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Approximate high flux corrections for multicomponent mass transfer models and some explicit methods

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Abstract

New approximate simplifications are made to the high flux correction matrix for the film model and the penetration model, as derived from the Maxwell–Stefan mass transfer theory. Approximations are valid for both predetermined total flux, when explicit method results, and equivalently when total fluxes must be iterated. These presented simplifications are simple enough so as to be always includable in the mass transfer calculations, and the zero total flux assumption (equimolar transfer) is never needed for computational reasons in practical calculations. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Multicomponent mass transfer can be calculated with the following equation:

$$(N) = c_t[k][\Xi_I](x_I - x_B) + N_t(x_I), \tag{1}$$

where $[k]$ is the matrix of mass transfer coefficients, and $[\Xi_I]$ is the matrix of high flux corrections (to the mass transfer coefficients). The mass transfer coefficient matrix is defined for the film theory as $[k] = [D]/\ell$, where $[D]$ is the matrix of diffusion coefficients and ℓ is the mass transfer film thickness. This film thickness is usually not known, and a correlation of dimensionless numbers must be used to calculate the mass transfer coefficient matrix. In the equations to follow, the mass transfer coefficient matrix is used straightforwardly, instead of the diffusion coefficient matrix and the film thickness separately. Benefit of this approach is that the mass transfer equations are similar for the film and for the penetration theories.

The high flux correction matrix for the linearized film model and for the exact Maxwell–Stefan film model is

$$[\Xi_I] = [\psi][\exp[\psi] - [I]]^{-1} \tag{2}$$

and for the penetration theory it is

$$[\Xi_I] = \exp\left(\frac{-[\Psi]^2}{\pi}\right)\left([I] + \mathrm{erf}\left(\frac{[\Psi]}{\sqrt{\pi}}\right)\right)^{-1}. \tag{3}$$

In these equations, $[\psi]$ is the matrix of mass transfer rate factors. For the linearized film model (where the changes in the total concentration and in the diffusion coefficient matrix along the film are neglected, and averages used), it is

$$[\psi] = N_t l/c_t\,[D_{\mathrm{av}}]^{-1} = N_t/c_t\,[k_{\mathrm{av}}]^{-1}. \tag{4}$$

For the exact Maxwell–Stefan equation, this matrix is more complicated. The high flux correction takes account of the curvature in the composition profiles in the mass transfer region. This curvature is due to convective flux and diffusional interactions effects. In the linearized model the composition profile curvature due to the changes in the diffusional interactions is neglected. (Taylor and Krishna, 1993, pp. 20, 163–165, 184–185; Krishna and Standart, 1976).

2. High flux correction matrix simplifications

The film model high flux correction matrix can be simplified by linearization. This cannot be done directly

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to the original form, but can be done by using exponential function series expansion

$$[\Xi] = [\Psi][\exp[\Psi] - [I]]^{-1} = [\Psi]\left[\sum_{k=0}^{\infty}\frac{[\Psi]^k}{k!} - [I]\right]^{-1}$$

$$= \left[\sum_{k=1}^{\infty}\frac{[\Psi]^{k-1}}{k!}\right]^{-1}. \tag{5}$$

If the last form is linearized at the origin $[\Psi] = [0]$, a very simple form is then obtained

$$[\Xi] = [I] - 1/2[\Psi]. \tag{6}$$

This corresponds to linearization at zero total flux for the linearized mass transfer theory.

Penetration theory high flux correction matrix may be simplified in several ways. The simplest may be the following. The exact correction form is linearized at the origin (zero total flux, or $[\Psi] = [0]$)

$$[\Xi] = [I] - 2/\pi[\Psi]. \tag{7}$$

These linearizations (and others) may be generalized to an unified form

$$[\Xi] = [\mathrm{I}] - a[\Psi]. \tag{8}$$

The high flux corrections are often multiplied with zero flux mass transfer coefficient matrix. The result is called the high flux mass transfer coefficient matrix. After recalling the definition of the mass transfer rate factor matrix this can be as

$$[k^{\bullet}_{\mathrm{av}}] = [k_{\mathrm{av}}][\Xi_I] = [k_{\mathrm{av}}] - aN_t/c_t[I]. \tag{9}$$

Taylor (1982) suggests that the penetration theory high flux correction matrix can be calculated from a rational approximation. In the method presented here, no matrix inversions are needed, conversely to Taylor's suggestion, and the high flux correction can be premultiplied to the high flux mass transfer coefficient matrix, which results in remarkably a simple form (9). This form make the derivation of a class of explicit methods possible.

3. Approximate explicit methods for the film- and the penetration models

Explicit methods can be derived only if the so-called bootstrap condition can be found. (Taylor and Krishna, 1993, pp. 147–149). In the following derivation for the linearized theory the high flux superscript is used as a reminder wherever the high flux correction is taken into account. For molar fluxes we write

$$N^{\bullet}_i = J^{\bullet}_i + x_{i,I}N_t. \tag{10}$$

The bootstrap condition states that the molar fluxes are not linearly independent, and it is written here as

$$\sum_{i=1}^{n} v_i N^{\bullet}_i = 0. \tag{11}$$

Summing up over all components we get

$$\sum_{i=1}^{n} v_i J^{\bullet}_i + N_t \sum_{i=1}^{n} v_i x_{i,I} = 0. \tag{12}$$

For $J^{\bullet}$ we can write in the general case

$$(J^{\bullet}) = c_t[k^{\bullet}_{\mathrm{av}}](\Delta x) = c_t[[k_{\mathrm{av}}] - aN_t/c_t](\Delta x)$$

$$= c_t[k_{\mathrm{av}}](\Delta x) - aN_t(\Delta x)$$

$$= (J) - aN_t(\Delta x). \tag{13}$$

Inserting this into Eq. (12) we get

$$\sum_{i=1}^{n} v_i(J_i - aN_t(x_{i,I} - x_{i,B})) + N_t \sum_{i=1}^{n} v_i x_{i,I} = 0, \tag{14}$$

$$N_t = -\frac{\sum_{i=1}^{n-1}(v_i - v_n)J_i}{\sum_{j=1}^{n} v_j((1-a)x_{j,I} + ax_{j,B})}. \tag{15}$$

Thus, mass transfer fluxes are obtained from zero total flux diffusion fluxes

$$N^{\bullet}_i = J^{\bullet}_i + x_i N_t = J_i - aN_t(x_I - x_B) + x_{i,I}N_t, \tag{16}$$

$$N^{\bullet}_i = J_i - \frac{\sum_{k=1}^{n-1}(v_k - v_n)((1-a)x_{i,I} + ax_{i,B})J_k}{\sum_{j=1}^{n} v_j((1-a)x_{j,I} + ax_{j,B})}. \tag{17}$$

A high flux bootstrap matrix can then be defined as

$$\beta^{\bullet}_{ik} = \delta_{ik} - ((1-a)x_I + ax_B)\Lambda_k, \tag{18}$$

$$\text{where} \qquad \Lambda_k = \frac{v_k - v_n}{\sum_{j=1}^{n} v_j((1-a)x_{j,I} + ax_{j,B})}. \tag{19}$$

Now the mass transfer fluxes can be calculated explicitly

$$(N^{\bullet}) = c_t[\beta^{\bullet}][k_{\mathrm{av}}](x_I - x_B), \tag{20}$$

where $[\beta^{\bullet}]$ is the high flux bootstrap matrix (the high flux correction matrix combined with the original bootstrap matrix). When these equations are compared to the original bootstrap equations, it can be seen that this high flux corrected bootstrap matrix may be calculated with the same algorithm than the original matrix, by using the following high flux corrected "pseudo mole fractions"

$$(x^{\bullet}) = (1-a)(x_I) + a(x_B). \tag{21}$$

This pseudo mole fractions approach is remarkably similar to the property averaging that is used, for example, by Young and Stewart (1986) for other properties. The pseudo mole fractions, however, takes the high flux correction into account in the bootstrap matrix.

When we use the value $a = 0.5$ in the above equation, we obtain, in fact, Krishna's explicit method. Krishna

(1981) obtained this result by simply assuming that the product of the bootstrap matrix and the mass transfer coefficient matrix is constant along the diffusion path. It should be noted that the high flux correction (9) with $a = 0.5$ is equivalent to Krishna's method when the determinancy condition cannot be predetermined explicitly. One more thing should be noted. Even though the linearization to the high flux correction was done in the origin (zero total flux) in the cases $a = 0.5$ for the film theory and $a = 2/\pi$ for the penetration theory, even then the high flux correction is taken into account approximately in the bootstrap matrix defined above, if the total flux is not zero in a practical application of the method.

Explicit solution for the exact Maxwell–Stefan film model can be obtained if the flux ratios are known. The result, however, needs somewhat more complicated matrix calculations than the general method derived above. Furthermore, compositions should be known at both ends of the film as well as the flux ratios. This seems to be of no practical importance, so it is considered to be more reasonable to retain the linearized solution.

4. Methods to obtain the linearization parameter

4.1. Statistical approach

If the total flux is not known, the parameter a may be optimized by purely statistical means. This is done by using a normally distributed weighting function. Weighting takes account of the fact that near equimolar mass transfer is more likely to occur than mass transfer with high total flux. This optimization is done for scalar Ψ, which may be interpreted as an eigenvalue of the $[\Psi]$ matrix. Different standard deviations are chosen, with expected value $\Psi = 0$. Values are calculated in 21 discrete points at the interval $\Psi \in [-1, 1]$ (which was considered to include almost all practical mass transfer situations), and the sum of squares of error is minimized. As the standard deviation approaches zero, the optimal parameter a value approaches those of the linearized models (6) and (7). When chosen standard deviation increases, a decreases. This parameter can then be chosen in the computer process simulation codes according to intuition of probable total flux variations. Optimized values for different standard deviations are shown in Fig. 1. It can be seen that good values for a lies somewhere between 0.5 and 0.46 for the film theory and 0.637 (or $2/\pi$) and 0.58 for the penetration theory. Parameter value $a = 0$ corresponds to the situation where the high flux correction is ignored. We recommend that $a = 0.48$ and 0.61 can be used if no information about the total flux direction or magnitude is available.

4.2. Known total flux

If the total flux is known from the previous step of iterative solution for a mass transfer device, the linearization parameter can be estimated. This is done by using a scalar approximation of the mass transfer rate factor, so that average value of mass transfer coefficients is used. This average can be obtained, for example, by dividing the trace of the mass transfer coefficient matrix by its rank. Correct values for a are then

$$a = \frac{1}{\Psi_{\text{ave}}} - \frac{1}{\exp(\Psi_{\text{ave}}) - 1} \tag{22}$$

for the film theory and

$$a = \frac{1}{\Psi_{\text{ave}}}\left(1 - \frac{\exp(\Psi_{\text{ave}}^2/\pi)}{(1 + \operatorname{erf}(\Psi_{\text{ave}}/\sqrt{\pi}))}\right) \tag{23}$$

for the penetration theory. Here

$$\Psi_{\text{ave}} = N_{t,\text{estimate}}(n-1)/(c_t \Sigma k_{ii}). \tag{24}$$

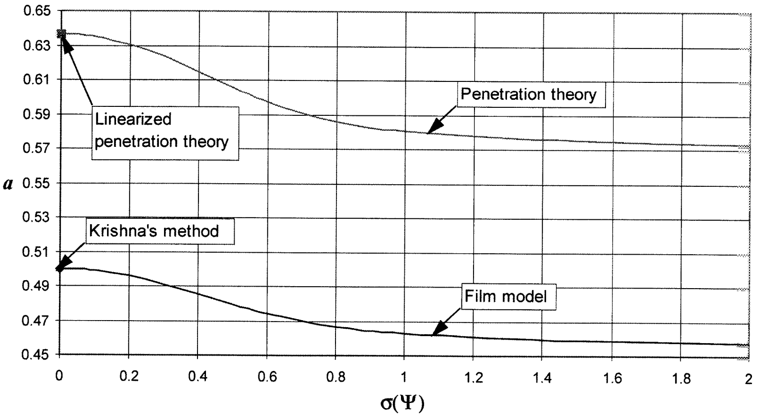

Fig. 1. Optimal a value as a function of standard deviation of the mass transfer rate factor, for the film and the penetration theory.

5. Numerical comparison

Extensive numerical comparison concerning different approximations is made by Smith and Taylor (1983). Among the seven tested methods there was the Krishna's explicit method, which was ranked third. As Krishna's method is only a special case of the methods presented here, it can be assumed that in general our methods are better or at least comparable to it.

Due to the simplicity of the Eqs. (8), (9) and (20), the approximate high flux correction can always be included in practical calculations. In terms of a scalar correction term Ψ (or an eigenvalue of a multicomponent matrix), quite high fluxes (absolute value of Ψ up to about 0.5) yields less than a 3% approximation error even if the total flux is not known. The exact high flux correction is then only needed if very high degree of accuracy is required. If the resulting high flux correction from these calculations has an effect on the fluxes that is more than 20–30%, and very high accuracy is needed, then the exact high flux correction can be used. When iterative solution to the balance equations is needed, the approximate flux values may then be used as initial estimates.

As the multicomponent mass transfer matrix calculations are shortened with the approximations of this paper, the computational time is expected to decrease. When a typical two-film mass transfer model with six components was simulated, the observed computational time was of the order 3–7 faster with the approximate solution than with the full solution. It can be assumed that computational times differ even more if the penetration theory is used, since the exact high flux correction is then more complicated requiring calculation of two matrix functions. If the number of components is increased from six which was used in our example, the difference in computation time is expected to increase. This is due to increased matrix sizes, since the exact solution spends relatively more time in the most time consuming matrix calculations, which are mostly $O(n^3)$ processes.

6. Conclusion

Approximate simplifications are presented for the film theory and the penetration theory high flux correction matrix, as derived from the Maxwell–Stefan mass transfer equations. Both predetermined total flux and iterated total flux are considered. In the previous case explicit methods can be obtained.

These methods are at least equivalent to Krishna's explicit method for the film model (which is a special case in the methods presented here) in terms of accuracy. The simplifications here are presented in a unified form. A statistical and an iterative approach for the optimal simplification is included.

These simplifications require no special matrix calculations for taking the high flux effects into account in the mass transfer calculations. Due to this, equimolar mass transfer need not be assumed for computational reasons even if the high flux correction is of minor importance. On the other hand, quite high total fluxes can be handled without excessive loss in accuracy. Even high flux correction effects of about 20–30% may be calculated approximately with very low risk of error. When the total flux is known in the iterative solution, even much higher approximate corrections can be made very accurately.

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Notation

(c)	column matrix of component concentrations, mol/m^3
$[D]$	matrix of Fick diffusion coefficients, as calculated from the Maxwell–Stefan equations, m^2/s
$[I]$	identity matrix, dimensionless
$[k]$	mass transfer coefficient matrix, m/s
$[k^\bullet]$	high flux mass transfer coefficient matrix, m/s
(x)	column matrix of component mole fractions, dimensionless
a	linearization parameter, dimensionless
c_t	total concentration, mol/m^3
J	diffusion flux, mol/m^{2}s
$J^\bullet$	diffusion flux calculated with high flux correction, mol/m^{2}s
l	film thickness, m
n	number of components
N	mass transfer flux, mol/m^{2}s
$N^\bullet$	mass transfer flux calculated with high flux correction, mol/m^{2}s
N_t	total flux, mol/m^{2}s
x	mole fraction, dimensionless
$x^\bullet$	high flux pseudo mole fraction, dimensionless

Greek letters

$[\beta]$	bootstrap matrix, dimensionless
δ_{ij}	Kronecker delta, dimensionless
ν	determinancy condition between fluxes, not defined
$[\Xi]$	high flux corrections matrix, dimensionless
σ	standard deviation, various
$[\Psi]$	mass transfer rate factor matrix, dimensionless

Sub- and superscripts, general

$()^{\bullet}$	refers to high flux value
$()_{\mathrm{av}}$	average value
$()_B$	bulk phase
$()_i$	refers to component *i*
$()_I$	interface
$()_L$	liquid phase
$()_t$	total

Mathematical notations

Δ	difference between some values, dimensionless
$[\,]$	square matrix, various
$()$	column matrix, various

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