t_k = \frac{z_k c_k \lambda_k}{\sum z_k c_k \lambda_k}.$$

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