

Multicomponent ionic diffusion in porewaters: Coulombic effects revisited

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Abstract

The diffusion of an ion in porewaters cannot occur independently of the other ions in solution as a result of Coulombic coupling, as well as from other effects not considered here. Unfortunately, a longstanding disagreement exists about the correct form and meaning of the equations that describe Coulombic coupling in porewaters, i.e., Ben-Yaakov [Am. J. Sci. 281 (1981) 974] vs. Lasaga [Am. J. Sci. 281 (1981) 981]. This paper re-examines this controversy by reformulating the problem starting from fundamental concepts of mass and charge conservation. We show that these antagonistic formulations are both valid and, in fact, equivalent, when the different interpretations of charge balance are resolved. Most of the disagreements between Ben-Yaakov and Lasaga are then shown to result from differing methods of solution, not fundamental disparities in their models. We note, however, that the explanation for the concept of “stationary” gradients of nonreacting ions as given Ben-Yaakov is inaccurate, and such gradients do lead to diffusive fluxes that are counterbalanced by electrochemical migrational fluxes to produce no *net* flux (excluding advective flux). We further find that the bicarbonate diffusive flux will not balance the diffusional charge flux of sulfate during its reduction *if advection is present*. This latter imbalance generates compensating fluxes in the other nonreacting ions. We have applied our theory to a simplified case of sulfate reduction in a marine sediment. The results show that nonreacting ions do diffuse and that with normally expected values of porewater advection, the ratio of the bicarbonate to the sulfate flux can be far different than the ideal value of -2 .

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1. Introduction

The Ben-Yaakov [1] vs. Lasaga [2] debate, which revolves around disparate interpretations of the theory of ionic diffusion in porewaters, is notable because of

its inexplicable and bothersome longevity; even today, few would say this clash has been resolved. Diffusion of solute ions constitutes an important, often dominant, means of mass transport during diagenesis [3–6]. Ionic diffusion is a specific case of multicomponent diffusion, whose theory has a long and distinguished history, associated with such prominent names as the Nobel laureates M. Planck, L. Onsager, and J. Kirkwood. Standard textbooks [7–12] and extensive reviews in papers (e.g., [13]), are readily available

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on this topic. Given this abundance of background information and the level of understanding it implies, any controversy with regard to the theory's implementation in diagenetic studies appears incongruous.

Ben-Yaakov [14] pioneered the application of the theory of multicomponent ionic diffusion to porewaters. Lasaga [15] extended this treatment to include ion pairs, but he also expressed substantial criticisms of Ben-Yaakov's earlier paper, which then engendered a formal Comment from Ben-Yaakov [1] and a related formal Reply from Lasaga [2]. Later publications by these authors [16–18] failed to resolve or even clarify the matter.

The contention centers on the following main aspects:

- (a) *Model formulation:* Lasaga [2,15] argues that one of the ionic species and its gradient is not independent of the others, and therefore, must be subtracted from governing formulas. Conversely, Ben-Yaakov [14] does not “eliminate” one of the ionic species and argues in [1] that such a procedure is erroneous.
- (b) *Model interpretation:* Ben-Yaakov states that ions that are not involved in chemical reactions can display a nonzero concentration gradient, but should have no resulting diffusive flux [1,14]. In contrast, Lasaga [2,15] states that nonreacting ions all diffuse because of “cross-coupling” effects. On a related point, these antagonists further argue about the “proper” form of cross-coupling diffusion coefficients.
- (c) *Model application:* In applying their respective versions of ionic diffusion theory to sulfate reduction, Ben-Yaakov [1,14] concludes that the diffusive flux of dissolved sulfate is balanced by twice the diffusive flux of bicarbonate, in the opposite direction, in order to maintain charge balance. Lasaga [2] counters that part of this charge balance will be born by the other ions in solution, so that the sulfate bicarbonate balance should not hold exactly.

The above disagreement needs to dissolve. Consequently, this paper presents a resolution by showing that the models are entirely equivalent and that these authors are debating (pointlessly) different solution

methods. Both parties have failed to appreciate this equivalence, in large part because of ambiguous treatments of electroneutrality.

2. Fick's law

Correct treatment of the problem begins with a precise statement of the system to be modelled and the introduction of a valid set of equations that govern the dependent variables in the system. The geochemical behaviour of a solute in the interstitial water of a porous medium is governed by the mass conservation equation for a multispecies multiphase mixture,

$$\frac{\partial \varphi C_i}{\partial t} = \frac{\partial J_i}{\partial x} + \varphi R_i \quad (1)$$

where t is time, x is depth (length), C_i is concentration of this particular solute, φ is the porosity, J_i denote the *total* flux of species i , R_i is the *net* rate of production/consumption, and the index i covers all solutes. For simplicity, we model the sediment in one vertical dimension, where the x -coordinate axis points downwards from the sediment–water interface. Furthermore, we assume an isothermal environment, with constant porosity and a constant porewater velocity u (defined below). The spatial variability of any “parameter” is not crucial to the present analysis, and parameters are then treated as constants.

Stating an equation like Eq. (1) for each of the n chemical constituents of the porewater results in a coupled set of n partial differential equations in the concentration variables C_i . To obtain explicit solutions for these concentrations, the production rates, R_i , must be stated, using kinetic reaction theory and experimental results as guides. Thereafter, the sole obstacle to solution is the specification of proper constitutive expressions for the mass fluxes J_i as functions of the set of concentrations C_i ($i=1, 2, \dots, n$).

The simplest expression for J_i is obtained for the case where the transport of porewater constituents is assumed to occur independently; that is, the motion of one solute species will not influence the transport of another solute. This assumption is reasonable for small, uncharged molecules in a *dilute* solution. Each molecule then constantly undergoes collisions with solvent molecules, resulting in random motions. The

total flux can then be decomposed into an advective part and a diffusive part

$$J_i = J_i^{\text{adv}} + J_i^{\text{dif}} = \phi u C_i + J_i^{\text{dif}} \quad (2)$$

where u is a reference velocity. Following [15], we employ the velocity of the solvent as the reference velocity u . (Note that for relatively dilute solutions, even seawater, this choice of u is numerically similar to the mass-averaged and the volume averaged velocities of the solution.) The diffusive flux, J_i^{dif} , thus represents the solute's deviation from the bulk motion of the porewater. Based on a statistical random-walk description, one can prove that the diffusive flux due to random collisions is given by Fick's first law [19,20]

$$J_i^{\text{dif}} = -\phi D_i \frac{\partial C_i}{\partial x} \quad (3)$$

where D_i is the diffusivity at infinite dilution, corrected for viscosity and the tortuosity of the pores [5,15].

3. Beyond Fick's law: simple Coulombic interactions

When charged species are present in solution, the simple random-walk model becomes unsatisfactory because additional physical constraints have to be satisfied. Electrolyte solutions must obey two additional electroneutrality conditions: (i) the total charge should vanish at every point in solution, and (ii) no electrical current should run through the solution, unless one is imposed externally. Thus, the concentration and flux of one ion become linked to those of the other ions to satisfy these two conditions. For example, in the simple NaCl–H₂O system with a salt gradient, the flux of Na⁺ must always balance the flux of Cl[−] to ensure that no current is present [9,13,15]. The simple constitutive Eqs. (2) and (3) are no longer strictly valid for electrolyte solutions.

In the geosciences, two approaches have been taken to address the effects of Coulombic forces: (i) a bottom-up approach, which is a simple and pragmatic extension of Fick's first law [14,15], and (ii) a top-down approach, based on first principles from the

theory of nonequilibrium thermodynamics [21]. The latter in-depth treatment of multispecies diffusion typically leads to a coupled system of equations for the diffusive mass fluxes in terms of thermodynamic driving forces, known as the generalized Stefan–Maxwell problem [22]. Drawbacks to this top-down approach are the complexity of the resulting expressions and the number of phenomenological transport coefficients that need to be determined, faced with scant experimental data. The top-down approach is not discussed further here, and the reader is referred to the literature on the subject (e.g., [21,22]).

Our main goal is to resolve the discrepancies between the treatments of Ben-Yaakov [1,14] and Lasaga [2,15], which both follow the pragmatic approach. With this method, a third migrational term J_i^{mig} is added to the constitutive expression for the total mass flux, i.e.,

$$J_i = J_i^{\text{adv}} + J_i^{\text{dif}} + J_i^{\text{mig}} \quad (4)$$

In Eq. (4), both the advective and diffusive fluxes retain their constitutive expressions given by Eqs. (2) and (3), respectively. The migrational term J_i^{mig} then accounts for the transport coupling between the ionic species and ensures that the electroneutrality requirements are fulfilled. The macroscopic effect of the Coulombic forces between the ions is typically modelled by incorporation of the electrical field; the migrational flux is then typically written as

$$J_i^{\text{mig}} = \phi z_i D_i C_i E^* \quad (5)$$

where z_i is the charge carried by the solute and E^* is the (modified) electrical field. The magnitude of the electrical field E^* expresses the amount of adjustment needed to the solutes' fluxes due to electroneutrality constraints (see below).

While arguably less satisfactory from a mechanistic point of view, the simple extension of Fick's first law as given by Eq. (5) does have the important advantage of model simplicity. Furthermore, the simple pragmatic method and the more sophisticated top-down approach are not unrelated. In fact, the former comprises a significantly abridged version of the nonequilibrium thermodynamic approach, using infinite dilution mobilities, neglecting off-diagonal Ons-

ager coefficients, and employing ideal chemical potentials [15,21,22].

Making use of Eqs. (4) and (5), the constitutive expression for the total mass flux becomes

$$J_i = \phi u C_i - \phi D_i \frac{\partial C_i}{\partial x} + \phi z_i D_i E^* C_i \quad (6)$$

Both Ben-Yaakov [1,14] and Lasaga [2,15] agree that Eq. (6) is the basic constitutive expression from which to develop any further theory. Eqs. (1) and (6) then lead to a mass conservation equation of the form

$$\frac{\partial C_i}{\partial t} = \frac{\partial}{\partial x} \left(D_i \frac{\partial C_i}{\partial x} - z_i D_i E^* C_i - u C_i \right) + R_i \quad (7)$$

Eq. (7) defines a set of diagenetic equations that is mathematically underdetermined, as it only contains n equations for $n+1$ variables, i.e., the n constituent concentrations C_i plus the electrical field E^* . Closure must be obtained by incorporation of an additional constraint, which should be derived from electroneutrality considerations.

4. Electroneutrality and current constraints

An important part of the misunderstanding between Ben-Yaakov [1] and Lasaga [2] originates from confusion surrounding the concept electroneutrality. Both authors refer to electroneutrality as an essential condition for their model, but on closer inspection, it is clear that they possess different interpretations of this concept. In fact, the term electroneutrality has been associated with *two separate* physical requirements: (1) that the total charge Z should vanish at every point in solution, i.e.,

$$Z \equiv \sum_{i=1}^n z_i C_i = 0 \quad (8)$$

and (2) that no electrical current I should run through the solution if none is applied, i.e.,

$$I \equiv \sum_{i=1}^n z_i J_i = 0 \quad (9)$$

The validity of Eq. (8) in a heterogeneous sediment where the solid surfaces may carry charge is provided in Appendix A.

Examination of their papers shows that Ben-Yaakov [1,14] employs the “no-current” condition Eq. (9) as the sole requirement for “electroneutrality”; in contrast, Lasaga [2,15] utilizes both Eqs. (8) and (9), calling Eq. (8) the condition for electroneutrality and Eq. (9) the “no-current” condition. The obvious question then is whether these distinct interpretations of electroneutrality engender fundamentally different models. To conduct this analysis, it is instructive to investigate the implications of either condition separately. Let us sum Eq. (1) for all porewater species, using the individual charges as weighing factors, to arrive at

$$\phi \frac{\partial}{\partial t} \left(\sum_{i=1}^n z_i C_i \right) = - \frac{\partial}{\partial x} \left(\sum_{i=1}^n z_i J_i \right) + \phi \sum_{i=1}^n z_i R_i \quad (10)$$

Basic stoichiometry requires that no net charge is created during chemical reactions, i.e.,

$$\sum_{i=1}^n z_i R_i = 0 \quad (11)$$

so that Eq. (10) readily reduces to

$$\phi \frac{\partial}{\partial t} \left(\sum_{i=1}^n z_i C_i \right) = - \frac{\partial}{\partial x} \left(\sum_{i=1}^n z_i J_i \right) \quad (12)$$

We will now examine the consequences of assuming that either Eq. (8) or Eq. (9) applies exclusively. In a first case, imposing only the “no-current” condition (Eq. (9)), Eq. (12) reduces to

$$\frac{\partial}{\partial t} \left(\sum_{i=1}^n z_i C_i \right) = \frac{\partial Z}{\partial t} = 0 \quad (13)$$

which immediately tells us that the total charge cannot be a function of time. Upon integration of Eq. (13), we obtain that

$$Z(x) = f(x) \quad (14)$$

where $f(x)$ is a prescribed function of space, but not time. Note that no constraints are imposed on the spatial dependence of $Z(x)$, and hence, the absence of charge is not guaranteed a priori; however, Eq. (13) does imply that if the *initial* ion concentration profiles satisfy the no-charge condition, i.e., $f(x)=0$ at $t=0$, then Eq. (8) is valid at all future times. In other words,

if one chooses physically sensible *initial conditions*, the no-current condition (Eq. (9)) ensures that the charge condition (Eq. (8)) is always true. The steady state case, as considered by Ben-Yaakov [1,14], can be considered simply as the long-time limit of the transient model.

Let us now consider the alternative case where only the “no-charge” condition, Eq. (8), is initially invoked. The combined mass balance (Eq. (10)) now reduces to

$$\frac{\partial}{\partial x} \left(\sum_{i=1}^n z_i J_i \right) = \frac{\partial I}{\partial x} = 0 \quad (15)$$

or, upon integration,

$$\sum_{i=1}^n z_i J_i(x, t) = I(t) \quad (16)$$

which requires that the total current $I(t)$ cannot vary with depth in the sediment. From a strict mathematical viewpoint, the current $I(t)$ can still vary with time, depending on the current imposed at the boundaries. However, if one does not impose a current at the boundaries at any time, $I(t)=0$ throughout. Consequently, if one adopts physically sensible *boundary conditions*, the no-charge condition (Eq. (8)) ensures that the no-current condition (Eq. (9)) is always fulfilled. In conclusion, both possible electroneutrality cases lead to identical models, given physically realistic boundary and initial conditions.

Clearly, there are no differences in the basic models adopted by Ben-Yaakov [1,14] and Lasaga [2,15]. Either starting from Eq. (9) and adopting $Z(x)=0$ in Eq. (14), or starting from Eq. (8) and assuming $I(t)=0$ in Eq. (16), one finds that Eq. (10) transforms to the simpler condition that

$$\sum_{i=1}^n \left(z_i D_i \frac{\partial C_i}{\partial x} \right) = \sum_{i=1}^n (z_i^2 D_i E^* C_i) \quad (17)$$

Eq. (17) states that if there is no current imposed and if the system has no initial charge, then the net charge flux created by diffusion is always balanced exactly by the net migrational flux. Advection plays no role, as the fluid is not charged. Eq. (17) is the

form employed explicitly in studies that use no current as the sole statement of electroneutrality (e.g., [23–26]).

5. Implementation

We have proven that the simple models of multi-component ionic diffusion given above are completely equivalent, with the result that Ben-Yaakov [1,14] and Lasaga [2,15] are, in fact, employing the same model. Yet, this does not explain the vehement disagreement between these authors and the continued confusion over their conflicting views. Our next step is to show that their major disagreements are related to different solution strategies, which nevertheless produce the same results as the underlying model is identical.

Elimination of a concentration: Lasaga [15] advances that one of the concentrations and its derivatives need to be eliminated from all the model equations in order to obtain a solution to a multicomponent ionic diffusion problem, a procedure hotly contested by Ben-Yaakov [1]. The debate centres on the appropriateness and physical significance of such an elimination procedure. We will illustrate below that both Lasaga’s and Ben-Yaakov’s apparently incompatible approaches are, in fact, procedural and, therefore, completely equivalent. The basis for their disagreement is divergent methods for solving their model equations, not differences in physical theory.

As a first step, it is instructive to assess the number of variables and equations in the model. On the variable side, there are n solute concentrations, $C_i(x, t)$, and the modified electrical field E^* , for a total of $n+1$ dependent variables. On the equation side, we have stated n mass conservation equations, to which the “no-charge” (Eq. (8)) and the “no-current” (Eq. (9)) conditions have been added. Apparently, this results in an overdetermined system, with the equations outnumbering the variables by one. Such an impression is, however, incorrect, as these $n+2$ equations are not linearly independent. The pivotal point is that the no-charge condition can be combined with the n conservation equations to obtain the no-current condition, and vice versa, under the physically sensible boundary and initial conditions discussed above.

One can resolve this apparent overdeterminacy in either of two ways, which are nevertheless completely equivalent. As a first approach, one can solve the complete set of n differential conservation equations (Eq. (1)) in combination with the “no-current” condition (Eq. (9)). From Eq. (17), the electrical field can be explicitly determined as

$$E^* = \frac{\sum_{i=1}^n z_i D_i \frac{\partial C_i}{\partial x}}{\sum_{j=1}^n z_j^2 D_j C_j} \quad (18)$$

assuming that the solution was initially charge neutral. Eq. (18) makes it evident that the modified electrical potential E^* in electrically neutral porewaters, and the migrational fluxes it generates, is the result of unequal ionic diffusion coefficients; that is, if all the D_i values were equal, E^* would then be identically zero and no migrational fluxes could be created. With Eq. (18), the expression for the mass flux (Eq. (6)) can then be written as

$$J_i = \varphi \left(u C_i - D_i \frac{\partial C_i}{\partial x} + \frac{z_i D_i C_i}{\sum_{j=1}^n z_j^2 D_j C_j} \sum_{k=1}^n z_k D_k \frac{\partial C_k}{\partial x} \right) \quad (19)$$

where the sums are taken independently, as indicated by the different indices.

Upon substitution of Eq. (19), the set of n conservation equations (Eq. (1)), only contain the n concentrations, C_i . The problem is now mathematically well posed, and thus the concentrations can be calculated as advanced by Ben-Yaakov [1,14]. Note that the “no-charge” constraint (Eq. (8)) is not explicitly employed. Yet, under the condition that one starts from charge neutral conditions, concentrations will satisfy the “no-charge” condition at each depth in the sediment.

Eq. (19) can be further rearranged into the following form

$$J_i = \varphi \left(u C_i - \sum_{j=1}^n D_{ij} \frac{\partial C_j}{\partial x} \right) \quad (20)$$

Note that the summation in Eq. (20) ranges over all solutes. The parameter D_{ij} is referred to as a cross-coupling diffusion coefficient because it specifies the dependence of the flux of a given solute i upon the concentration gradient of another solute j . Comparison of Eqs. (19) and (20) leads to the following explicit expression for the cross-coupling coefficients,

$$D_{ij} = \delta_{ij} D_i - \frac{z_i z_j D_i D_j C_i}{\sum_{k=1}^n z_k^2 D_k C_k} \quad (21)$$

where δ_{ij} is the Dirac delta function, which has values of 1 if $i=j$ and 0 if $i \neq j$ (see [5]). Nevertheless, the cross-coupling coefficients in Eqs. (20) and (21) are mathematically not unique, as will be illustrated below.

In a second possible approach, as advocated by Lasaga [2,15], both the no-charge and no-current conditions are employed explicitly. If we decide to retain both Eqs. (8) and (9), then in combination with the n conservation equations, we now obtain an overdetermined system of equations; consequently, one of the concentration equations must be eliminated. Lasaga [15] has further interpreted this to mean that the concentration that is governed by the equation being eliminated must also be removed from all the remaining equations; this latter procedure is not, however, a mathematical or physical necessity. It is instead one possible route to solve the new set of equations.

Elimination of a concentration is possible because Eq. (8) imposes a rigid interdependence between the concentration profiles of the ions in solution. In other words, it is possible to remove a particular “dependent” ion from the model, and accordingly, the knowledge of the concentrations of the remaining ions will allow the complete determination of the concentration profile for that eliminated ion. Following Lasaga [15], the chloride ion can be arbitrarily chosen as the dependent ion, and the no-charge constraint then leads to condition that

$$C_{\text{Cl}^-} = -\frac{1}{z_{\text{Cl}^-}} \sum_{i=1}^{n-1} z_i C_i = \sum_{i=1}^{n-1} z_i C_i \quad (22)$$

With Eq. (22) and its derivative, the flux equation for all species, except the “dependent” species Cl^- , is given by

$$J_i = \varphi u C_i - \varphi D_i \frac{\partial C_i}{\partial x} + \frac{\varphi z_i D_i C_i}{\sum_{j=1}^{n-1} (D_{\text{Cl}^-} + z_j D_j) z_j C_j} \times \left[\sum_{k=1}^{n-1} z_k (D_k - D_{\text{Cl}^-}) \frac{\partial C_k}{\partial x} \right] \quad (23)$$

Eq. (23) no longer contains the chloride concentration or its derivatives. Hence, one can now solve a reduced set of $n - 1$ differential equations to obtain the $n - 1$ principal concentrations. The chloride concentration is then simply calculated by means of the no-charge constraint, Eq. (22). Eq. (23) can be rearranged to a form similar to Eq. (20), although the summation now only includes $n - 1$ gradients

$$J_i = \varphi \left(u C_i - \sum_{j=1}^{n-1} D'_{ij} \frac{\partial C_j}{\partial x} \right) \quad (24)$$

Accordingly, a new set of cross-coupling coefficients D'_{ij} can be defined

$$D'_{ij} = \delta_{ij} D_i - \frac{z_i z_j D_i (D_j - D_{\text{Cl}^-}) C_i}{\sum_{k=1}^{n-1} (D_{\text{Cl}^-} + z_k D_k) z_k C_k} \quad (25)$$

Note that this $(n - 1) \times (n - 1)$ matrix D'_{ij} is numerically different from the $(n) \times (n)$ matrix of coefficients D_{ij} defined in Eq. (21). Yet, being entirely equivalent representations of the transport problem, the actual choice between the two representations given by Eqs. (21) and (25) for the flux J_i is completely arbitrary, as long as one uses the corresponding set of concentration gradients and diffusion constants. The particular form of these cross-coupling coefficients is a result of a choice of solution technique, not a fundamental physical constraint. This is why there is no unique matrix of cross-coefficients, and why the representations offered by Ben-Yaakov and Lasaga are equivalent. (These statements do not preclude the existence of specifically defined cross-coupling coefficients either from nonideal chemical potentials [21] or from the Maxwell–Stefan model of multicomponent ionic diffusion [22].)

“*Nondiffusing*” ions: Another point of disagreement between Ben-Yaakov [1,14] and Lasaga [2,15] concerns the question of whether an ion can have a nonzero diffusive flux although that ion does not participate in chemical reactions. Ben-Yaakov [1] (pp. 976–977) claimed that the answer must be negative, while Lasaga [2,15] concluded the opposite. We will address this point by considering Ben-Yaakov’s treatment of so-called *stationary gradients*.

In general, can an ion that does not participate in diagenetic reactions, $R_i = 0$, still have a diffusive flux, J_i^{dif} ? Contrary to statements by Ben-Yaakov [1] (pp. 974, 976–977), the answer is yes; on this point, Ben-Yaakov gets the mathematics right, but the interpretation wrong. Let us consider the conservation equation for a nonreacting ion and let us assume steady state for mathematical simplicity. That ion’s conservation equation is then

$$\frac{d}{dx} (J_i^{\text{adv}} + J_i^{\text{dif}} + J_i^{\text{mig}}) = 0 \quad (26)$$

Assume that there exists a depth, L , in the sediment, including $L = \infty$, where the gradients disappear; then Eq. (26) can be integrated to obtain:

$$J_i^{\text{adv}}(x) + J_i^{\text{dif}}(x) + J_i^{\text{mig}}(x) = J_i^{\text{adv}}(L) \quad (27)$$

because both the diffusive and migrational fluxes must disappear at L , where gradients disappear. Ben-Yaakov [14] implicitly assumes that advection is absent, $u = 0$. Setting $J_i^{\text{adv}}(x) = 0$, the balance for this nonreacting ion now reads as

$$J_i^{\text{dif}}(x) = -J_i^{\text{mig}}(x) \quad (28)$$

or, substituting Eq. (6),

$$D_i \frac{dC_i}{dx} = z_i D_i E^* C_i \quad (29)$$

which is Eq. (12) in Ben-Yaakov’s work ([1], p. 977). Our Eqs. (28) and (29) clearly state that the diffusive flux of an unreactive ion (left-hand side), i.e., one that is not “involved in diagenetic processes” as defined by Ben-Yaakov ([1], p. 974), exists and is balanced by an opposing migrational flux (right-hand side), due to the electrical potential gradient, such that there is no *net* flux of the unreactive ion in the absence of

advection. However, only if E^* is zero is there no *diffusional* flux of the unreactive ion; given that another ion in the system has a gradient, resulting from chemical reaction or imposed boundary conditions, E^* will be nonzero and the unreactive ion will have a diffusive flux, but no net flux. This interpretation is consistent with the theory of electrodes, cited by Ben-Yaakov [1], which usually refers to steady state with no bulk fluid motions (see [9,13]).

The conclusions reached with respect to Eqs. (28) and (29) are valid only in the *absence of advection*. With nonzero advection, Eq. (27) indicates that first, the migrational flux of a nonreacting ion does not, in general, balance its diffusional flux, and the difference is accounted for by the ion's advective flux. Second, advection causes a net flux of magnitude equal to the advective flux at depth L , i.e., $J_i^{\text{adv}}(L) = u(L)C_i(L)$, that is lost from the reaction zone of the sediment. Only if the advective flux were the same at each depth would this conclusion be untrue; that is, the advective fluxes would then cancel from both sides of Eq. (27). That might at first appear to be possible, because u is a constant at each depth under the assumption of constant porosity and steady state [3,5]; however, both Lasaga [2,14] and Ben-Yaakov [1] state that there will be nonzero gradients of nonreactive ions, which means, in general, that $C_i(x) \neq C_i(L)$ and the advective fluxes on both sides of Eq. (27) do not normally cancel, i.e.,

$$J_i^{\text{adv}}(x) \neq J_i^{\text{adv}}(L) \quad \text{for all } x < L \quad (30)$$

If the gradient of the ion is overall positive, i.e., $C_i(0) < C_i(L)$, then there will be an excess burial flux of the nonreactive ion over that being buried (advected) at the sediment water interface. If the gradient is overall negative, i.e., $C_i(0) > C_i(L)$, then there will be a deficit. Lasaga's ([2], p. 987) treatment allows for this possibility. There is nothing magical about these "excess" burial fluxes of nonreacting ions. The migrational term in Eq. (4) creates a coupling between *all* ions in solution (see Eq. (18)). If the distributions of some ions are modified by reactions, then the nonreacting ions are forced to help maintain the charge balance via this coupling and gradients of nonreacting ions are produced. Given a nonzero gradient, the amount ultimately *buried* is

different than the advective flux at the sediment–water interface.

Sulfate and bicarbonate fluxes: Now let us turn to reacting ions, and specifically the hotly debated question of the balance between the sulfate and bicarbonate fluxes during sulfate reduction; that is, does $J_{\text{HCO}_3} = -2J_{\text{SO}_4}$? To analyze this condition, we begin with the conservation equations for bicarbonate and sulfate, respectively,

$$\phi \frac{\partial C_{\text{HCO}_3}}{\partial t} = \frac{\partial J_{\text{HCO}_3}}{\partial x} + 2\phi R_{\text{red}} \quad (31)$$

$$\phi \frac{\partial C_{\text{SO}_4}}{\partial t} = \frac{\partial J_{\text{SO}_4}}{\partial x} - \phi R_{\text{red}} \quad (32)$$

where R_{red} is the rate of sulfate reduction and where we have assumed that no other significant reactions affect these reactants; this latter assumption is significant for bicarbonate, which can be affected by suboxic organic matter decay reactions, carbonate dissolution and precipitation, and even reverse weathering. As a first procedural step, eliminate the reaction terms between these equations by multiplying Eq. (32) by 2 and adding the result to Eq. (31),

$$\phi \frac{\partial (C_{\text{HCO}_3} + 2C_{\text{SO}_4})}{\partial t} = \frac{\partial (J_{\text{HCO}_3} + 2J_{\text{SO}_4})}{\partial x} \quad (33)$$

Eq. (33) states that the depth change in the weighted sum of the *net* fluxes of sulfate and bicarbonate is related to the time change in the weighted sum of their concentrations. Therefore, in the transient state, the net bicarbonate flux does not ordinarily equal twice the flux of sulfate (net or otherwise).

Notably, if steady state is now assumed, then Eq. (33) reduces to

$$\frac{d(J_{\text{HCO}_3} + 2J_{\text{SO}_4})}{dx} = 0 \quad (34)$$

Eq. (34) guarantees that there is no change with depth in this weighted sum of the total fluxes, but that does not necessarily equate to an equality of the fluxes themselves. We now need to integrate Eq. (34), making use of the conditions at $x=L$, as in the previous case. We assume that the gradients disappear at $x=L$, such that both diffusional and migrational fluxes disappear at this depth. This vanishing of

gradients is the third assumption in this derivation and limits the conditions under which $J_{\text{HCO}_3} = -2J_{\text{SO}_4}$ even further; for example, it excludes situations where freshwater seeps into seawater and vice versa. Thus,

$$J_{\text{HCO}_3}(x) + 2J_{\text{SO}_4}(x) = J_{\text{HCO}_3}^{\text{adv}}(L) + 2J_{\text{SO}_4}^{\text{adv}}(L) \quad (35)$$

which proves that, even at steady state, the net bicarbonate flux, $J_{\text{HCO}_3}(x)$, will not normally be exactly double the sulfate flux if porewater is being *buried*, i.e., $J_{\text{HCO}_3}^{\text{adv}}(L) \neq 0$, even if $J_{\text{SO}_4}^{\text{adv}} = 0$, due to complete sulfate reduction. Eq. (35) represents the general reality of diagenesis, because burial occurs in most sediments. This is the point argued by Lasaga [15], pp. 343–344; [2], p. 987.

If there is burial of porewater, then the bicarbonate to sulfate flux ratio is given by rearranging Eq. (35) into the form

$$\frac{J_{\text{HCO}_3}}{J_{\text{SO}_4}} = \underbrace{-2}_{\text{Ideal Ratio}} + \underbrace{\frac{J_{\text{HCO}_3}^{\text{adv}}(L) + 2J_{\text{SO}_4}^{\text{adv}}(L)}{J_{\text{SO}_4}}}_{\text{Correction for Advection}} \quad (36)$$

Eq. (36) governs the ratio of the total fluxes, and in general, this ratio is a function of depth. If and only if the advection velocity is nil does Eq. (35) reduce to

$$J_{\text{HCO}_3} = -2J_{\text{SO}_4} \quad (37)$$

as advanced by Ben-Yaakov [14]. Later, in [1,2], the argument was shifted to a comparison of the diffusive fluxes of bicarbonate and sulfate; however, the theory given above deals with total, not simply diffusive fluxes. Statements about the ratio of diffusive fluxes depend on additional assumptions regarding the relative magnitude of migrational and advective terms.

In summary, the required conditions for the validity of Eq. (37) are (a) *no reactions* affecting bicarbonate or sulfate other than sulfate reduction, (b) *fading gradients* with depth, (c) *steady state*, and (d) *no advection* of porewater, $J_i^{\text{adv}}(x) = 0$. We have proven with Eq. (36) that the bicarbonate flux cannot provide an *exactly* counterbalancing charge flux to the sulfate fluxes caused by sulfate reduction if the porewaters advect due to burial, compaction or hydrological flow. This imbalance necessitates fluxes of the other charged ions.

6. Example

In order to provide the reader with an appreciation for the numerical magnitude of the Coulombic effects discussed above, we illustrate the solution for a simplified porewater system subject to sulfate reduction,



We allow five ionic solutes (Na^+ , Cl^- , Mg^{2+} , SO_4^{2-} , HCO_3^-), diffusion, migration, porewater advection, constant porosity, and steady-state diagenesis. Sulfate reduction is represented as a depth-decreasing exponential [3]. We state the governing equations using the Lasaga approach for reasons discussed further below:

$$\frac{d}{dx} \left[D_{\text{Na}} \frac{d[\text{Na}]}{dx} - z_{\text{Na}} D_{\text{Na}} [\text{Na}] E^* - u[\text{Na}] \right] = 0 \quad (39)$$

$$\frac{d}{dx} \left[D_{\text{Mg}} \frac{d[\text{Mg}]}{dx} - z_{\text{Mg}} D_{\text{Mg}} [\text{Mg}] E^* - u[\text{Mg}] \right] = 0 \quad (40)$$

$$\frac{d}{dx} \left[D_{\text{SO}_4} \frac{d[\text{SO}_4]}{dx} - z_{\text{SO}_4} D_{\text{SO}_4} [\text{SO}_4] E^* - u[\text{SO}_4] \right] - R_0 e^{-\alpha x} = 0 \quad (41)$$

$$\frac{d}{dx} \left[D_{\text{HCO}_3} \frac{d[\text{HCO}_3]}{dx} - z_{\text{HCO}_3} D_{\text{HCO}_3} [\text{HCO}_3] E^* - u[\text{HCO}_3] \right] + 2R_0 e^{-\alpha x} = 0 \quad (42)$$

plus Eq. (18) to calculate E^* , Eq. (22) to calculate Cl^- , and the boundary conditions

$$[C_i](x=0) = [C_i]_0 \quad (43)$$

$$\partial[C_i]/\partial x = 0 \quad \text{at } x = L \quad (44)$$

We solve this model for a seawater-like case with simple disappearance of all gradients at a depth $L = 115$ cm and where $[\text{Na}]_0 = [\text{Cl}]_0 = 0.5$ mmol cm^{-3} , $[\text{Mg}]_0 = 0.03$ mmol cm^{-3} , $[\text{SO}_4]_0 = 0.029$ mmol cm^{-3} , and $[\text{HCO}_3]_0 = 0.002$ mmol cm^{-3} at the sediment–water interface and $u = 0.1$ cm year^{-1} . Furthermore, we set $R_0 = 1.25 \times 10^{-3}$ mmol cm^{-3}

year^{-1} , and $\alpha = 0.01$ to produce marine profiles similar to those at the FOAM site [3]. Diffusion coefficients are calculated at 10 °C using the equations in [5]. The resulting equations are solved by numerical integration with the FORTRAN code PDECOL [27]. This solution methodology does not lead to a matrix of cross-coupling coefficients as in Eqs. (21) and (25),

again illustrating the solution-related nature of these coefficients.

Fig. 1 illustrates the calculated fluxes of sulfate (Panel A) and sodium (Panel B) for this marine case. Diffusion dominates the sulfate flux, and the small difference between the diffusion and the total flux is attributable to advection. The migrational and diffu-

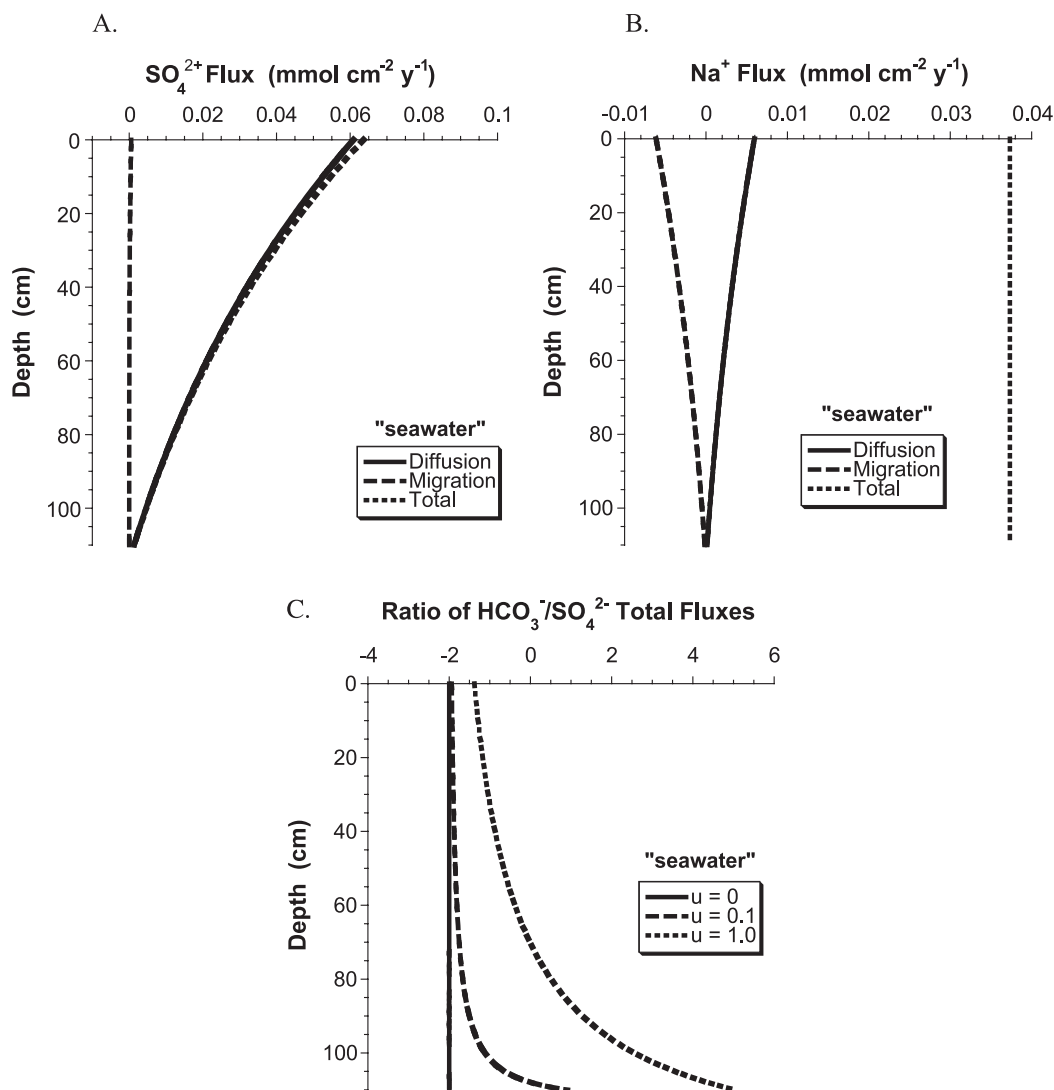


Fig. 1. Illustrations of selected solution components for the simplified porewater model (Eqs. (39)–(43)) as applied to a marine sediment subject to sulfate reduction. Parameter values are given in the text, but the porewater velocity, u , is 0.1 cm year⁻¹, unless otherwise stated. Panel A displays the diffusional, migrational and total fluxes of dissolved sulfate, a reacting ion, as a function of depth, while Panel B provides the same information about sodium, a nonreacting ion. Panel C shows the calculated ratios of the bicarbonate and sulfate total fluxes as a function of depth and three values of the porewater velocity, u .

sive fluxes of sodium are equal and opposite, as demanded by Eq. (29), and its total (net) flux results only from advection (burial) of the porewater. Fig. 1C displays the calculated ratio of the total fluxes of bicarbonate and sulfate for three different porewater advection velocities. The curve labelled $u=0$ has no porewater advection, and the ratio in this case is indistinguishable from the ideal value of -2 . The other two curves in this figure illustrate the effects of porewater advection (downward) of 0.1 and 1.0 cm year⁻¹, which arguably bracket the range for near-shore sediments. The deviations caused by these advectons become appreciable with depth and are related to the fact that fluxes become dominated by advection at depth (see Eq. (36)). We repeated these calculations for “freshwater” sediments by reducing the sodium and chloride concentrations by a factor of 100, but the results were insignificantly different than the illustrated seawater case (not shown).

By comparison, the solution of the above example via the Ben-Yaakov approach is problematical. The conservation equations for the system are then Eqs. (39)–(42), Eq. (18), plus a conservation equation for Cl⁻,

$$\frac{\partial [\text{Cl}]}{\partial t} = \frac{\partial}{\partial x} \left[D_{\text{Cl}} \frac{\partial [\text{Cl}]}{\partial x} - z_{\text{Cl}} D_{\text{Cl}} [\text{Cl}] E^* - u [\text{Cl}] \right] = 0 \quad (45)$$

One solution to Eqs. (39)–(45) is given by

$$[\text{Na}] = [\text{Na}]_0 \text{ (a constant)} \quad (46)$$

$$[\text{Mg}] = [\text{Mg}]_0 \text{ (a constant)} \quad (47)$$

$$[\text{SO}_4] = [\text{SO}_4]_0 + \frac{x R_0 e^{-\alpha L}}{D_{\text{SO}_4} \alpha} - \frac{R_0}{D_{\text{SO}_4} \alpha^2} (1 - e^{-\alpha x}) \quad (48)$$

$$[\text{HCO}_3] = [\text{HCO}_3]_0 - \frac{2 R_0 x e^{-\alpha L}}{D_{\text{HCO}_3} \alpha} + \frac{2 R_0}{D_{\text{HCO}_3} \alpha^2} (1 - e^{-\alpha x}) \quad (49)$$

$$[\text{Cl}] = [\text{Cl}]_0 \text{ (a constant)} \quad (50)$$

which can be verified by substitution. This solution is also the solution when $E^*=0$, i.e., no Coulombic coupling. Now, the Coulombically coupled and the noncoupled models cannot have the same solution and be different models; how is this situation possible? Notice that Eqs. (46)–(50) are not solutions to the problem when posed in the same way as Lasaga, i.e., Eqs. (18), (22), (39)–(42). Therefore, the problem is related specifically to the Ben-Yaakov formulation.

To explain this result, recall how Eq. (18) was derived; one starts by multiplying each conservation equation by z_i and summing to obtain

$$\frac{\partial}{\partial t} \left(\sum_{i=1}^n z_i C_i \right) = \frac{\partial}{\partial x} \left(\sum_{i=1}^n z_i \left[D_i \frac{\partial C_i}{\partial x} - z_i D_i E^* C_i - u C_i \right] \right) + \sum_{i=1}^n z_i R_i \quad (51)$$

Now introduce (1) no charge, (2) no creation of charge by reactions, and then integrate using (3) the no-current condition to obtain Eq. (17), which leads to Eq. (18) with an embedded condition of no-charge.

However, there is at least one alternative derivation of Eq. (51). Assume instead the conditions of (1) steady state, (2) no advection, (3) no-charge creation, and then integrate using (4) the no-current condition; Eq. (51) again reduces to Eq. (17). Thus, two independent sets of conditions/assumptions lead to the same equation, Eq. (17). The model cannot fulfil both sets of assumptions simultaneously, and the effect of assuming *steady state* and *no advection* is to remove or mask the embedded no-charge information in the Ben-Yaakov approach. Conversely, when you bring back the no-charge condition explicitly, as in the Lasaga statement of this problem, all the conditions, i.e., no-charge, no-current, charge-balanced reactions, steady state and no advection, can be fulfilled. The important lesson from this latter result is that supplementary assumptions, beyond those present in the theory of Coulombic interactions and diffusion, e.g., steady state and no advection, can have serious consequences to the solution of ionic diffusion–reaction equations. Such assumptions cannot then be made arbitrarily, and their consequences to the theory need to be fully appreciated.

7. Conclusions

The longstanding disagreement between Ben-Yaakov [1,14] and Lasaga [2,15] treatments of multicomponent ionic diffusion is baseless. We show that both model formulations are entirely equivalent, and the only difference is in the solution strategy. The Ben-Yaakov procedure solves the conservation equations for each of the N ions in solutions in combination with the “no-current” condition. The “no-charge” condition is implicitly fulfilled in this approach. Lasaga’s treatment retains only $N - 1$ conservation equations, but explicitly employs both the “no-current” condition and the “no-charge” constraint. Both modelling approaches lead, however, to entirely identical solutions if no further assumptions are invoked, e.g., steady state and no advection.

We have calculated the effects of Coulombic interactions in a simplified “marine” sediment subject to sulfate reduction. Coulombic effects, such as migration and diffusion of nonreacting ions, clearly exist in our results, but they are sufficiently modest that they generally can be ignored in most diagenetic modelling exercises, except perhaps studies of pH and speciation. This conclusion cannot be extrapolated to the case where large salinity gradients are present. We also find that the total bicarbonate and sulfate fluxes have a ratio different from the ideal -2 value demanded by Ben-Yaakov [1,14] with porewater advection velocities expected for nearshore marine sediments. Thus, the theoretical -2 ratio is excepted only in the steady state, with no porewater advection, no competing reactions, and the absence of boundary forcing, such as seepage of freshwater into marine porewaters.

We end this paper with a note of caution: we have restricted ourselves to pure Coulombic effects, and our conclusions apply only to those effects. Additional influences from ion pairing [15,18], or specific ion interactions, i.e., nonideal chemical potentials [21,22], or fast reversible reactions [28] should also be considered in a realistic diagenetic model of multicomponent ionic diffusion and these effects can be nontrivial.

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[BOYLE]

Appendix A

It is easy to show that Eq. (8) is the appropriate form for the no-charge condition, even in porewaters of a clayey sediment. To gain overall electroneutrality, the charge on the surface of the solids must be balanced by adsorbed ions, while any residual charge is counterbalanced by the remaining ions in solution, i.e. [11],

$$\frac{(1 - \phi)}{\phi} \left[-S(x) - F \sum_{i=1}^N z_i \bar{C}_i \right] - F \sum_{i=1}^N z_i C_i = 0 \quad (\text{A1})$$

where $S(x)$ is the fixed charge density associated with any charges on the surface of the sediment particles, e.g., the negative charges usually present on the surface of clay “platelets” (units of C per unit volume of solid sediment), F is Faraday’s constant, and \bar{C}_i is the adsorbed concentration of ions at the sites given by $S(x)$, in units of moles per unit volume of solids.

Now, it is generally assumed [29] that the counterbalancing ions in solution are concentrated in an electrical double layer around each sediment particle, such that the porewater outside the double layers is electrically neutral, i.e.,

$$\frac{(1 - \phi)}{\phi} \left[-S(x) - F \sum_{i=1}^N z_i \bar{C}_i \right] - F \sum_{i=1}^N z_i [C_i]_{\text{edl}} = 0 \quad (\text{A2})$$

and, by definition,

$$\sum_{i=1}^N z_i [C_i]_{\text{bpw}} \equiv 0 \quad (\text{A3})$$

where the subscript edl indicates the mean value in the electrical double layers and the subscript bpw indicates the mean in the bulk porewater outside the electrical double layers.

Eq. (A3) expresses the general state of porewaters if the electrical double layer occupies a small fraction of the porewater volume at any depth, and this is indeed the case. Specifically, Stumm and Morgan [29] state that the thickness x_{edl} (the linear dimension) of an electrical double layer is approximately given by

$$x_{\text{edl}} = \left(\frac{\varepsilon \varepsilon_0 R T}{2 F I \times 10^3} \right)^{\frac{1}{2}} \quad (\text{A4})$$

where ε_0 is the vacuum permittivity, ε is the dielectric constant for the porewater, and I is the ionic strength. Typical values for the parameters in Eq. (A4) are $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$, $T = 298 \text{ K}$, $\varepsilon_0 = 8.854 \times 10^{-10} \text{ C}^2 \text{ J}^{-1} \text{ cm}^{-1}$, and $\varepsilon \approx 80$, $F = 969,490 \text{ C mol}^{-1}$, while I varies from 0.7 in seawater to 0.01 in freshwater. Stumm and Morgan ([29], p. 555) calculate that x_{edl} is of the order of 10 nm for freshwater and 0.4 nm in seawater. By comparison, a linear pore dimension is of the order of the clay platelet size or larger; for clays, this is no less than 10^{-6} m , or at least 2 to 3 orders of magnitude larger than x_{edl} . Thus, electrical double layers occupy a small fraction of the pore space and most of the porewater is well described by Eq. (A3); consequently, we can drop the subscript bpw in Eq. (A3) without problem—which is Eq. (8). Eq. (A2) plays no further role in our development.

References

- [1] S. Ben-Yaakov, Discussion—diffusion of seawater ions: significance and consequences of cross coupling effects, *Am. J. Sci.* 281 (1981) 974–980.
- [2] A.C. Lasaga, Reply—diffusion of seawater ions: significance and consequences of cross coupling effects: further comments and clarifications, *Am. J. Sci.* 281 (1981) 981–988.
- [3] R.A. Berner, *Early Diagenesis: A Theoretical Approach*, Princeton Univ. Press, Princeton, NJ, 1980, 241 pp.
- [4] D.E. Anderson, Chapter 6—diffusion in electrolyte mixtures, in: A.C. Lasaga, R.J. Kirkpatrick (Eds.), *Kinetics of Geochemical Processes, Reviews in Mineralogy*, vol. 8, Mineral. Soc. Am., Washington, D.C., 1981, pp. 211–260.
- [5] B.P. Boudreau, *Diagenetic Models and Their Implementation*, Springer-Verlag, Heidelberg, 1997, 414 pp.
- [6] A.C. Lasaga, *Kinetic theory in the Earth Sciences*, Princeton Univ. Press, Princeton, NJ, 1998, 811 pp.
- [7] H.S. Harned, B.B. Owen, *The Physical Chemistry of Electrolytic Solutions*, 3rd ed., Reinhold Publ., New York, 1958, 803 pp.
- [8] R.A. Robinson, R.H. Stokes, *Electrolytic Solutions*, 2nd ed., Butterworths, London, 1959, 571 pp.
- [9] V.G. Levich, *Physicochemical Hydrodynamics*, Prentice-Hall, Englewood Cliffs, NJ, 1962, 700 pp.
- [10] J.O'M. Bockris, A.K.N. Reddy, *Modern Electrochemistry*, vol. 1, Plenum/Rosetta, London, 1973, 622 + xxviii pp.
- [11] I. Rubinstein, *Electro-diffusion of ions*, SIAM Studies Appl. Math., vol. 11, Soc. Indus. Appl. Math., Philadelphia, 1990, 254 pp.
- [12] R. Taylor, R. Krishna, *Multicomponent Mass Transfer*, Wiley, New York, 1993, 579 pp.
- [13] J. Newman, Transport processes in electrolyte solutions, *Adv. Electrochem. Electrochem. Eng.* 5 (1967) 87–135.
- [14] S. Ben-Yaakov, Diffusion of sea water ions: I. Diffusion of sea water into dilute solution, *Geochim. Cosmochim. Acta* 36 (1972) 1395–1406.
- [15] A.C. Lasaga, The treatment of multicomponent diffusion and ion pairs in diagenetic fluxes, *Am. J. Sci.* 279 (1979) 324–346.
- [16] A. Katz, S. Ben-Yaakov, Diffusion of seawater ions: Part II. The role of activity coefficients and ion pairing, *Mar. Chem.* 8 (1980) 263–280.
- [17] A.C. Lasaga, Influence of diffusion coupling on diagenetic concentration profiles, *Am. J. Sci.* 281 (1981) 553–575.
- [18] K.R. Applin, A.C. Lasaga, The determination of SO_4^{2-} , NaSO_4 , and MgSO_4 tracer diffusion coefficients and their application to diagenetic flux calculations, *Geochim. Cosmochim. Acta* 48 (1984) 2151–2162.
- [19] W. Feller, *An Introduction to Probability Theory and Its Applications*, vol. 1, 3rd edition, Wiley, New York, 1968, 704 pp.
- [20] C.W. Gardiner, *Handbook of stochastic methods for physics, Chemistry and the Natural Sciences*, 2nd ed., Springer Series in Synergetics, vol. 13, Springer Verlag, Berlin, 1985, 442 pp.
- [21] A.R. Felmy, J.H. Weare, Calculation of multicomponent ionic diffusion from zero to high concentration: I. The system Na–K–Ca–Mg–Cl– SO_4 – H_2O at 25 °C, *Geochim. Cosmochim. Acta* 55 (1991) 113–131.
- [22] R. Krishna, J.A. Wesselingh, The Maxwell–Stefan approach to mass transfer, *Chem. Eng. Sci.* 52 (1997) 861–911.
- [23] R. Mills, A. Perera, J.P. Simonin, L. Orcil, P. Turq, Coupling of diffusion processes in multicomponent electrolyte solutions, *J. Phys. Chem.* 89 (1985) 2722–2725.
- [24] D.G. Leaist, B. Wiens, Interdiffusion of acids and bases. HCl and NaOH in aqueous solution, *Can. J. Chem.* 64 (1986) 1007–1011.
- [25] J.-P. Simonin, J.-F. Gaillard, P. Turq, E. Soualhia, Diffusion

- coupling in electrolyte solutions: 1. Transient effects on a tracer ion: sulfate, *J. Phys. Chem.* 92 (1988) 1696–1700.
- [26] P. Van Cappellen, J.-F. Gaillard, Biogeochemical dynamics in aquatic systems, in: P.C. Lichtner, C.I. Steefel, E.H. Oelkers (Eds.), *Reactive Transport in Porous Media, Reviews in Mineralogy, Mineral. Soc. Am.*, vol. 34, Washington D.C., 1996, pp. 335–376.
- [27] N.K. Madsen, R.F. Sincovec, Algorithm 540, PDECOL, general collocation software for partial differential equations, *ACM Trans. Math. Softw.* 5 (1979) 326–351.
- [28] B.P. Boudreau, A steady-state diagenetic model for dissolved carbonate species and pH in the porewaters of oxic and suboxic sediments, *Geochim. Cosmochim. Acta* 51 (1987) 1985–1996.
- [29] W. Stumm, J.J. Morgan, *Aquatic Chemistry*, 3rd ed., Wiley-Interscience, Wiley, 1996, 1022 pp.