Chapter 2

Transport of large molecules through membranes with narrow pores: The sphere-in-tube analogy

The Maxwell-Stefan transport equations

There are many apparently different ways of describing transport through membranes. In a review by Mason and Lonsdale (Mason 1990) it is shown that they can all be derived from the Generalised Maxwell-Stefan equations. These in turn can be derived from either statistical-mechanics (Mason 1978) or from Thermodynamics of Irreversible Processes (Lightfoot 1974).

The Maxwell-Stefan transport equations are force balances on the individual species in a mixture. They can be written in the form:

\[
\begin{bmatrix}
\text{driving force on a species } i \\
\text{friction with all other species } j
\end{bmatrix} = \begin{bmatrix}
\zeta_{i,j} x_j (u_i - u_j)
\end{bmatrix}
\]

In addition, the equations assume that the friction force exerted by any species \( j \) on the species \( i \) is proportional to the fraction of \( j \) in the mixture. It is also proportional to the difference in velocity between the two species. The simplest case is in a fluid mixture. This mixture will be homogeneous on a small scale (which should however, still be large compared with the size of molecules). The Maxwell-Stefan equations for an isothermal mixture can then be written as:

\[
F_i = \sum_j x_j \zeta_{i,j} (u_i - u_j)
\]

The driving force \( F_i \) is equal to the electrochemical potential gradient for component \( i \) in the system under consideration. It can contain contributions.
from several gradients, such as those due to the chemical potential, the pressure and the electrical potential:

\[ F_i = -\nabla p \mu_i - V_i \nabla P - Z_i F \nabla \Psi \]  

(2)

Here the chemical potential gradient is taken at constant pressure; the effect of any pressure gradient is given separately by the second term. This term is proportional to the molar volume \( V_i \) of the species. The third term contains the Faraday constant \( F \) and the charge number of the species \( Z_i \). As can be easily checked, the force is in Newton per mole of the species \( i \). The fraction \( x_j \) is usually a mole or mass fraction, but the equation can also be written using concentrations. The parameter \( \zeta_{i,j} \) is a friction coefficient that describes the interaction between the species \( i \) and \( j \). If \( i \) consists of small spheres and \( j \) is a viscous liquid, then the friction coefficient is given by Stokes’ law:

\[ \zeta_{i,j} = N_A \frac{3 \pi \eta d_i}{N_A} \]  

(3)

The Avogadro number \( N_A \) enters because we are dealing with a mole of a species and not with a single sphere. In fluids, friction coefficients obey the Onsager reciprocal relation:

\[ \zeta_{i,j} = \zeta_{j,i} \]  

(4)

The Maxwell-Stefan equation can now be written in terms per mole of mixture:

\[ x_i (-\nabla p \mu_i - V_i \nabla P - Z_i F \nabla \Psi) = \sum_j x_i x_j \zeta_{i,j} (u_i - u_j) \]  

(5)

In many texts, the friction coefficients are replaced by Maxwell-Stefan diffusivities:

\[ D_{i,j} = \frac{RT}{\zeta_{i,j}} \]  

(6)
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The velocities \( u_i \) and \( u_j \) are diffusive velocities. To obtain absolute velocities, we need to add the viscous velocity \( v_f \) of the mixture as a whole:

\[
w_i = u_i + v_f
\]  

(7)

As noted, the equations above are for transport in fluids. In application to porous media (such as ultrafiltration membranes) there are complications. These are considered in the next paragraph.

The two forms of the transport equation

If we want to describe transport of a mixture through membranes, the membrane itself can be considered in two ways. We can account for the detailed structure and base our description on it. The membrane is taken to be a separate phase. Diffusive and viscous transport are described separately: we will call this the structured approach. On the other hand we can regard the mixture of permeants and the membrane matrix to be homogeneous on a sufficiently small scale, and set up the equations for this mixture. In this description no distinction is made between diffusive and viscous selectivities. We will call this approach the overall model.

The structured model

This model describes diffusive transport in the pores with the Generalised Maxwell Stefan equation:

\[
- y_i \nabla p \mu_i - y_i V_i \nabla P - y_i z_i F \nabla \Psi = \sum_k \zeta_{i,k} y_i y_k (u_i - u_k) + \zeta_{i,m} y_i u_i
\]  

(8)

Besides diffusive transport, viscous flow is also important in pressure driven membrane processes. The convective transport of the fluid as a whole, \( v \), is related to the total force on this mixture. This can be written as:

\[
F_{tot} = \zeta_v v
\]  

(9)
Where $\zeta_v$ is defined as the viscous friction coefficient. The total force on the mixture is equal to $\Sigma_j y_j F_j$. Viscous flow through uncharged membranes is then described by:

$$F_{tot} = -\frac{1}{C_{tot}} \nabla P = \zeta_v v$$ \hfill (10)$$

The situation is different for charged membranes. Inside the pores the electroneutrality condition should hold, which means that the sum of all electrical charges should add up to zero. Inside a charged pore, part of this charges is fixed to the wall. This means that the fluid inside is not electrically neutral as it has to compensate the charges on the pore wall. This also implies that the total force on the fluid mixture will contain an electrical term. The total force is then equal to:

$$F_{tot} = -\frac{1}{C_{tot}} \nabla P - \sum_j y_j z_j F \nabla \Psi$$ \hfill (11)$$

So the equation for viscous flow through charged pores reads:

$$-\frac{1}{C_{tot}} \nabla P - \sum_j y_j z_j F \nabla \Psi = \zeta_v v$$ \hfill (12)$$

The viscous friction coefficient $\zeta_v$ is equal to $\eta/(C_{tot}B_0)$, where $B_0$ is the hydraulic permeability. For cylindrical pores, usually Poiseuille flow is assumed. Then the velocity depends parabolically on the radial position in the pore and is described in terms of mean velocity and radial position as:

$$v(r) = 2v \left( 1 - \left( \frac{r}{R_{pore}} \right)^2 \right)$$ \hfill (13)$$

This velocity profile is visualised in fig. 1. The velocity of the fluid is the highest near the central axis of the pore and drops to zero near the pore wall due to friction with this wall.
Fig. 1. Flow pattern inside a pore. Velocity profile of the fluid is indicated by the dashed line. At the pore wall the velocity of the fluid is zero due to friction with the wall. In the centre the velocity reaches a maximum. Larger solute molecules (the darker spheres) stay predominantly near the centre and obtain a higher viscous velocity.

Larger components tend to move along the pore axis and have a higher viscous velocity than other components and the mean velocity of the fluid. This difference is expressed by the factor $\alpha_i$, which is called the viscous selectivity of component $i$. The viscous velocity of each component $i$ can be expressed as:

$$v_i = \alpha_i v$$  \hspace{1cm} (14)

As the sum of the viscous velocities has to add up to the mean fluid velocity $v_f$ (which equals $v$) the relationship between the viscous selectivities is:

$$\sum_i \Omega_i \alpha_i = 1$$  \hspace{1cm} (15)

Here $\Omega_i$ is the volume fraction of component $i$.

The total velocity of component $i$, $w_i$, is equal to the sum of its diffusive and viscous velocities: $w_i = u_i + \alpha_i v$. We can substitute for $u_i$ in the Maxwell-Stefan equation, which yields:
In his review, Mason (1990) presented a form of the Maxwell-Stefan equation, which also accounts for the selective character of viscous flow. He put an empirical ‘bugger factor’, $\alpha'_{i}$, in the pressure term of the driving force. His form is presented below (with friction coefficients instead of diffusivities which occur in the notation of Mason):

$$\sum_k \xi_{i,k} y_i y_k (w_i - w_k) + \xi_{i,m} y_i w_i +$$

$$+ \left\{ \sum_k \left[ \xi_{i,k} y_i y_k (\alpha_i - \alpha_k) \right] + \xi_{i,m} y_i \alpha_i \right\} \frac{1}{\xi_v} \left( \frac{1}{C_{tot}} \nabla P + \sum_j y_j z_j F V \nabla \Psi \right)$$

(16)

The ‘bugger factor’, $\alpha'_{i}$, is related to the viscous selectivities $\alpha$ by:

$$\alpha'_{i} = \frac{1}{\xi_{i,m}} \left\{ \sum_k \left[ \xi_{i,k} y_i y_k (\alpha_i - \alpha_k) \right] + \xi_{i,m} \alpha_i \right\}$$

(18)

The overall component velocities $w_i$ are usually replaced by molar fluxes, $N_i$:

$$N_i = y_i w_i C_{tot}$$

(19)

Equation (17) then gives:

$$- \frac{y_i}{RT} \nabla p \mu_i - \frac{V_i}{RT} \nabla P - \frac{y_i z_i F}{RT} \nabla \Psi =$$

$$\sum_k \xi_{i,k} \frac{N_i - y_i N_k}{C_{tot}} \xi_{i,m} \frac{N_i}{C_{tot}} + \alpha'_{i} \frac{\xi_{i,m} y_i}{\xi_v} \left( \frac{1}{C_{tot}} \nabla P + \sum_j y_j z_j F V \nabla \Psi \right)$$

(20)
For transport through uncharged pores this equation reduces to:

\[
-\frac{y_i}{RT} \nabla_{T,p} \mu_i - \frac{V_i}{RT} \nabla P - \frac{y_i z_i F}{RT} \nabla \Psi = \sum_k \zeta_{i,k} \left( \frac{y_k N_i - y_i N_k}{C_{tot}} \right) + \zeta_{i,m} \frac{N_i}{C_{tot}} + \alpha_i' \frac{\zeta_{i,m} y_i}{\zeta_v} \frac{1}{C_{tot}} \nabla P
\]  

(21)

The overall model

In the overall model the total velocity of component \( i \), \( w_i \), is directly related to the driving force \( F_i \), without any discrimination between the diffusive and convective contributions. The general form of this type of description is:

\[
F_i = \sum_k \xi_{i,k} y_k (w_i - w_k) + \xi_{i,m} w_i
\]

(22)

\[
F_i = -\nabla p \mu_i - V_i \nabla P - Z_i F \nabla \Psi
\]

(23)

The overall friction coefficients, \( \xi \), are related to their diffusive counterparts by the relations given in the next paragraph.

In terms of molar fluxes, the ‘overall’ description is given by:

\[
F_i = \sum_k \xi_{i,k} \left( \frac{y_k N_i - y_i N_k}{C_{tot}} \right) + \xi_{i,m} \frac{N_i}{C_{tot}}
\]

(24)

Relations between the two sets of transport equations

Mason et al (Mehta 1976, Mason 1978) have derived the relation between the overall friction coefficients and the diffusive friction coefficients. They have derived these accounting for viscous selectivities by the 'bugger'-factor \( \alpha_i' \). Below, we present these relations in terms of the real viscous selectivities, \( \alpha_i \). These can be derived following the method presented in (Mehta 1976, Mason 1978). The complete relations are given in the appendix. Below, the results for
a binary solution are presented. The solvent is indicated by subscript ‘1’, the solute by subscript ‘2’.

\[
\xi_{1,2} = \xi_{1,2} + \frac{\alpha_1 \xi_{1,m} \xi_{2,m} + y_2 \xi_{1,2} \xi_{2,m} (\alpha_1 - \alpha_2)}{\xi_v + \alpha_1 y_1 \xi_{1,m} + \alpha_2 y_2 \xi_{2,m}} \tag{25}
\]

\[
\xi_{2,1} = \xi_{2,1} + \frac{\alpha_2 \xi_{1,m} \xi_{2,m} + y_1 \xi_{2,1} \xi_{1,m} (\alpha_2 - \alpha_1)}{\xi_v + \alpha_1 y_1 \xi_{1,m} + \alpha_2 y_2 \xi_{2,m}} \tag{26}
\]

\[
\xi_{1,m} = \frac{\xi_{1,m} \xi_v + y_2 \xi_{1,m} \xi_{2,m} (\alpha_2 - \alpha_1) + (\alpha_2 - \alpha_1) \xi_{1,2} \xi_{1,m} y_1 y_2 + \xi_{2,m} y_2^2}{\xi_v + \alpha_1 y_1 \xi_{1,m} + \alpha_2 y_2 \xi_{2,m}} \tag{27}
\]

\[
\xi_{2,m} = \frac{\xi_{2,m} \xi_v + y_1 \xi_{1,m} \xi_{2,m} (\alpha_1 - \alpha_2) + (\alpha_1 - \alpha_2) \xi_{1,2} \xi_{2,m} y_1 y_2 + \xi_{1,m} y_1^2}{\xi_v + \alpha_1 y_1 \xi_{1,m} + \alpha_2 y_2 \xi_{2,m}} \tag{28}
\]

The above equations can be simplified greatly by making some assumptions, valid for filtration of dilute solutions in pressure-driven membrane processes:

\[
y_1 \approx 1 \tag{29}
\]

\[
\alpha_1 \approx 1 \tag{30}
\]

\[
\xi_{1,m} \rightarrow \infty \tag{31}
\]

The last approximation is the application of the no-slip boundary condition for the flow of solvent through the porous channel. With these approximations, relations (21)-(24) reduce to:

\[
\xi_{1,2} = \xi_{1,2} + \xi_{2,m} \tag{32}
\]
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\[ \xi_{2,1} = \alpha_2 (\zeta_{2,1} + \zeta_{2,m}) \]  
\[ \xi_{1,m} = \xi_v \]  
\[ \xi_{2,m} = (\zeta_{2,m} + \zeta_{1,2})(1 - \alpha_2) \]  

A reasonable assumption for the friction coefficients \( \zeta_{1,2} \) and \( \zeta_{2,1} \) is that these are equal to the friction coefficients in free solution:

\[ \zeta_{1,2} = \zeta_{2,1} = \zeta_{2,1}^0 \]  

**Estimation of viscous selectivities and membrane friction coefficients from hydrodynamics**

To describe transport of molecules through narrow pores, more information is needed on the diffusive friction coefficients and viscous selectivities. These can be estimated by making an analogy with the hydrodynamic problem of a hard sphere, moving in a liquid flowing through a narrow tube. In the past, several numerical calculations have been carried out on this problem. In his review Deen presents some of the most important results ([Deen 1987](#)). The results from Bungay and Brenner ([Bungay 1973](#)) are the most interesting ones as they are applicable over the entire range of solute to pore size ratio's. This ratio is expressed by the symbol \( \lambda \):

\[ \lambda = r_s / r_p \]  

For a sphere, on which a driving force \( F_s \) is exerted, transport through a tube filled with a moving fluid (e.g. water) is described by the following equation:

\[ F_s = -6\pi \eta r_s K(w_s - Gw_w) \]  

The driving force \( F_s \) is equal to the friction the sphere experiences from both the fluid and the tube wall. If we suppose that the sphere experiences no
friction then it will adopt the local fluid velocity at the position at which it is located. The ratio of particle to mean fluid velocity will then be equal to the viscous selectivity, $\alpha_s$. Setting $F_s$ zero in above equation (no driving force, no friction) gives the result that selectivity $\alpha_s$ is equal to $G$.

A second limiting case is the transport of a sphere through a stagnant fluid. This case is the hydrodynamic equivalent to diffusive transport of solutes through pores. The fluid velocity, $w_w$, equals zero and the transport relation reads:

$$F_s = 6\pi \eta r_s K w_s = \frac{kT}{D_{s,w}} Kw_s = \frac{kT}{D_{eff,t}} w_s$$  \hspace{1cm} (39)

Transport of this sphere in an unbounded liquid, under the same driving force $F_s$, is given by:

$$F_s = 6\pi \eta r_s w_{s,\infty} = \frac{kT}{D_{s,w}} w_{s,\infty}$$  \hspace{1cm} (40)

As the driving force on the particle is the same in both cases, eqns. (39) and (40) can be combined to give:

$$\frac{w_s}{w_{s,\infty}} = \frac{D_{eff}}{D_{s,w}} = \frac{1}{K}$$  \hspace{1cm} (41)

So the ratio of the diffusivity of a sphere in an unbounded fluid relative to the effective diffusivity of this sphere in a tube equals $K$.

We can write eqn. (38), for one mole of spheres, in the form of the overall Maxwell-Stefan equation:

$$N_A F_s = -N_A 3\pi \eta d_s K G (w_s - w_w) - N_A 3\pi \eta d_s K (1 - G) (w_s - w_w)$$  \hspace{1cm} (42)

The overall friction coefficients are seen to be given by:
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\[ \xi_{i,w} = N_A 3\pi \eta d_s K \]  \hspace{1cm} (43)

\[ \xi_{i,m} = N_A 3\pi \eta d_s K(1 - G) \]  \hspace{1cm} (44)

To obtain diffusive friction coefficients, we need more information on viscous selectivities and the diffusive hindrance factor \( K \).

**Viscous selectivities**

From the calculations of Bungay and Brenner, an expression can be deduced for the ratio of particle velocity to fluid velocity, \( G_0 \), of a sphere moving along the centreline of a tube. This factor \( G_0 \) is in fact the viscous selectivity of that sphere when it moves along the centre-line; it is equal to \( v_s / v_f(0) \). In the next analysis, the velocity of the fluid is assumed to be a parabolic function of the radial distance (Poiseuille flow) and the fluid velocity along the centreline is represented by \( v_f(0) \). Deen assumes that the ratio of particle velocity to fluid velocity is constant over the entire pore area, so if a particle is positioned at a distance \( r \) off the central axis, the viscous part of its velocity can be expressed as:

\[ v_s(r) = G_0 v_f(r) = G_0 2v_f \left( 1 - \left( \frac{r}{r_p} \right)^{2} \right) \]  \hspace{1cm} (45)

The coefficient \( G_0 \) can be deduced from the relations of Bungay and Brenner:

\[ G_0 = \frac{K_s}{2K_t} \]  \hspace{1cm} (46)

\[
\left( \frac{K_t}{K_s} \right) = \frac{9}{4} \pi^2 \sqrt{2} (1 - \lambda)^{-5/2} \left[ 1 + \sum_{n=1}^{2} \left( a_n b_n \right) (1 - \lambda)^n \right] + \sum_{n=0}^{4} \left( a_{n+3} b_{n+3} \right) \lambda^n \]  \hspace{1cm} (47)

The coefficients \( a_n \) and \( b_n \) are given in table 1.
Table 1. Values of the coefficients in eqn. (47)

<table>
<thead>
<tr>
<th>n</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_n$</td>
<td>-1.2167</td>
<td>1.5336</td>
<td>-22.5083</td>
<td>-5.6117</td>
<td>-0.3363</td>
<td>-1.216</td>
<td>1.647</td>
</tr>
<tr>
<td>$b_n$</td>
<td>0.1167</td>
<td>-0.00442</td>
<td>4.0180</td>
<td>-3.9788</td>
<td>-1.9215</td>
<td>4.392</td>
<td>5.006</td>
</tr>
</tbody>
</table>

Bowen and Sharif have also performed calculations, using the centreline approach for values of $\lambda$ up to 0.8 (Bowen 1994). Their numerical values for the 'centre-line' selectivity can be approximated by:

$$G_0 = 1 - 0.255\lambda^2 - 1.279\lambda^{2.5} + 1.035\lambda^3$$  \hspace{1cm} (48)

Both relations are presented as a function of $\lambda$ in fig. 2a. The results coincide as expected.

To obtain the viscous selectivity $\alpha_i$ the ratio of $v_s(r)/\langle v_f \rangle$ is averaged over the entire pore area:

$$\alpha_i = \frac{\int_0^{1-\lambda} G_0 \left(1 - \beta^2\right) \beta d\beta}{\int_0^{1-\lambda} \beta d\beta}$$ which leads to $\alpha_i = \frac{(2 - \phi_i) K_s}{2 K_t}$  \hspace{1cm} (49)

The viscous selectivity is plotted as a function of $\lambda$ in fig. 2b. For small solutes the viscous selectivity has the value of one. As there is no adsorption, the solute will be distributed evenly over the cross section of the pore and its velocity will be equal to that of the fluid. At higher values of $\lambda$ the viscous selectivity increases and reaches a maximum of about 1.5 near $\lambda = 0.5$. Here the solute stays near the centre of the pore; its own centre has to stay at least one solute radius away from the pore wall. As a result, the velocity of the solute is larger than the average velocity of the fluid. Finally, when the solute size approaches that of the pore, the viscous selectivity drops to one again. Now the solute occupies the whole pore cross section and its velocity must be equal to the average fluid velocity.
Fig. 2. The viscous selectivity at the centerline $G_\alpha$ (a), the overall viscous selectivity $\alpha_i$ (b), and the diffusive hindrance factor $K_d$ (c), as calculated from the descriptions of Bungay and Brenner and Bowen.
Diffusive hindrance factor

The diffusive hindrance factor, $K_d$, is obtained from the Bungay and Brenner equations by using the following expression (Deen 1987):

$$K_d = \frac{6\pi}{K_t} \tag{50}$$

Bowen obtained the following relation:

$$K_d = 1 - 2.30\lambda + 1.154\lambda^2 + 0.224\lambda^3 \tag{51}$$

Both relations are compared in fig. 2c. They coincide for values of $\lambda$ up to 0.8. Beyond that point the relation of Bowen is not valid. In overall descriptions usually an effective diffusivity of a spherical solute $s$ in a pore is defined as:

$$D_{s,p} = K_d D_{s,f}^{\infty}$$

Diffusive friction coefficients

The relations obtained for the viscous selectivity and the diffusive hindrance factor, eqns. (46), (50), can now be substituted in eqns. (43), (44) to obtain the overall friction coefficients. The diffusive hindrance coefficient can now be obtained from relations (32)-(36). The results are depicted in figs. 3 a and b.

These coefficients are seen to be a strong function of $\lambda$ and to vary several orders in magnitude. The overall friction coefficient $\xi_{i,m}$ is negative due to the fact that the viscous selectivity is always larger than one.
Fig. 3. Overall friction factors, $\xi_{i,w}/\xi_{i,w}^0$ and $\xi_{i,m}/\xi_{i,w}^0$ (a) and diffusive friction factor $\zeta_{i,m}/\zeta_{i,w}^0$ (b) as a function of $\lambda$. 

- $\xi_{i,w}/\xi_{i,w}^0$ indicates the ratio of overall friction to the friction coefficient in the absence of factors.
- $\xi_{i,m}/\xi_{i,w}^0$ represents the ratio of the overall friction to the friction coefficient in the absence of factors.
- $\zeta_{i,m}/\zeta_{i,w}^0$ signifies the ratio of the diffusive friction factor to the friction coefficient in the absence of factors.
Special cases of the Maxwell-Stefan equations

There are several descriptions, other than the Maxwell-Stefan theory, of pressure driven membrane processes. The hydrodynamic description (Deen 1987) has been given in the last paragraph. Other examples are the Kedem-Katchalsky approach (Kedem 1958, Spiegler 1966) and the Nernst-Planck description for charged solutes. All these descriptions make the following assumptions:

- water flow is assumed to be viscous,
- solutions are assumed to be dilute,
- the molar volumes of the solutes are considered small enough to neglect the pressure term in the potential gradient.

The equation of Kedem and Katchalsky is applied by Nakao et al. (Nakao 1981) to describe the transport of neutral solutes through ultrafiltration membranes. It is given by:

\[ N_i = -P_i(C_{i,l}^P - C_{i,l}^C) + (1 - \sigma)J_v C_{i,l} \]  

(52)

The molar flux, \( N_i \), and the volumetric flux \( J_v \) are superficial fluxes, they are relative to the total membrane surface area. In this equation the concentration difference is that between the two outsides of the membrane. \( C_{i,l}^P \) and \( C_{i,l}^C \) are the concentrations in the permeate and the concentrate flows, respectively. The relation between the concentrations in the membrane and the outer liquid can be expressed by the partition coefficient \( \Phi \):

\[ C_{i,m} = \Phi C_{i,l} \]  

(53)

The coefficient \( \Phi_i \) is determined by geometrical factors, electrical interactions (when both solute and membrane pore wall are electrically charged) and other specific interactions of solute and pore wall. For spherical solutes in cylindrical pores, the relation of Ferry is often used (Ferry 1936):

\[ \Phi_i = (1 - \lambda_i)^2 \]  

(54)
The above relation gives the distribution coefficient, determined by geometrical factors only.

The concentration difference in eqn. (52) has to be rewritten in terms of concentrations in the membrane phase. In addition it can be rewritten in terms of a gradient:

\[
\frac{dC_{i,m}}{dz} \approx \frac{\Phi(C^p_{i,l} - C^c_{i,l})}{\tau \delta_m}
\]  

(55)

The membrane thickness \(\delta_m\) is multiplied by a tortuosity factor, \(\tau\), to account for the fact that the pores are not straight and perpendicular to the membrane surface. The transport length is thus larger than the thickness of the membrane. The approximation above is valid only for not-too-large gradients. Since we are dealing with gradients instead of concentration differences we also have to replace the mean concentration, \(C_{i,l}\), by the local concentration inside the membrane:

\[
\bar{C}_{i,l} = \frac{C_{i,m}}{\Phi}
\]

(56)

Substitution of eqns (53), (55) and (56) into eqn. (52) gives, after rearrangement:

\[
-\frac{dC_{i,m}}{dz} = \frac{N_i - \frac{(1 - \sigma_i)}{\Phi} J VC_{i,m}}{P \tau \delta_m \Phi}
\]

(57)

The concentration gradient for the solute can be rewritten as a chemical potential gradient, bearing in mind that the molar volume of the solute is small enough to neglect the pressure term:

\[
\frac{dC_{i,m}}{dz} = C_{\text{tot}} \frac{dy_i}{dz} \approx C_{\text{tot}} \frac{y_i}{RT} \frac{d\mu_i}{dz}
\]

(58)
For dilute solutions the following approximation for the flux can be made:

\[ J_v C_{i,m} \approx y_i N_w \quad (59) \]

Using above equations, the Kedem-Katchalski equation can now be rearranged as:

\[
-\frac{y_i}{R T} \frac{d\mu_i}{dz} = \frac{(1 - \sigma_i)}{\Phi C_{tot} \frac{P \tau \delta_m}{\Phi}} (N_i - y_i N_w) + \frac{1 - (1 - \sigma_i)}{C_{tot} \frac{P \tau \delta_m}{\Phi}} N_i \quad (60)
\]

To compare above equation to the Maxwell-Stefan equation the superficial molar fluxes have to be replaced by real molar fluxes inside the pores, \( N_i \). Their relation is:

\[ N_i = \varepsilon N_i \quad (61) \]

Finally eqn. (60) becomes:

\[
-\frac{y_i}{R T} \frac{d\mu_i}{dz} = \frac{(1 - \sigma_i)}{\Phi C_{tot} \frac{P \tau \delta_m}{\varepsilon}} (N_i - y_i N_w) + \frac{1 - (1 - \sigma_i)}{C_{tot} \frac{P \tau \delta_m}{\varepsilon}} N_i \quad (62)
\]

This has the same form as the Maxwell-Stefan equation (24). The friction coefficients are seen to be equal to:

\[
\xi_{i,w} = RT \frac{(1 - \sigma_i)}{P \tau \delta_m} \quad (63)
\]

\[
\xi_{i,m} = RT \frac{1 - (1 - \sigma_i)}{P \tau \delta_m} \quad (64)
\]
A description that is often used for membrane filtration of charged solutes is the Nernst-Planck equation:

\[ N_i = -D_{i,\text{eff}} \frac{dC_{i,m}}{dz} - C_{i,m}D_{i,\text{eff}} \frac{Z_i F}{RT} \frac{d\Psi}{dz} + C_{i,m} \alpha_i J_v \]  \hspace{1cm} (65)

This equation can be rewritten in Maxwell-Stefan terms as:

\[ -\frac{dy_i}{dz} - y_i \frac{Z_i F}{RT} \frac{d\Psi}{dz} = \frac{N_i - C_i \alpha_i J_v}{C_{\text{tot}} D_{i,\text{eff}}} = \frac{\alpha_i}{C_{\text{tot}} D_{i,\text{eff}}} (N_i - y_i N_w) + \frac{1 - \alpha_i}{C_{\text{tot}} D_{i,\text{eff}}} N_i \]  \hspace{1cm} (66)

In this equation \( D_{i,\text{eff}} \) is the effective diffusivity of component \( i \) in the pore. It is equal to \( K_d D_{i,w} \). The expressions for the friction coefficients \( \xi_{i,w} \) and \( \xi_{i,m} \) are given by:

\[ \xi_{i,w} = RT \frac{\alpha_i}{D_{i,\text{eff}}} \]  \hspace{1cm} (67)

\[ \xi_{i,m} = RT \frac{1 - \alpha_i}{D_{i,\text{eff}}} \]  \hspace{1cm} (68)

All descriptions above are seen to be special cases of the Maxwell-Stefan equation, according to the ‘overall’ approach.

**Applications of the Maxwell-Stefan equations**

*Prediction of falling rates of particles in tubes*

The equation for the falling of a single particle in a bounded liquid can be written as:

\[ F_s = \frac{\xi_{s,f}}{N_A} (u_s - u_f) + \frac{\xi_{s,t}}{N_A} u_s = u_s \left( \frac{\xi_{s,f} + \xi_{s,t}}{N_A} \right) \]  \hspace{1cm} (69)
In an unbounded liquid the above equation reduces to:

\[ F_s = \frac{\zeta_{s,f}}{N_A} u_{s,\infty} \]  

\[ (70) \]

From these equations, an expression for the tube friction factor, \( f_t \), can be found:

\[ f_t = \frac{u_s}{u_{s,\infty}} = \frac{\zeta_{s,f}}{\zeta_{s,f} + \zeta_{s,t}} \]

\[ (71) \]

This relation can be tested against experimental data. Chhabra et al presented experimental data on the reduction of falling rate velocity of various particles (glass, PVC, sapphire and steel) as a function of \( \lambda \) (Chhabra 1981). Lali (Lali 1989) also measured the velocities, both in Newtonian and non-Newtonian liquids. The experimental data points on Newtonian liquids were not presented, instead a correlation is given, which should be valid within 10%. This correlation reads:

\[ f_w = \frac{v_s}{v_{s,\infty}} = (1 - \lambda)^{2.2} \]

\[ (72) \]

**Fig. 4.** Experimental friction factors for falling spheres in narrow tubes, compared to predictions based on the Maxwell-Stefan description. Experimental data are presented by symbols, the Maxwell-Stefan predictions by the solid line, the relation of Lali by the dashed line.
Transport of large molecules through narrow pores

In fig. 4 the data of Chhabra and the correlation of Lali were compared with a prediction made with eqns. (69)-(71). The prediction based upon the Maxwell-Stefan theory compares quite well to the data of Chhabra. The relation of Lali (dashed line) starts to deviate at higher $\lambda$.

Diffusion of solids through membrane pores

Various studies have been performed on diffusion of different solutes through track etched membranes (Beck 1972, Bohrer 1984, Cannell 1980). Track etched membranes are very suitable for diffusion studies as their pores are nearly cylindrical in shape, are almost perpendicular to the membrane surface and have a very narrow size distribution. The pore diameter is usually determined by pure water flow measurements, assuming Poiseuille flow. Deen (Deen 1987) has shown that, especially for non-polymeric solutes, the hydrodynamic approach gives a good description of the diffusivities of these molecules from the given pore radii of the membranes and solute sizes. This comparison is depicted in figs 5a and b. Plotted is the product $\Phi D_{s,p} / D_{s,w}^\infty$; the multiplication by $\Phi$ is needed as, in the formulation of Beck and Schultz, the concentration gradient is related to the concentration in the liquid on the outside of the membrane.

![Fig. 5a. Comparison of experimental diffusivities with theoretical predictions for non-polymeric solutes. Experimental data are indicated by symbols, the predictions by the solid line.](image-url)
Fig. 5b. Comparison of experimental diffusivities with theoretical predictions for polymeric solutes. Experimental data are indicated by symbols, the predictions by the solid line.

For polymeric solutes, the situation is somewhat different. Ficoll is a cross-linked polymer and a nearly spherical molecule (Deen 1987). It follows the hydrodynamic description. The other polymers do not, the situation is worst for dextran. It is clear that for linear polymers, such as dextran, the description breaks down.

**Pressure driven membrane filtration**

In the process discussed in this section, transport of different components is governed by a combination of diffusion and viscous flow. In this section we consider nanofiltration data obtained by the Netherlands Institute for Dairy Research (NIZO) in Ede, the Netherlands. Experiments have been performed on different oligosaccharides using a Desal G10 nanofiltration membrane (Donkers 1997, Noordman 1999).

For a model description the following equations are required:

I. Two Maxwell-Stefan equations (one for the solute and one for the solvent). For solute $s$ it reads:
Transport of large molecules through narrow pores

\[ -y_s \nabla \ln y_s - y_s V_s \nabla P = \]

\[ \sum_k \zeta_{s,w} y_s y_w (w_s - w_w) + \zeta_{s,p} y_s w_s + \alpha'_s \frac{\zeta_{s,p} y_s}{\zeta_w} \nabla P \]  \hfill (73)

with \( \alpha'_s = \frac{1}{\zeta_{s,p}} (\zeta_{s,w} y_w (\alpha_s - \alpha_w) + \zeta_{s,p} \alpha_s) \)

The Maxwell-Stefan equation for water \( w \) is obtained by interchanging subscripts \( s \) and \( w \) in above equations. The gradients in the Maxwell-Stefan equations are approximated by a central difference scheme according to Wesselingh and Krishna (Wesselingh 1990).

II. A description of the viscous selectivities and diffusive hindrance factors coefficient. We use the centreline calculations of Bungay and Brenner, eqns. (46) and (47) and:

\[ \alpha_s = G_0 \]  \hfill (74)

III. A calculation of the ‘overall’ friction coefficients and from these the ‘structured’ friction coefficients:

\[ \frac{\xi_{s,w}}{\zeta_{s,w}} = \frac{\alpha_s}{K_d} \]  \hfill (75)

\[ \frac{\xi_{s,p}}{\zeta_{s,w}} = \frac{(1 - \alpha_s)}{K_d} \]  \hfill (76)

The structured friction coefficients can be obtained from the set of eqns.(25)-(28), assuming \( \alpha_w \approx 1 \) and \( \zeta_{1,m} \rightarrow \infty \):

\[ \xi_{w,s} = \xi_{w,s} + \xi_{s,m} \]  \hfill (77)
\[ \xi_{s,w} = \alpha_s (\xi_{s,w} + \xi_{s,m}) \]  
\[ \xi_{w,m} = \xi_v \]  
\[ \xi_{s,m} = (\xi_{s,m} + \xi_{w,s}) (1 - \alpha_s) \]

The friction coefficients \( \zeta_{1,2} \) and \( \zeta_{2,1} \) are set equal to the friction coefficients in free solution, according to eqn. (36).

IV. A relation for the pure water flux:

\[ v_f = -\frac{\varepsilon}{\tau} \frac{B_0}{\eta} \nabla P, \text{ with } B_0 = \frac{r_p^2}{8} \]

Integrating above equation yields:

\[ v_f = -\frac{\varepsilon}{\tau \delta_m} \frac{r_p^2}{8\eta} \Delta P \]

V. A mass balance at the end of the membrane to correlate the molar fluxes of solute to the concentration in the permeate stream:

\[ \frac{N_{i}}{N_{j}} = \frac{x_i^p}{x_j^p} \]

VI. partition equations to determine the distribution of solute over liquid phase and membrane phase at both the feed side and the permeate side of the membrane:

\[ y_i = x_i \Phi_i \]
VII. constraint relations: the mole fractions have to add up to unity everywhere in the system:

\[ \sum_i x_i = 1 \quad \text{and} \quad \sum_i y_i = 1 \] (85)

The complete set of equations was solved for the molar fluxes, local mole fractions, pressures and electrical potentials, using the Newton-Raphson method (Press 1987). In fig. 6, the rejection of different oligosaccharides is shown as a function of permeate flux. The experimental results are indicated by symbols and the model predictions by the solid lines. For the model description two membrane parameters are to be determined, the pore diameter and the effective membrane length. These two parameters are interrelated by the pure water flux equation. The pore diameter can now be found by comparison of the experimental rejection data with the model description using an optimisation procedure (in this work the Marquardt-Levenberg method). For this membrane the pore diameter is determined to be 1.81 nm.

![Fig. 6. Rejection of different oligosaccharides as measured for a Desal G10 nanofiltration membrane. Number of glucose units: (◊), 2; (•), 3; (▽), 4; (□), 5; (▲), 6.](image)

The effective pore length, \((\tau/\varepsilon)\delta_m\) can be calculated from eqn. (81) to be 14.6 \(\mu\text{m}\) (the pure water flux of this membrane is equal to 2.83 L m\(^{-2}\)hr\(^{-1}\) bar\(^{-1}\) at 25 \(^o\text{C}\)). As can be seen from fig. 6 a good description can be obtained with the pore diameter as the only adjustable parameter. Experiments on filtration of
uncharged solutes such as oligosaccharides and subsequent analysis of the data with the model presented are useful as a tool to characterise a membrane (Timmer 1999, Noordman 1999).

Nakao and Kimura (Nakao 1981) have performed experiments with several uncharged solutes to determine the mean pore diameter of an ultrafiltration membrane. The results of Nakao and Kimura were analysed in terms of the description of Kedem and Katchalski, eqn. (52). The constants $P$ and $\sigma$ were obtained for each solute by a fitting procedure and summarised in table 2.

Table 2. Parameters as determined by Nakao and Kimura (Nakao 1981)

<table>
<thead>
<tr>
<th>solute</th>
<th>$r_s$ (nm)</th>
<th>$P$ (µm/s)</th>
<th>$\sigma$</th>
<th>$\tau\delta_m/\varepsilon$ (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEG4000</td>
<td>1.63</td>
<td>0.52</td>
<td>0.93</td>
<td></td>
</tr>
<tr>
<td>Vitamin B12</td>
<td>0.74</td>
<td>3.0</td>
<td>0.81</td>
<td>0.91</td>
</tr>
<tr>
<td>Raffinose</td>
<td>0.58</td>
<td>7.8</td>
<td>0.66</td>
<td>2.08</td>
</tr>
<tr>
<td>Sucrose</td>
<td>0.47</td>
<td>17</td>
<td>0.63</td>
<td>2.86</td>
</tr>
<tr>
<td>Glucose</td>
<td>0.36</td>
<td>17</td>
<td>0.30</td>
<td>8.07</td>
</tr>
<tr>
<td>Glycerin</td>
<td>0.26</td>
<td>55</td>
<td>0.18</td>
<td>5.78</td>
</tr>
</tbody>
</table>

# these values are fitted from the experimental rejection data,
$\tau\delta_m/\varepsilon$ as determined from the hydraulic permeability is equal to 11.4 µm.

From these parameters, the friction coefficients for the Maxwell-Stefan equation, in ‘overall’ description, can be obtained from eqns. (63) and (64). The diffusive hindrance factor, $K_d$, and the viscous selectivity, $\alpha_s$, are equal to:

$$K_d D_{s,w} = \frac{P\tau\delta_m}{\varepsilon\Phi}$$

(86)

$$\alpha_s = \frac{1 - \sigma}{\Phi}$$

(87)

Nakao and Kimura analysed their data with the approach of Verniory et al. for the hindrance factors and the viscous selectivity. They determined the pore diameter to be 2.32 nm to give the best description of the data by the Kedem-Katchalsky model. With this diameter all data are well described except for those of PEG4000 where the apparent diameter of this molecule is larger than
the pore. The viscous selectivities are plotted in fig. 7. It can be seen that they are well predicted, except for one point, which is that of sucrose.

The diffusive hindrance factor $K_d$ causes more problems. Besides a pore diameter also the effective membrane length $\tau\delta_m/\varepsilon$ is needed. In our description of the nanofiltration data obtained at NIZO this was determined from the hydraulic permeability once the pore diameter is known. Descriptions of the work of Nakao and Kimura fail on this point, however. From the hydraulic permeability and the given pore diameter an effective pore length of 11.4 µm was obtained. With this length, values for $K_d$ close to unity are obtained and the rejection is poorly described. Nakao and Kimura improved their description by fitting the effective pore length separately. The values obtained are indicated by a # in table 2. With these values they obtained a better description of their rejection data.

![Viscous selectivity as determined from parameters $P$ and $\sigma$ as given by Nakao et al. (Nakao 1981) compared to the description of Bungay and Brenner (Bungay 1973).](image)

**Fig. 7.** Viscous selectivity as determined from parameters $P$ and $\sigma$ as given by Nakao et al. (Nakao 1981) compared to the description of Bungay and Brenner (Bungay 1973).

The resulting $K_d$ values are compared in fig. 8. They are close to the Bungay and Brenner values (Bungay 1973), which is not surprising as the approach of Verniory, which Nakao and Kimura (Nakao 1981) have used, give results comparable to Bungay and Brenner. The values of $\tau\delta_m/\varepsilon$ are all smaller than those obtained from hydraulic permeability measurements and decrease with increasing solute size. Nakao and Kimura postulated that this was because the
main pores of the membrane are interconnected by smaller pores, which are accessible for water but not for the larger solutes. As the solutes are transported through the main pores, water can flow through the smaller pores and thus experience a longer transport length than the solutes. This mechanism can explain the difference in transport length found for different solutes, however, the question might be raised why the transport length of the solvent would be so much larger as most of the solvent will probably also seek the route with the lower resistance.

![Figure 8](image_url)  
**Fig. 8.** Diffusive hindrance factor, $K_d$, as determined from parameters $P$ and $\sigma$ as given by Nakao et al. (Nakao 1981) compared to the description of Bungay and Brenner (Bungay 1973). $K_d#$ is calculated using the values of $\tau \delta_m / \epsilon$ as given in table 2, $K_d$ is calculated using the values of $\tau \delta_m / \epsilon$ as obtained from the hydraulic permeability.

**Conclusions**

This chapter first describes the Maxwell-Stefan equations for diffusive transport in fluids. It then considers the changes that are required for porous media such as membranes. It considers two different forms of the equations for porous media, defined as the structured approach and the overall approach. In the structured approach the membrane is taken to be a structure with defined pores. Diffusive and viscous transport are considered separately in this description. In the overall approach, the membrane and permeants are
considered to form one, pseudo-homogeneous phase. This description does not distinguish between diffusive and viscous transport, instead it combines these mechanisms in one overall transport velocity. Viscous selectivity is incorporated in the Maxwell-Stefan equations and the relation of the ‘true’ selectivities, $\alpha$, to the bugger factor, $\alpha'$, of Mason is presented.

The different approaches make use of different friction coefficients. In this chapter it is shown how they are interrelated. Values for the friction coefficients can be estimated using hydrodynamic models and simulations like those of Bungay and Brenner.

Other descriptions of pressure driven membrane processes are the hydrodynamic description of Deen, the description of Kedem and Katchalsky and the Nernst-Planck equation for charged solutes and membranes. These are all shown to be special cases of the Maxwell-Stefan equations.

The Maxwell-Stefan equations were applied to the following examples:
1. The falling rates of spheres in narrow tubes
2. The diffusion of particles through track etched membranes with straight cylindrical pores and
3. The rejection of uncharged components in pressure driven membrane processes.

It is shown that falling rates of spheres in tubes and diffusion of spherical solutes through track etched membranes are well described. The diffusion of non spherical polymers through these membranes was less well predicted. Finally experimental rejection data for nanofiltration of sugar solutions were well described by using only one adjustable parameter, the pore diameter. This provides a method to characterise a membrane by a simple filtration experiment.
Symbols

\( B_0 \) : membrane permeability, m\(^2\)

\( C \) : concentration mol m\(^{-3}\)

\( D \) : diffusion coefficient, m\(^2\) s\(^{-1}\)

\( F \) : force on a component, N

\( F \) : Faraday constant, C mol\(^{-1}\)

\( G \) : viscous selectivity (equal to \( \alpha \) and \( K_c \))

\( J_v \) : volumetric flux, m\(^3\) m\(^{-2}\) s\(^{-1}\)

\( K_c \) : viscous selectivity (equal to \( \alpha \) and \( G \))

\( K_d \) : diffusive hindrance factor

\( La \) : Avogadro number

\( M_w \) : Molecular Weight, g mol\(^{-1}\)

\( N \) : molar flux, mol m\(^{-2}\) s\(^{-1}\)

\( P \) : pressure, Pa

\( r \) : radius, m

\( R \) : gas constant J mol\(^{-1}\) K\(^{-1}\)

\( T \) : temperature, K

\( u \) : diffusive volume flux, m s\(^{-1}\)

\( V \) : partial molar volume, m\(^3\) mol\(^{-1}\)

\( v \) : viscous volume flux, m s\(^{-1}\)

\( w \) : overall volume flux, m s\(^{-1}\)

\( x \) : mole fraction in boundary layer

\( y \) : mole fraction in membrane

\( z \) : axial co-ordinate in distance, m

\( Z \) : charge number of ion

\( \alpha \) : viscous selectivity (equal to \( G \) and \( K_c \))

\( \delta_m \) : thickness of the membrane

\( \varepsilon \) : porosity of membrane

\( \Phi \) : partition coefficient of solute

\( \eta \) : viscosity, Pa s

\( \lambda \) : ratio of solute to pore radius

\( \mu \) : chemical potential, J mol\(^{-1}\)

\( \tau \) : tortuosity of membrane

\( \Psi \) : electrical potential, V
Transport of large molecules through narrow pores

ζ : friction coefficient, J mol⁻¹ m⁻² s, structured approach
ξ : friction coefficient, J mol⁻¹ m⁻² s, overall approach
Ω : Volume fraction of a component in solution

subscripts

f : fluid
i,j : component index
l : liquid
m : membrane
p : pore
s : sphere
t : tube
tot : total
w : water
∞ : unbounded fluid

superscripts

c : concentrate
p : permeate
0 : infinite dilution

References.


Transport of large molecules through narrow pores


Appendix: Derivation of relation between $\xi$, $\zeta$ and $\alpha$

We start with the diffusive Maxwell Stefan equation:

$$\xi_{i,m,y_iu_i} + \sum_k \zeta_{i,k,y_iy_k}(u_i - u_k) = -\nabla \mu_i$$  \hspace{1cm} (A1)

The relation of the diffusive velocity to the overall velocity is given by:

$$w_i = u_i + v_i$$  \hspace{1cm} (A2)

$$v_i = -\frac{\alpha_i B_0}{\eta} \nabla P = -\frac{\alpha_i}{C_{tot} \bar{v}}$$  \hspace{1cm} (A3)

At this stage it is handy to use Mason’s bugger factor $\alpha_i'$ instead of the true viscous selectivity $\alpha_i$. The relation is given by:

$$\alpha_i' = \frac{1}{\xi_{i,m}} \left\{ \sum_k \left[ \zeta_{i,k,y_k(\alpha_i - \alpha_k)} + \zeta_{i,m} \alpha_i \right] \right\}$$  \hspace{1cm} (A4)

Incorporating viscous flow into the Maxwell-Stefan equation by using Mason’s bugger factor yields:

$$\sum_k \zeta_{i,k,y_iy_k(w_i - w_k)} + \zeta_{i,m,y_iw_i} = -y_i \nabla \mu_i - \frac{\zeta_{i,m} y_i}{\bar{v}} \left( \frac{1}{C_{tot}} \nabla P - F_{el} \right)$$  \hspace{1cm} (A5)

The electrical force is defined as $F_{el} = -\sum_j y_j z_j F \nabla \Psi$

Next this equation may be summed over all $v$ components. Bearing in mind that:

$$\sum_{i=1}^{v} \sum_{k=1}^{v} \zeta_{i,k,y_iy_k(w_i - w_k)} = 0$$  \hspace{1cm} (A6)

and
\[ - \sum_{i=1}^{v} x_i \nabla \mu_i = - \frac{1}{C_{tot}} \nabla P + F_{el} = F_{tot} \quad (A7) \]

the result is:

\[ \sum_{i=1}^{v} \zeta_{i,m} y_i w_i = F_{tot} \left( 1 + \sum_{i=1}^{v} \frac{\zeta_{i,m} y_i}{\zeta_v} \right) = \chi F_{tot} \quad (A8) \]

The constant \( \chi \) is equal to:

\[ \chi = \left( 1 + \sum_{i=1}^{v} \frac{\zeta_{i,m} y_i}{\zeta_v} \right) \quad (A9) \]

Equation (A8) can be solved for \( F_{tot} \) and substituted, together with eqn. (A7), in the Maxwell Stefan equation for an individual component \( i \):

\[ \sum_k \zeta_{i,k} y_i y_k (w_i - w_k) + \zeta_{i,m} y_i w_i = -y_i \nabla \mu_i + \alpha_i' \frac{\zeta_{i,m} y_i}{\zeta_v} \frac{1}{\chi} \sum_{i=1}^{v} \zeta_{i,m} y_i w_i \quad (A10) \]

This equation can be rearranged to have the driving force on one side and the velocity terms to the other:

\[ -y_i \nabla \mu_i = \sum_k \zeta_{i,k} y_i y_k (w_i - w_k) + \zeta_{i,m} y_i w_i - \alpha_i' \frac{\zeta_{i,m} y_i}{\zeta_v} \frac{1}{\chi} \sum_{i=1}^{v} \zeta_{i,m} y_i w_i \quad (A11) \]

Now the last term on the right hand side has to be split into two new terms, one proportional to \((w_i - w_k)\), one to \(w_i\):

\[ -\alpha_i' \frac{\zeta_{i,m} y_i}{\zeta_v} \frac{1}{\chi} \sum_{i=1}^{v} \zeta_{i,m} y_i w_i = -\alpha_i' \frac{\zeta_{i,m}}{\zeta_v} \frac{1}{\chi} \sum_{k=1}^{v} y_i y_k \zeta_{k,m} w_k \]

\[ = \alpha_i' \frac{\zeta_{i,m}}{\zeta_v} \frac{1}{\chi} \sum_{k=1}^{v} y_i y_k \zeta_{k,m} (w_i - w_k) - \alpha_i' \frac{\zeta_{i,m}}{\zeta_v} \frac{1}{\chi} \sum_{k=1}^{v} y_i y_k \zeta_{k,m} w_i \quad (A12) \]
Rearrangement of the Maxwell-Stefan equation (A11) yields:

\[- y_i \nabla \mu_i = \sum_k \zeta_{i,k} y_i y_k (w_i - w_k) + \alpha_i' \frac{\zeta_{i,m}}{\zeta_v} \frac{1}{\chi} \sum_{k=1}^\nu y_i y_k \zeta_{k,m} (w_i - w_k) \]

\[+ \zeta_{i,m} y_i w_i - \alpha_i' \frac{\zeta_{i,m}}{\zeta_v} \frac{1}{\chi} \sum_{k=1}^\nu y_i y_k \zeta_{k,m} w_i \]

(A13)

Now this form can be compared with the overall description:

\[- y_i \nabla \mu_i = \sum_k \zeta_{i,k} y_i y_k (w_i - w_k) + \zeta_{i,m} y_i w_i \]

(A14)

The relation between the overall coefficients \(\zeta\) and the structured coefficients \(\xi\) can now be derived:

\[\xi_{i,k} = \zeta_{i,k} + \alpha_i' \frac{\zeta_{i,m}}{\zeta_v} \frac{1}{\chi} \zeta_{k,m} \]

(A15)

\[\xi_{i,m} = \zeta_{i,m} - \alpha_i' \frac{\zeta_{i,m}}{\zeta_v} \frac{1}{\chi} \sum_{k=1}^\nu y_k \zeta_{k,m} \]

(A16)

The relation to the true viscous selectivities can be derived by the substitution:

\[\alpha_i' = \frac{1}{\zeta_{i,m}} \left\{ \sum_k [\xi_{i,k} y_k (\alpha_i - \alpha_k)] + \zeta_{i,m} \alpha_i \right\} \]

(A17)

Next we can rewrite \(\chi\):

\[\zeta_v \chi = \left( \zeta_v + \sum_{i=1}^\nu \alpha_i' \xi_{i,m} y_i \right) = \left( \zeta_v + \sum_{i=1}^\nu \left\{ \sum_k [\xi_{i,k} y_i y_k (\alpha_i - \alpha_k)] + y_i \xi_{i,m} \alpha_i \right\} \right) \]

(A18)

Since \(\sum_{i=1}^\nu \sum_{k=1}^\nu [\xi_{i,k} y_i y_k (\alpha_i - \alpha_k)]\) is equal to zero, the above equation reduces to:
Substituting this, together with eqn. (A4), into eqn. (A15) yields the relation between $\xi_{i,k}$, the different $\zeta$ coefficients and the true viscous selectivities $\alpha$:

$$
\xi_{i,k} = \frac{\zeta_{k,m} \left\{ \sum_k \left[ \xi_{i,k} y_k (\alpha_i - \alpha_k) \right] + \zeta_{i,m} \alpha_i \right\}}{\zeta_v + \sum_{k=1}^{v} y_k \zeta_{k,m} \alpha_k}
$$

(A20)

The expression for $\xi_{i,m}$ becomes:

$$
\xi_{i,m} = \frac{\zeta_{i,m} \alpha_i \sum_{k=1}^{v} y_k \zeta_{k,m} + \left\{ \sum_{k=1}^{v} y_k \zeta_{k,m} \right\} \left[ \sum_{k=1}^{v} y_k \zeta_{i,k} (\alpha_i - \alpha_k) \right]}{\zeta_v + \sum_{k=1}^{v} y_k \zeta_{k,m} \alpha_k}
$$

(A21)