

Supplementary Material accompanying: Mass Transport of Gases Across the Air-Water Interface: Implications for Aldehyde Emissions in the Uinta Basin, Utah, USA.

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S1. Solutions to the reaction-diffusion equations in one phase

In all the one-phase solutions, we adopt the convention that positive flux points in the direction of increasing z , where z measures distance from the interface.

S1.1. One compound in one phase

Because we work with only one compound in one phase, here we drop the “1,” “2,” “A,” and “W” subscripts.

Let the thin film have thickness L . Solute molecules are present with concentration $C(z)$, where z is the distance from the interface. At all $z > L$, the phase is assumed to be turbulent and well mixed; the eddy diffusivity is effectively infinite; $C(z) = C_\infty$. At all $z < L$, the film is assumed to be stagnant; solute transport occurs only by molecular diffusion; the eddy diffusivity equals the molecular diffusivity, D .

The concentration of the solute obeys the steady-state diffusion equation

$$\frac{d^2 C}{dz^2} = 0, \quad z \in (0, L)$$

with the boundary conditions $C(z = 0) = C_0$, $C(z \geq L) = C_\infty$. The solution to the diffusion equation is

$$C(z) = C_0 + \frac{(C_\infty - C_0)z}{L}$$

And the flux at any $z \in (0, L)$ is

$$F(z) = -D \frac{dC}{dz} = -\frac{(C_\infty - C_0) D}{L}$$

S1.2. Two reacting compounds in one phase prior to the imposition of boundary conditions

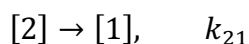
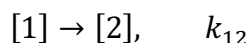
Hoover and Berkshire [1969] treated this case, but with the assumption that the two species have the same molecular diffusivity. This assumption is permissible because diffusivities for small compounds lie in a rather narrow range. Nevertheless, for more generality, I assume arbitrary diffusivities. With two compounds, the subscripts “1” and “2” are necessary.

The case of two interacting compounds obeys the coupled steady-state reaction-diffusion equations:

$$D_1 \frac{d^2 C_1}{dz^2} + k_{21} C_2 - k_{12} C_1 = 0$$

$$D_2 \frac{d^2 C_2}{dz^2} - k_{21} C_2 + k_{12} C_1 = 0$$

$C_1(z)$ and $C_2(z)$ are the concentrations of compounds 1 and 2 at position z ; D_1 and D_2 are their diffusivities; k_{12} and k_{21} are reaction rates for the two reactions



The reaction-diffusion equations are to be solved over the domain $z \in (0, L)$.

The chemical equilibrium constant is

$$K = \frac{k_{12}}{k_{21}}$$

Write

$$Q = \frac{D_1}{D_2}$$

as the ratio of the two diffusivities. The following two quantities have units of distance:

$$d_1 = \left(\frac{D_1}{k_{12}} \right)^{1/2}, \quad d_2 = \left(\frac{D_2}{k_{21}} \right)^{1/2}$$

They establish the length scale over which species 1 or 2 diffuse before reacting. The combined distance

$$d = (d_1^{-2} + d_2^{-2})^{-1/2}$$

appears in the solution to the reaction-diffusion equations. Obviously, d is always smaller than the lesser of d_1 and d_2 , but never more than by a factor of about 0.7. When d_1 and d_2 differ by an order of magnitude or more, then d is very close to the lesser of d_1 and d_2 . Therefore, d acts as a reaction distance for both compounds in the film.

The general solution, obtained for example using Laplace transforms, is given by

$$C_1(z) = \beta + \frac{\gamma z}{d} + \delta \cosh\left(\frac{z}{d}\right) + \varepsilon \sinh\left(\frac{z}{d}\right)$$

$$C_2(z) = K\beta + \frac{K\gamma z}{d} - Q\delta \cosh\left(\frac{z}{d}\right) - Q\varepsilon \sinh\left(\frac{z}{d}\right)$$

At this stage, β , γ , δ , and ε are arbitrary coefficients whose values become fixed when we impose boundary conditions. The terms linear in z have been normalized by a factor d^{-1} so that β , γ , δ , and ε all have units of concentration. The fluxes of compounds 1 and 2 are

$$F_1(z) = -D_1 \frac{\partial C_1}{\partial z} = -\frac{D_1}{d} \left[\gamma + \delta \sinh\left(\frac{z}{d}\right) + \varepsilon \cosh\left(\frac{z}{d}\right) \right]$$

$$F_2(z) = -\frac{D_2}{d} \left[K\gamma - Q\delta \sinh\left(\frac{z}{d}\right) - Q\varepsilon \cosh\left(\frac{z}{d}\right) \right]$$

The net flux at any z is independent of z as expected:

$$F_t = F_1(z) + F_2(z) = -(D_1 + D_2 K) \frac{\gamma}{d} = -(1 + KQ) \frac{\gamma D_1}{d}$$

The individual fluxes through $z = 0$ are

$$F_1(0) = -\frac{D_1}{d} (\gamma + \varepsilon)$$

$$F_2(0) = -\frac{D_2}{d} (K\gamma - Q\varepsilon)$$

S1.3. Two compounds in one phase; case N boundary conditions (compound [2] does not pass through the interface)

The far-field concentrations, or concentrations at a large distance from the boundary, are assumed to be the constants $C_{1\infty}$ and $C_{2\infty}$. Boundary conditions on the diffusion equations are

$$C_1(0) = C_{10}, \quad \left. \frac{dC_2}{dz} \right|_{z=0} = 0, \quad C_1(L) = C_{1\infty}, \quad C_2(L) = C_{2\infty}$$

A zero-slope, zero-flux reflecting boundary condition is applied on C_2 at $z = 0$ since [2] molecules are unable to cross the boundary. In this case, the four boundary conditions lead

to the following expressions for the coefficients. We add the subscript N (no-pass) to distinguish these values from those of case P (pass) for which [2] can pass through the interface. $\Lambda = L/d$ is a reduced film thickness.

$$\delta_N = -(C_{1\infty} - C_{10}) \left(1 + \frac{Q\Lambda}{K \tanh \Lambda}\right)^{-1}$$

$$\varepsilon_N = \frac{-\delta_N}{\tanh \Lambda}$$

$$\beta_N = C_{10} - \delta_N$$

$$\gamma_N = \frac{Q\varepsilon_N}{K}$$

The general solutions have the appearance of asymptotic divergence: For $z \gg d$, the cosh and sinh functions are exponentially large in z . However, it turns out that the relationship $\delta_N = -\varepsilon_N \tanh \Lambda$ is fine-tuned to prevent any “catastrophes.” We can combine the terms in cosh and sinh to produce these expressions:

$$C_1(z) = \beta_N + \gamma_N \lambda + \delta_N g(\lambda, \Lambda)$$

$$C_2(z) = K\beta_N + K\gamma_N \lambda - Q\delta_N g(\lambda, \Lambda)$$

where

$$g(\lambda, \Lambda) = \cosh \lambda - \frac{\sinh \lambda}{\tanh \Lambda} = \frac{\sinh(\Lambda - \lambda)}{\sinh \Lambda} = \frac{e^{-\lambda} - e^{-(2\Lambda - \lambda)}}{1 - e^{-2\Lambda}}$$

and where λ represents the reduced distance $\lambda = z/d$ and where $\Lambda = L/d$. The range of λ is $\lambda \in [0, \Lambda]$. Figure S1 displays the g function for different values of Λ . In contrast to the single-compound result, the C_1 and C_2 functions can be curved, with all curvature entering through the g function. For any Λ less than about 1, we have $g \cong 1 - \lambda/\Lambda$ and negligible curvature. Of the several equivalent expressions given above for $g(\lambda, \Lambda)$, the one involving exponential functions has the best numerical stability.

The fluxes through $z = 0$ are:

$$F_1 = -\frac{D_1(Q + K)}{(LQ + Kd \tanh \Lambda)} (C_{1\infty} - C_{10}), \quad F_2 = 0$$

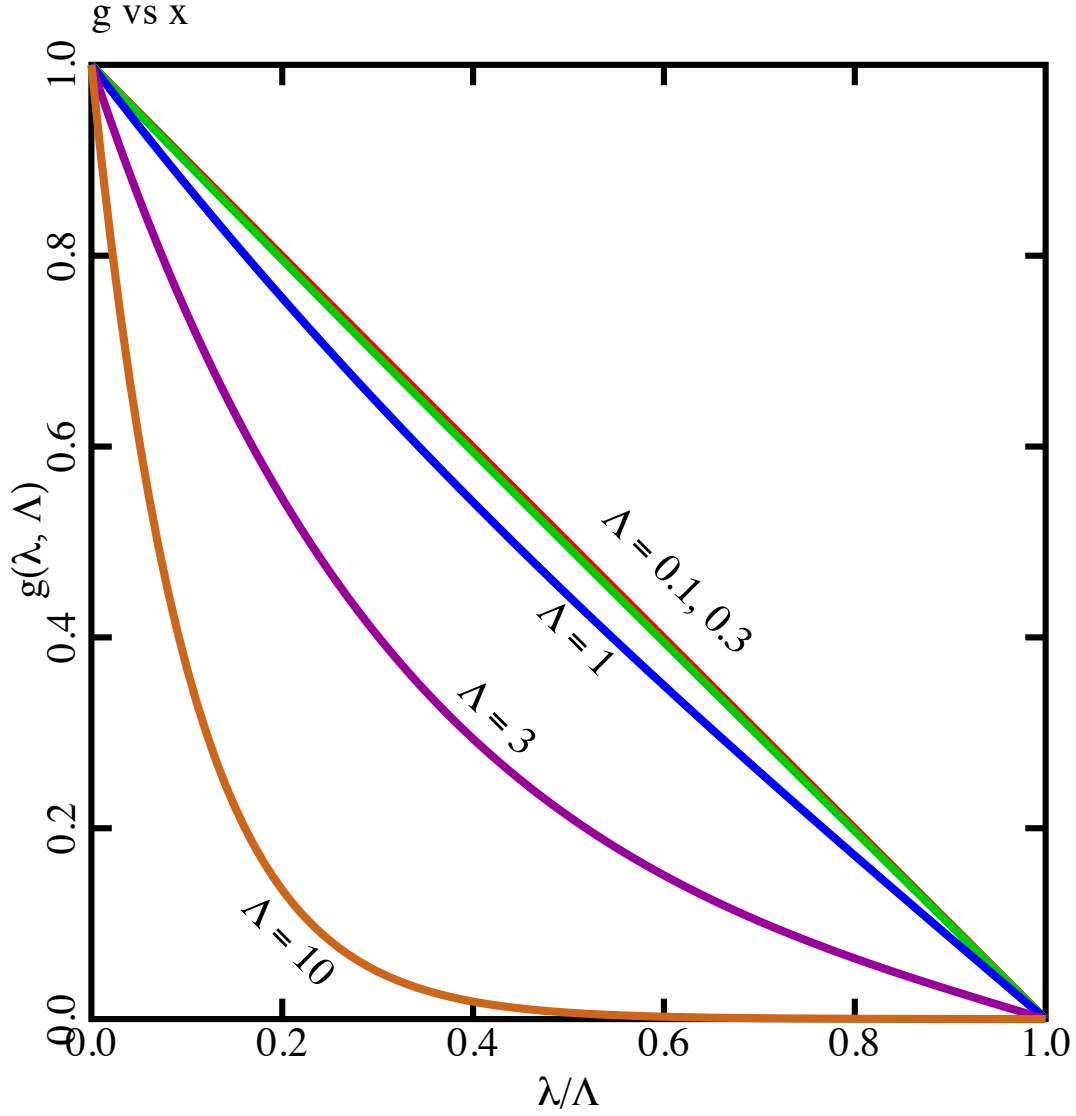


Figure S1. Plots of the $g(\lambda, \Lambda)$ functions for various values of Λ .

S1.4. Two compounds in one phase; case P boundary conditions (compound [2] passes through the interface).

The far-field concentrations, or concentrations at a large distance from the boundary, are assumed to be the constants $C_{1\infty}$ and $C_{2\infty}$. Boundary conditions on the diffusion equations are

$$C_1(0) = C_{10}, C_2(0) = C_{20}, C_1(L) = C_{1\infty}, C_2(L) = C_{2\infty}$$

Species 1 and 2 are assumed to be in chemical equilibrium at all $z > L$:

$$C_{2\infty} = KC_{1\infty}$$

The coefficients β , γ , δ , and ε are selected to satisfy the four boundary conditions, and we use the subscript P to distinguish from Case N:

$$\beta_P = \frac{QC_{10} + C_{20}}{Q + K}$$

$$\delta_P = \frac{KC_{10} - C_{20}}{Q + K}$$

$$\varepsilon_P = \frac{-\delta_P}{\tanh(\Lambda)}$$

$$\gamma_P = \frac{1}{\Lambda} [C_{1\infty} - C_{10} + \delta_P]$$

The same relationship between δ and ε is obtained, meaning that asymptotic divergence is avoided and that the sinh and cosh terms can again be grouped into the g function:

$$C_1(z) = \beta_P + \gamma_P \lambda + \delta_P g(\lambda, \Lambda)$$

$$C_2(z) = K\beta_P + K\gamma_P \lambda - Q\delta_P g(\lambda, \Lambda)$$

The fluxes through $z = 0$, in all Case-P situations, are

$$F_1(0) = -\frac{D_1}{d} (\gamma_P + \varepsilon_P) = -\frac{D_1}{L} [(C_{1\infty} - C_{10}) + Z\delta_P]$$

$$F_2(0) = -\frac{D_2}{d} (K\gamma_P - Q\varepsilon_P) = -\frac{D_2}{L} [(K(C_{1\infty} - C_{10})) + Y\delta_P]$$

where

$$Z = 1 - \frac{\Lambda}{\tanh \Lambda}, \quad Y = K + \frac{Q\Lambda}{\tanh \Lambda}$$

S2. Two-phase solutions

To construct two-phase solutions, we have to patch together two of the one-phase solutions given above in Sections S1.1 through S1.4. There are now two z -coordinates: z_A and z_W , each measuring distance into the phase away from the interface and pointing in opposite directions. Subscripts “A” and “W,” representing air- and water-phase properties, must now appear on all variables. Since z_W and z_A point in opposite directions, the sign convention for the flux must be redefined:

$$\begin{aligned} F_W(\text{new convention}) &= -F_W(\text{old convention}) \\ F_A(\text{new convention}) &= F_A(\text{old convention}) \end{aligned}$$

Now, positive flux flows from the water to the air phase.

When two phases are patched together at steady state, the fluxes at the interface must match. This leads to a reduction in the number of independent variables. For example, when we create model A4 from two of the case-P solutions, all results are initially given in terms of the eight concentrations: $C_{1\infty W}$, $C_{1\infty A}$, $C_{2\infty W}$, $C_{2\infty A}$, C_{10W} , C_{10A} , C_{20W} , C_{20A} . Only four of these are independent, because of the four conditions listed at the bottom of Table 2 in the main document. Matching fluxes adds two more constraints:

$$F_{1W}(0) = F_{1A}(0), \quad F_{2W}(0) = F_{2A}(0)$$

and we are left with only two independent concentration variables. As independent concentration variables, we will take the two far-field concentrations of compound 1, $C_{1\infty W}$ and $C_{1\infty A}$. The same is true for models A1, A2, and A3; we are always left with two independent concentration variables which we choose to be $C_{1\infty W}$ and $C_{1\infty A}$.

To facilitate comparison between models, it is useful to introduce the following ζ -notation.

$$\zeta_A = \frac{D_{2A}}{L_A}, \zeta_W = \frac{D_{2W}}{L_W}, Q_A \zeta_A = \frac{D_{1A}}{L_A}, Q_W \zeta_W = \frac{D_{1W}}{L_W}$$

S2.1. Model A1.

Model A1 was originally developed by Whitman (1923). Figure S2 displays a schematic of the solution.

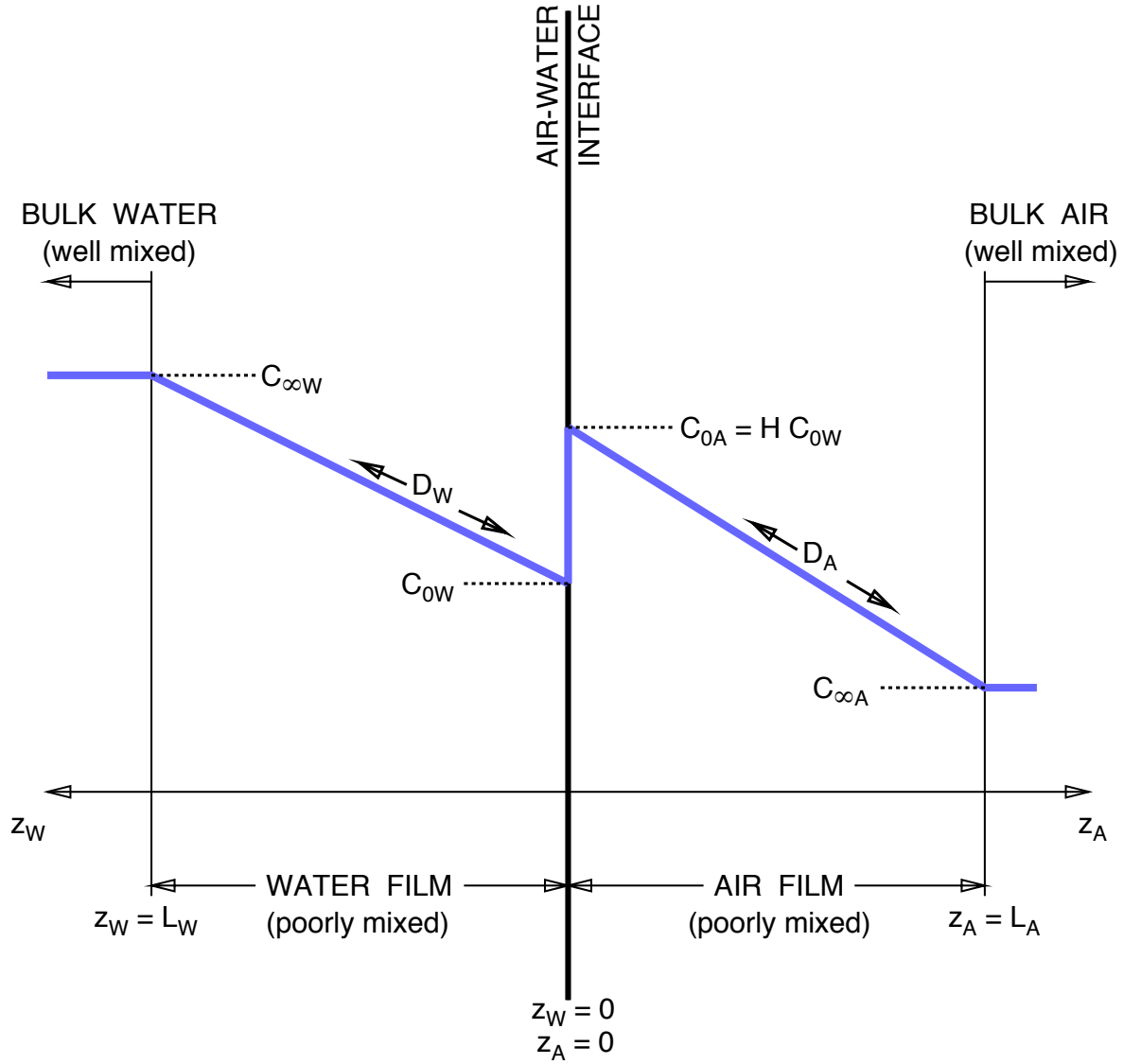


Figure S2. Schematic of the concentration profiles predicted by model A1.

To form model A1, patch together two of the one-compound-one-phase solutions given in Section S1.1. This value of C_{0W} leads to flux matching:

$$C_{0W} = \frac{C_{\infty A} k_A + C_{\infty W} k_W}{H k_A + k_W}$$

where

$$k_W = \frac{D_W}{L_W}, k_A = \frac{D_A}{L_A}, C_{0A} = H C_{0W}$$

The expression for the flux is

$$F = \frac{k_W k_A}{(H k_A + k_W)} (H C_{\infty W} - C_{\infty A})$$

The concentration profiles are linear in z_A and z_W and are given by the straight-line equations in Section S1.1. The flux vanishes when $H C_{\infty W} = C_{\infty A}$. Then the concentrations in the two phases are completely uniform and in equilibrium. To facilitate comparison between models, we take

$$m = \frac{C_{\infty A}}{H C_{\infty W}}$$

and rewrite the flux expression as

$$F = f_{A1} C_{\infty W} (1 - m), \quad \text{where } f_{A1} = \frac{k_W H k_A}{k_W + H k_A}$$

f_{A1} is one possible definition of the mass transfer coefficient. The subscript “A1” indicates that this expression applies to model A1. The parameter m tunes the flow between the two phases. When $m < 1$, the atmospheric concentration is in deficit, and net flow is from water to air. When $m > 1$, the water concentration is in deficit, and net flow is from air to water. When $m = 1$, the concentrations in the two phases are in physical equilibrium. Observe that f depends only on system variables.

Air-side control occurs when the term $k_W \gg H k_A$. Then $f_{A1} = H k_A$. Water-side control occurs when the term $k_W \ll H k_A$. Then $f_{A1} = k_W$.

S2.2 Model A1E

The main document describes how model A1E is developed from model A1, with the result that

$$f_{A1e} = \frac{\zeta_{eW} \zeta_{eA}}{(H_e \zeta_{eA} + \zeta_{eW})} H_1 (1 + K_A)$$

or

$$\frac{1}{f_{A1e}} = \frac{1}{(Q_A + K_A) H_1 \zeta_A} + \frac{1}{(Q_W + K_W) \zeta_W}$$

A more natural definition of the mass-transfer coefficient would define it relative to $C_{1\infty W} + C_{2\infty W}$, but the above form is appropriate for comparison with the other models.

The following hold for model A1E in cases of either water- or air-side control:

$$\begin{aligned} f_{A1e} &\rightarrow \zeta_A H_1 (Q_A + K_A) & (\text{air}) \\ f_{A1e} &\rightarrow \zeta_W (Q_W + K_W) & (\text{water}) \end{aligned}$$

S2.3. Model A2.

To form model A2 patch together a one-compound solution for the air phase and a case-N-two-compound solution for the water phase, selecting the value of C_{10W} that leads to flux matching. The development parallels that of model A1, except that k_W is redefined:

$$k_W = E_W \left(\frac{D_{1W}}{L_W} \right) = E_W Q_W \zeta_W$$

$$k_A = \left(\frac{D_{1A}}{L_A} \right) = Q_A \zeta_A$$

$$E_W = \frac{\Lambda_W (Q_W + K_W)}{\Lambda_W Q_W + K_W \tanh \Lambda_W}$$

The flux-matching condition and the expression for the flux read the same as for model A1 but with redefined k_A and k_W :

$$C_{10W} = \frac{C_{1\infty A} k_A + C_{1\infty W} k_W}{H k_A + k_W}$$

and the flux becomes

$$F = f_{A2} C_{1\infty W} (1 - m)$$

with

$$f_{A2} = \frac{k_W H_1 k_A}{k_W + H_1 k_A}$$

$$\frac{1}{f_{A2}} = \frac{1}{H_1 Q_A \zeta_A} + \frac{1}{E_W Q_W \zeta_W}$$

For any positive x , $\tanh x < x$. It follows that $E_W > 1$. For this reason, E_W is sometimes called the enhancement factor; it enhances the value of k_W .

S2.4. Model A3.

The derivation for Model A3 parallels that of A2, except that we now have two enhancement factors:

$$k_W = E_W \left(\frac{D_{1W}}{L_W} \right) = E_W Q_W \zeta_W$$

$$k_A = E_A \left(\frac{D_{1A}}{L_A} \right) = E_A Q_A \zeta_A$$

$$E_W = \frac{\Lambda_W (Q_W + K_W)}{\Lambda_W Q_W + K_W \tanh \Lambda_W}$$

$$E_A = \frac{\Lambda_A (Q_A + K_A)}{\Lambda_A Q_A + K_A \tanh \Lambda_A}$$

$$F = f_{A3} C_{1\infty W} (1 - m)$$

$$f_{A3} = \frac{k_W H_1 k_A}{k_W + H_1 k_A}$$

or

$$\frac{1}{f_{A3}} = \frac{1}{H_1 E_A Q_A \zeta_A} + \frac{1}{E_W Q_W \zeta_W}$$

S2.5. Rank-2 matrix identities

As will be seen in Section 2.6, the exact computational algorithm for model A4 involves rank-2 matrices. In this section, I lay out a number of helpful matrix identities. They are given here without proof, but at rank-2, they can all be easily verified by direct computation. The names of all matrices and vectors appear in boldface.

Adjugate of a 2x2 matrix

$$\text{adj} \begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{bmatrix} = \begin{bmatrix} a_{22} & -a_{12} \\ -a_{21} & a_{11} \end{bmatrix}$$

Inverse of a 2x2 matrix

$$\mathbf{A}^{-1} = \frac{1}{\det(\mathbf{A})} \text{adj}(\mathbf{A})$$

Derivative of an inverse matrix

$$\frac{\partial \mathbf{M}^{-1}}{\partial x} = -\mathbf{M}^{-1} \cdot \frac{\partial \mathbf{M}}{\partial x} \cdot \mathbf{M}^{-1}$$

Many of the matrices used in model A4 are outer products of a column and a row. All of the following identities apply to such matrices. Let $\mathbf{C}_1, \mathbf{C}_2$, etc., represent arbitrary 2x1 columns and $\mathbf{R}_1, \mathbf{R}_2$, etc., represent arbitrary 1x2 rows. \otimes signifies the matrix outer product.

The determinant of an arbitrary outer product.

$$\det(\mathbf{C}_1 \otimes \mathbf{R}_1) = 0$$

The determinant of a sum of two outer products. (This is a special case of the matrix determinant lemma, cf. Wikipedia.)

$$\begin{aligned} \det(\mathbf{C}_1 \otimes \mathbf{R}_1 + \mathbf{C}_2 \otimes \mathbf{R}_2) \\ &= \mathbf{R}_1 \cdot \text{adj}(\mathbf{C}_2 \otimes \mathbf{R}_2) \cdot \mathbf{C}_1 \\ &= \mathbf{R}_2 \cdot \text{adj}(\mathbf{C}_1 \otimes \mathbf{R}_1) \cdot \mathbf{C}_2 \end{aligned}$$

The following relationships hold for an arbitrary row \mathbf{R}_1 and an arbitrary column \mathbf{C}_1 :

$$\begin{aligned} \mathbf{R}_1 \cdot \text{adj}(\mathbf{C}_1 \otimes \mathbf{R}_1) &= 0 \\ \text{adj}(\mathbf{C}_1 \otimes \mathbf{R}_1) \cdot \mathbf{C}_1 &= 0 \end{aligned}$$

The above forms simplify further:

$$\mathbf{R}_1 \cdot \text{adj}(\mathbf{C}_1 \otimes \mathbf{R}_2) \cdot \mathbf{C}_2 = (\mathbf{R}_1 \times \mathbf{R}_2) \cdot (\mathbf{C}_2 \times \mathbf{C}_1)$$

Before writing the previous expression, it was important to distinguish between row and column vectors. But now I introduce cross products of two rows or of two columns. In this context, rows and columns are treated as simple 2-vectors in the plane, and \times represents their cross product. Since they are interpreted as 2-vectors, their cross products are all normal to the plane, and the dot products are simple products of the magnitudes.

S2.6. Model A4. Computational algorithm.

We now patch together two case-P solutions. The result is much more algebraically complex than the previous models. Table S1 contains a self-contained, exact algorithm for calculating the fluxes. Remember that the input variables must satisfy the following constraints:

$$K_A = \frac{k_{12A}}{k_{21A}}, K_W = \frac{k_{12W}}{k_{21W}}$$

$$H_2 K_W = H_1 K_A$$

The computation proceeds using rank-2 matrices. Table S2 defines an extended list of variables, with units, useful for (1) calculating concentration profiles, (2) calculating individual fluxes of the two compounds, or (3) understanding the derivation of model A4. Following the tables, I sketch out the derivation.

Two separate expressions appear for f_{A4} :

$$f_{A4} = \zeta_W(Q_W + K_W + \mathbf{W} \cdot \mathbf{r}_0)$$

$$f_{A4} = -\zeta_A \mathbf{A} \cdot \mathbf{r}_0$$

They are exactly equal, and either may be used to calculate the flux.

Table S1. Algorithm to calculate f_{A4} .

<p>1. Inputs to the model are these system variables:</p> $D_{1A}, D_{2A}, D_{1W}, D_{2W}, k_{12A}, k_{21A}, k_{12W}, k_{21W}, H_1, H_2, L_A, L_W$ <p>See the main text for definitions, etc.</p>
<p>2. Calculate all the following scalars:</p> $K_A = \frac{k_{12A}}{k_{21A}}, K_W = \frac{k_{12W}}{k_{21W}}, Q_A = \frac{D_{1A}}{D_{2A}}, Q_W = \frac{D_{1W}}{D_{2W}}$ $J_A = (Q_A + K_A)^{-1}, J_W = (Q_W + K_W)^{-1}, \zeta_A = \frac{D_{2A}}{L_A}, \zeta_W = \frac{D_{2W}}{L_W}$ $d_{1A} = \left(\frac{D_{1A}}{k_{12A}}\right)^{1/2}, d_{1W} = \left(\frac{D_{1W}}{k_{12W}}\right)^{1/2}, d_{2A} = \left(\frac{D_{2A}}{k_{21A}}\right)^{1/2}, d_{2W} = \left(\frac{D_{2W}}{k_{21W}}\right)^{1/2}$ $d_A = (d_{1A}^{-2} + d_{2A}^{-2})^{-1/2}, d_W = (d_{1W}^{-2} + d_{2W}^{-2})^{-1/2}$ $\Lambda_A = \frac{L_A}{d_A}, \Lambda_W = \frac{L_W}{d_W}, x_A = \frac{\Lambda_A}{\tanh \Lambda_A}, x_W = \frac{\Lambda_W}{\tanh \Lambda_W}$
<p>3. Calculate these rows and columns:</p> $\mathbf{W} = [Q_W, 1], \mathbf{A} = [H_1 Q_A, H_2], \mathbf{V}_A = \begin{bmatrix} Q_A \\ K_A \end{bmatrix}, \mathbf{V}_W = \begin{bmatrix} Q_W \\ K_W \end{bmatrix}, \mathbf{S} = \begin{bmatrix} -1 \\ 1 \end{bmatrix}$ $\boldsymbol{\Theta}_W = [K_W, -1], \boldsymbol{\Theta}_A = H_2 \boldsymbol{\Theta}_W$
<p>4. Calculate these two square matrices:</p> $\mathbf{M}_A = \zeta_A J_A [-\mathbf{V}_A \otimes \mathbf{A} + x_A Q_A \mathbf{S} \otimes \boldsymbol{\Theta}_A]$ $\mathbf{M}_W = \zeta_W J_W [-\mathbf{V}_W \otimes \mathbf{W} + x_W Q_W \mathbf{S} \otimes \boldsymbol{\Theta}_W]$
<p>5. Take the matrix sum:</p> $\mathbf{M} = \mathbf{M}_A + \mathbf{M}_W$
<p>6. Invert \mathbf{M} to form \mathbf{M}^{-1}</p>
<p>7. Calculate the column vector $\boldsymbol{\tau}_0$. Of several expressions, this one is preferred:</p> $\boldsymbol{\tau}_0 = \zeta_W \mathbf{M}^{-1} \cdot \mathbf{V}_W$
<p>8. Calculate f_{A4} by either of these two equivalent formulas.</p> $f_{A4} = \zeta_W (Q_W + K_W + \mathbf{W} \cdot \boldsymbol{\tau}_0)$ $f_{A4} = -\zeta_A \mathbf{A} \cdot \boldsymbol{\tau}_0$

Table S2. A more complete list of variables.	Units
SYSTEM VARIABLES (inputs to algorithm)	
$D_{1A}, D_{2A}, D_{1W}, D_{2W}$	$\text{cm}^2 \text{s}^{-1}$
$k_{12A}, k_{21A}, k_{12W}, k_{21W}$	s^{-1}
H_1, H_2	Dimensionless
L_A, L_W	cm
CONCENTRATION VARIABLES	
$C_{1\infty W}, C_{1\infty A}, C_{2\infty W}, C_{2\infty A}, C_{10W}, C_{10A}, C_{20W}, C_{20A}$	mol cm^{-3}
SCALARS	
$Q_A = \frac{D_{1A}}{D_{2A}}, Q_W = \frac{D_{1W}}{D_{2W}}$	Dimensionless
$K_A = \frac{k_{12A}}{k_{21A}}, K_W = \frac{k_{12W}}{k_{21W}}$	Dimensionless
$\zeta_A = \frac{D_{2A}}{L_A}, \zeta_W = \frac{D_{2W}}{L_W}, Q_A \zeta_A = \frac{D_{1A}}{L_A}, Q_W \zeta_W = \frac{D_{1W}}{L_W}$	cm s^{-1}
$d_{1A} = \left(\frac{D_{1A}}{k_{12A}} \right)^{1/2} \quad d_{1W} = \left(\frac{D_{1W}}{k_{12W}} \right)^{1/2}$ $d_{2A} = \left(\frac{D_{2A}}{k_{21A}} \right)^{1/2} \quad d_{2W} = \left(\frac{D_{2W}}{k_{21W}} \right)^{1/2}$ $d_A = (d_{1A}^{-2} + d_{2A}^{-2})^{-1/2} \quad d_W = (d_{1W}^{-2} + d_{2W}^{-2})^{-1/2}$	cm
$\Lambda_A = \frac{L_A}{d_A}, \Lambda_W = \frac{L_W}{d_W}, Z_A = 1 - \frac{\Lambda_A}{\tanh \Lambda_A}, Z_W = 1 - \frac{\Lambda_W}{\tanh \Lambda_W}$ $Y_A = K_A + \frac{Q_A \Lambda_A}{\tanh \Lambda_A}, Y_W = K_W + \frac{Q_W \Lambda_W}{\tanh \Lambda_W}$	Dimensionless

Table S2, cont'd. A more complete list of variables.	Units
MORE SCALARS	
$J_A = (Q_A + K_A)^{-1}, J_W = (Q_W + K_W)^{-1}$	Dimensionless
$\delta_{PA} = J_A(K_A C_{10A} - C_{20A}), \delta_{PW} = J_W(K_W C_{10W} - C_{20W})$ $\delta_{PA} = -J_A C_{1\infty W} \boldsymbol{\Theta}_A \cdot \mathbf{T}, \quad \delta_{PW} = -J_W C_{1\infty W} \boldsymbol{\Theta}_W \cdot \mathbf{T}$	mol cm^{-3}
$x_A = \frac{\Lambda_A}{\tanh \Lambda_A}, \quad x_W = \frac{\Lambda_W}{\tanh \Lambda_W}$	Dimensionless
$m = \frac{C_{1\infty A}}{H_1 C_{1\infty W}}$	Dimensionless
First component of \mathbf{T} : $T_1 = \mathbf{R} \cdot \mathbf{T}$	Dimensionless
Fluxes of individual compounds: $F_{1A} = -\zeta_A Q_A C_{1\infty W} [H_1(m + T_1) - J_A Z_A \boldsymbol{\Theta}_A \cdot \mathbf{T}]$ $F_{2A} = -\zeta_A C_{1\infty W} [K_A(m + T_1) - Y_A J_A \boldsymbol{\Theta}_A \cdot \mathbf{T}]$ $F_{1W} = \zeta_W Q_W C_{1\infty W} (1 + T_1 - J_W Z_W \boldsymbol{\Theta}_W \cdot \mathbf{T})$ $F_{2W} = \zeta_W C_{1\infty W} [K_W(1 + T_1) - Y_W J_W \boldsymbol{\Theta}_W \cdot \mathbf{T}]$ Combined fluxes: $F_t = F_{1A} + F_{2A} = F_{1W} + F_{2W}$ $F_t = C_{1\infty W} (1 - m) f_{A4}$	$\text{mol cm}^{-2} \text{s}^{-1}$
$f_{A4} = \zeta_W (Q_W + K_W + \mathbf{W} \cdot \boldsymbol{\tau}_0)$ $f_{A4} = -\zeta_A \mathbf{A} \cdot \boldsymbol{\tau}_0$	cm s^{-1}

Table S2, cont'd. A more complete list of variables.	Units
ROW VECTORS	
$\Theta_W = [K_W, -1], \quad \Theta_A = [K_A H_1, -H_2] = H_2 \Theta_W,$ $\mathbf{W} = [Q_W, 1], \quad \mathbf{A} = [H_1 Q_A, H_2], \quad \mathbf{R} = [1, 0]$	Dimensionless
COLUMN VECTORS	
$\mathbf{T} = \mathbf{M}^{-1} \cdot \mathbf{V} \cdot \begin{bmatrix} m H_1 \\ 1 \end{bmatrix}$ $\tau_0 = \mathbf{M}^{-1} \cdot \mathbf{V} \cdot \mathbf{V}_D = \zeta_W \mathbf{M}^{-1} \cdot \mathbf{V}_W$ $\mathbf{V}_A = \begin{bmatrix} Q_A \\ K_A \end{bmatrix}, \quad \mathbf{V}_B = \begin{bmatrix} 1 \\ K_W \end{bmatrix}, \quad \mathbf{V}_C = \begin{bmatrix} H_1 \\ 1 \end{bmatrix} = \mathbf{V}_D + H_1 \mathbf{V}_E$ $\mathbf{V}_D = \begin{bmatrix} 0 \\ 1 \end{bmatrix}, \quad \mathbf{V}_E = \begin{bmatrix} 1 \\ 0 \end{bmatrix}, \quad \mathbf{V}_W = \begin{bmatrix} Q_W \\ K_W \end{bmatrix}, \quad \mathbf{S} = \begin{bmatrix} -1 \\ 1 \end{bmatrix}$	Dimensionless
SQUARE MATRICES	
$\mathbf{M}_A = \zeta_A J_A [-\mathbf{V}_A \otimes \mathbf{A} + x_A Q_A \mathbf{S} \otimes \Theta_A]$ $\mathbf{M}_W = \zeta_W J_W [-\mathbf{V}_W \otimes \mathbf{W} + x_W Q_W \mathbf{S} \otimes \Theta_W]$ $\mathbf{M} = \mathbf{M}_A + \mathbf{M}_W$ $\mathbf{V} = \begin{bmatrix} Q_A \zeta_A & Q_W \zeta_W \\ K_A \zeta_A & K_W \zeta_W \end{bmatrix}$	cm s^{-1}
\mathbf{M}^{-1}	s cm^{-1}
$\frac{\partial \mathbf{M}_A}{\partial \zeta_A} = J_A [-\mathbf{V}_A \otimes \mathbf{A} + x_A Q_A \mathbf{S} \otimes \Theta_A], \quad \frac{\partial \mathbf{M}_A}{\partial \zeta_W} = 0$ $\frac{\partial \mathbf{M}_W}{\partial \zeta_A} = 0, \quad \frac{\partial \mathbf{M}_W}{\partial \zeta_W} = J_W [-\mathbf{V}_W \otimes \mathbf{W} + x_W Q_W \mathbf{S} \otimes \Theta_W]$	dimensionless

S2.7. Model A4. Derivation.

The starting point is these expressions for the fluxes through the boundary, bundled into column vectors:

$$\begin{bmatrix} F_1 \\ F_2 \end{bmatrix}_A = \begin{bmatrix} -Q_A \zeta_A [(C_{1\infty A} - C_{10A}) + Z_A \delta_{PA}] \\ -\zeta_A [K_A (C_{1\infty A} - C_{10A}) + Y_A \delta_{PA}] \end{bmatrix}$$

$$\begin{bmatrix} F_1 \\ F_2 \end{bmatrix}_W = \begin{bmatrix} \zeta_W Q_W [(C_{1\infty W} - C_{10W}) + Z_W \delta_{PW}] \\ \zeta_W [K_W (C_{1\infty W} - C_{10W}) + Y_W \delta_{PW}] \end{bmatrix}$$

The boundary conditions at L_A and L_W are:

$$\begin{bmatrix} C_{1\infty W} \\ C_{2\infty W} \end{bmatrix} = C_{1\infty W} \begin{bmatrix} 1 \\ K_W \end{bmatrix}, \quad \begin{bmatrix} C_{1\infty A} \\ C_{2\infty A} \end{bmatrix} = C_{1\infty A} \begin{bmatrix} 1 \\ K_A \end{bmatrix}$$

The expressions above remove $C_{2\infty W}$ and $C_{2\infty A}$ as independent variables, leaving for the moment, six independent concentration variables. If we assume a fast equilibrium for molecules crossing the interface, then the following relation holds:

$$\begin{bmatrix} C_{10A} \\ C_{20A} \end{bmatrix} = \begin{bmatrix} H_1 C_{10W} \\ H_2 C_{20W} \end{bmatrix}$$

This removes C_{10A} and C_{20A} as independent concentration variables, now leaving four independent concentration variables. When we enforce flux-matching (this time for both compounds independently), we also remove C_{10W} and C_{20W} . The only remaining independent concentration variables are $C_{1\infty W}$ and $C_{1\infty A}$.

To enforce flux matching, we treat $C_{1\infty W}$ and $C_{1\infty A}$ as givens, and adjust C_{10W} and C_{20W} to balance the flux of both compounds. The flux-matching condition is

$$\begin{bmatrix} F_1 \\ F_2 \end{bmatrix}_W = \begin{bmatrix} F_1 \\ F_2 \end{bmatrix}_A$$

The matrices defined in Table S2 permit us to encode the flux-matching condition in this way:

$$-\mathbf{V} \cdot \begin{bmatrix} C_{1\infty A} \\ C_{1\infty W} \end{bmatrix} = \mathbf{M} \cdot \begin{bmatrix} C_{10W} \\ C_{20W} \end{bmatrix}$$

We also introduce the notation

$$m = \frac{C_{1\infty A}}{H_1 C_{1\infty W}}$$

and use it to remove $C_{1\infty A}$ in favor of $C_{1\infty W}$ as throughout. Flux matching imposes this expression for the interfacial concentrations:

$$\begin{bmatrix} C_{10W} \\ C_{20W} \end{bmatrix} = -\mathbf{M}^{-1} \cdot \mathbf{V} \cdot \begin{bmatrix} C_{1\infty A} \\ C_{1\infty W} \end{bmatrix} = -C_{1\infty W} \mathbf{T}$$

for \mathbf{T} as given in Table S2. The expressions in the table for fluxes and for δ_{PW} and δ_{PA} follow.

The next step is to show that the term $(1 - m)$ factors out of the flux expressions. We define a column vector $\boldsymbol{\tau}$ such that

$$\mathbf{T} = -m \mathbf{V}_B + \boldsymbol{\tau}$$

(This expression was motivated by the empirical observation during numerical calculations that $\mathbf{T} \approx -m\mathbf{V}_B$ in many cases and that \mathbf{V}_B is orthogonal to $\boldsymbol{\Theta}_A$ and $\boldsymbol{\Theta}_W$.) All expressions are implicitly linear in m . Redefine $\boldsymbol{\tau}$ to show the m -dependence explicitly:

$$\boldsymbol{\tau} = \boldsymbol{\tau}_0 + m\boldsymbol{\tau}_1$$

$\boldsymbol{\tau}$, $\boldsymbol{\tau}_0$, and $\boldsymbol{\tau}_1$ are to be determined. We also make use of this equation which is easily verifiable:

$$\mathbf{M} \cdot \mathbf{V}_B = -\mathbf{V} \cdot \mathbf{V}_C$$

Two different identities can now be written for $\mathbf{M} \cdot \mathbf{T}$:

$$\mathbf{M} \cdot \mathbf{T} = \mathbf{V} \cdot \mathbf{V}_D + mH_1 \mathbf{V} \cdot \mathbf{V}_E$$

$$\mathbf{M} \cdot \mathbf{T} = \mathbf{M} \cdot \boldsymbol{\tau}_0 + m\mathbf{M} \cdot \boldsymbol{\tau}_1 + m\mathbf{V} \cdot \mathbf{V}_C$$

Both are valid at arbitrary m , so the constant terms and the terms in m are both independently equal. The following expressions all follow.

$$\mathbf{M} \cdot \boldsymbol{\tau}_0 = \mathbf{V} \cdot \mathbf{V}_D$$

$$\mathbf{M} \cdot \boldsymbol{\tau}_1 = H_1 \mathbf{V} \cdot \mathbf{V}_E - \mathbf{V} \cdot \mathbf{V}_C = -\mathbf{V} \cdot \mathbf{V}_D$$

$$\boldsymbol{\tau}_0 = \mathbf{M}^{-1} \cdot \mathbf{V} \cdot \mathbf{V}_D = \zeta_W \mathbf{M}^{-1} \cdot \mathbf{V}_W, \quad \boldsymbol{\tau}_1 = -\boldsymbol{\tau}_0, \quad \boldsymbol{\tau} = (1 - m)\boldsymbol{\tau}_0$$

$$\boldsymbol{\Theta}_W \cdot \mathbf{T} = (1 - m) \boldsymbol{\Theta}_W \cdot \boldsymbol{\tau}_0, \quad \boldsymbol{\Theta}_A \cdot \mathbf{T} = (1 - m)H_2 \boldsymbol{\Theta}_W \cdot \boldsymbol{\tau}_0, \quad T_1 = -m + (1 - m)\tau_{01}$$

When these expressions are inserted into the flux equations, the term $(1 - m)$ factors out.

In most instances, we are only interested in the total flux, $F_1 + F_2 = F_t$, and the equations for the sum F_t turn out to be simpler than those for either F_1 or F_2 . We obtain the expressions

$$F_{tW} = C_{1\infty W}(1 - m)f_{tW}, \quad F_{tA} = C_{1\infty W}(1 - m)f_{tA}$$

$$f_{tW} = \zeta_W(Q_W + K_W + \mathbf{W} \cdot \boldsymbol{\tau}_0), \quad f_{tA} = -\zeta_A \mathbf{A} \cdot \boldsymbol{\tau}_0$$

Now either f_{tW} or f_{tA} can also be written f_{A4} .

S2.8. Model A4. Air- or water-side control.

Model A4 also becomes air- or water-side dominant when crossing one barrier or the other is the rate-limiting step. I use the following two derivatives

$$R_A = \frac{\partial \ln f_{A4}}{\partial \ln \zeta_A} = -\frac{\zeta_W}{f_{A4}}(\mathbf{W} \cdot \mathbf{M}^{-1} \cdot \mathbf{M}_A \cdot \boldsymbol{\tau}_0) = 1 + \frac{\zeta_A}{f_{A4}}(\mathbf{A} \cdot \mathbf{M}^{-1} \cdot \mathbf{M}_A \cdot \boldsymbol{\tau}_0)$$

$$R_W = \frac{\partial \ln f_{A4}}{\partial \ln \zeta_W} = 1 + \frac{\zeta_W}{f_{A4}}(\mathbf{W} \cdot \boldsymbol{\tau}_0 - \mathbf{W} \cdot \mathbf{M}^{-1} \cdot \mathbf{M}_W \cdot \boldsymbol{\tau}_0) = 1 + \frac{\zeta_A}{f_{A4}}(\mathbf{A} \cdot \mathbf{M}^{-1} \cdot \mathbf{M}_W \cdot \boldsymbol{\tau}_0)$$

to indicate the extent of air or water dominance. (The two different versions of f_{A4} provide two versions each of R_A and R_W .) Write f_{A4} as an explicit function of ζ_A and ζ_W . Then

$$f_{A4} = f(\zeta_A, \zeta_W) = \lambda^{-1} f(\lambda \zeta_A, \lambda \zeta_W)$$

Where λ is an arbitrary scale factor. We know this because f_{A4} has units length/time and that ζ_A and ζ_W are the only variables from which units of length/time can enter the final result. We can always think of λ as representing a change of units, in which case the above expression becomes obvious. It is not hard to show that any function with this property obeys

$$R_A + R_W = 1$$

R_A and R_W are the slopes of f_{A4} vs. ζ_A and ζ_W on a log-log plot. Therefore, R_A near 1 implies R_W near 0 and air-side control, and vice versa. When neither is near 1, the system exhibits no clear dominance of one side over the other.

S3. Numerical properties of model A4.

I have performed Monte Carlo calculations to study model A4. All results given below were obtained using system variables distributed according to Table S3.

Table S3. Distribution of variables employed for studying numerical properties of model A4. H_1 through k_{21A} were selected from the indicated log-normal distributions. K_W , k_{12A} , and H_2 were then assigned as shown.

Variable	μ	σ
H_1	0.0	2.0
$D_{1W}/(\text{cm}^2 \text{ s}^{-1})$	0.0	2.0
$D_{2W}/(\text{cm}^2 \text{ s}^{-1})$	0.0	2.0
$D_{1A}/(\text{cm}^2 \text{ s}^{-1})$	0.0	2.0
$D_{2A}/(\text{cm}^2 \text{ s}^{-1})$	0.0	2.0
k_{12W}/s^{-1}	0.0	2.0
k_{21W}/s^{-1}	0.0	2.0
K_A	0.0	2.0
L_W/cm	0.0	2.0
L_A/cm	0.0	2.0
k_{21A}/s^{-1}	0.0	2.0
K_W	$\frac{k_{12W}}{k_{21W}}$	
k_{12A}/s^{-1}	$K_A k_{21A}$	
H_2	$\frac{H_1 K_A}{K_W}$	

S3.1. Numerical stability of model A4.

The equations given in tables S1 and S2 are exact for model A4. However, in practice I have found that numerical calculations can be subject to roundoff errors that commonly accumulate in the sum of two quantities of nearly equal magnitude but opposite sign. This usually happens here in one of two ways:

- (1) $\det(\mathbf{M})$ is near zero. (One way this happens is when \mathbf{M} , written exactly as the sum of four outer products, is dominated by only one of the four. As pointed out in Section S2.5, the determinant of an outer product is zero.)
- (2) \mathbf{W} or \mathbf{A} are occasionally nearly orthogonal to \mathbf{T} or to $\boldsymbol{\tau}_0$, so the dot products such as $\mathbf{W} \cdot \mathbf{T}$, $\mathbf{A} \cdot \mathbf{T}$, $\mathbf{W} \cdot \boldsymbol{\tau}_0$, and $\mathbf{A} \cdot \boldsymbol{\tau}_0$ are near zero.

To understand the severity of this problem, I coded the calculations to estimate significant figures at each step in the calculation. All computations were performed in double-precision arithmetic, which allows for a nominal 15-digit accuracy. So, at the beginning of

the calculation, all variables were assumed to have 15 significant figures, and then the standard rules for significant figure estimation were followed. Fortunately, the algorithm provides two separate equations for f_{A4} . The code calculates both and returns the one with the better accuracy. As shown in Figure S3, there can be considerable loss of accuracy in the calculation of f_{A4} , but at least one of the calculations always has 10-figure accuracy or better.

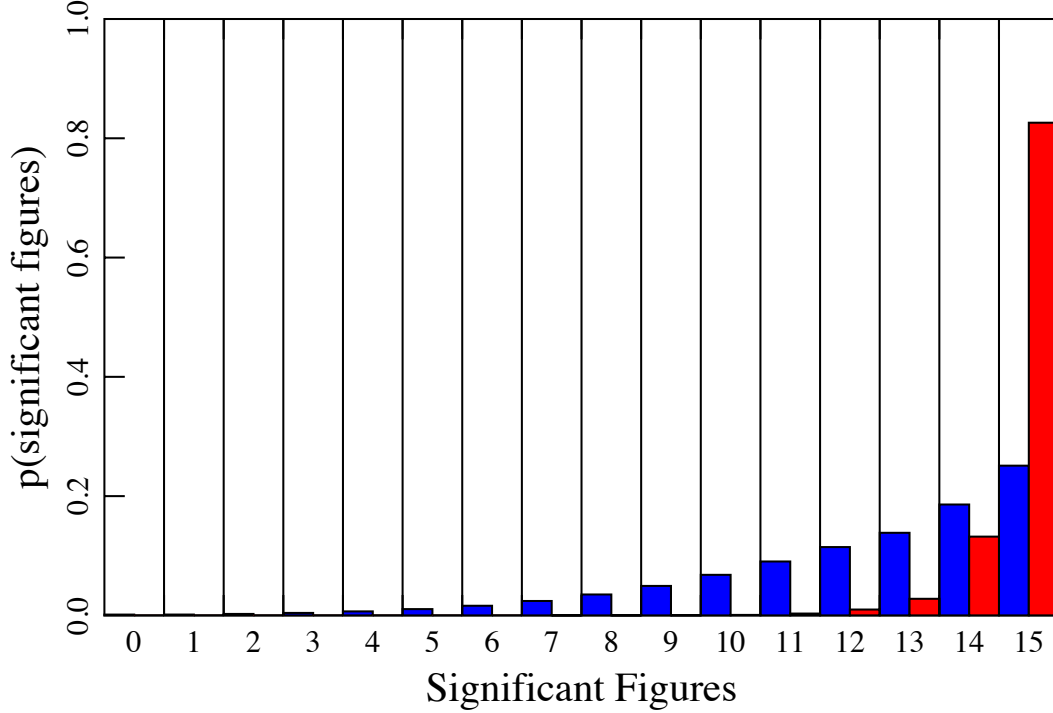


Figure S3. Accuracy of the calculation of f_{A4} . f_{A4} can be calculated via two separate expressions. Blue and red bars respectively represent the probability that the less accurate and more accurate calculation has a given number of significant figures.

S3.2. Model A4 simplifications

The A4 algorithm is very complicated, but there are limiting cases in which the matrix identities given in Section 2.5 produce simplifications. The complete \mathbf{M} matrix is a sum of four outer-product matrices. Interesting simplifications occur when only two of the four outer products are important. (When we approximate \mathbf{M} with only one of the four outer products, the resulting \mathbf{M} is non-invertible.) Now consider two of these cases:

Air-side control. (\mathbf{M}_A irrelevant relative to \mathbf{M}_W .)

$$\mathbf{M} \cong \mathbf{M}_W$$

$$\mathbf{M} \cong \zeta_W J_W [-\mathbf{V}_W \otimes \mathbf{W} + x_W Q_W \mathbf{S} \otimes \mathbf{\Theta}_W]$$

$$\begin{aligned}
\det \mathbf{M} &\cong -\zeta_W^2 J_W^2 x_W Q_W (\mathbf{W} \times \boldsymbol{\Theta}_W) \cdot (\mathbf{V}_W \times \mathbf{S}) = \zeta_W^2 x_W Q_W \\
\mathbf{M}^{-1} &\cong \zeta_W^{-1} x_W^{-1} Q_W^{-1} [-J_W \text{adj}(\mathbf{V}_W \otimes \mathbf{W}) + J_W x_W Q_W \text{adj}(\mathbf{S} \otimes \boldsymbol{\Theta}_W)] \\
\boldsymbol{\tau}_0 &\cong \zeta_W \mathbf{M}^{-1} \cdot \mathbf{V}_W \cong J_W \text{adj}(\mathbf{S} \otimes \boldsymbol{\Theta}_W) \cdot \mathbf{V}_W \\
f_{A4} &= -\zeta_A \mathbf{A} \cdot \boldsymbol{\tau}_0 \cong -\zeta_A J_W \mathbf{A} \cdot \text{adj}(\mathbf{S} \otimes \boldsymbol{\Theta}_W) \cdot \mathbf{V}_W = -\zeta_A J_W (\mathbf{A} \times \boldsymbol{\Theta}_W) \cdot (\mathbf{V}_W \times \mathbf{S}) \\
f_{A4} &\cong \zeta_A H_1 (Q_A + K_A)
\end{aligned}$$

Water-side control. (\mathbf{M}_W irrelevant relative to \mathbf{M}_A).

$$\begin{aligned}
\mathbf{M} &\cong \mathbf{M}_A \\
\mathbf{M} &\cong \zeta_A J_A [-\mathbf{V}_A \otimes \mathbf{A} + x_A Q_A \mathbf{S} \otimes \boldsymbol{\Theta}_A] \\
\det \mathbf{M} &\cong -\zeta_A^2 J_A^2 x_A Q_A (\mathbf{A} \times \boldsymbol{\Theta}_A) \cdot (\mathbf{V}_A \times \mathbf{S}) = \zeta_A^2 x_A Q_A H_1 H_2 \\
\mathbf{M}^{-1} &\cong \zeta_A^{-1} x_A^{-1} Q_A^{-1} H_1^{-1} H_2^{-1} J_A [-\text{adj}(\mathbf{V}_A \otimes \mathbf{A}) + x_A Q_A \text{adj}(\mathbf{S} \otimes \boldsymbol{\Theta}_A)] \\
\boldsymbol{\tau}_0 &\cong (\zeta_A x_A Q_A H_1 H_2)^{-1} \zeta_W J_A [-\text{adj}(\mathbf{V}_A \otimes \mathbf{A}) \cdot \mathbf{V}_W + x_A Q_A \text{adj}(\mathbf{S} \otimes \boldsymbol{\Theta}_A) \cdot \mathbf{V}_W] \\
f_{A4} &= -\zeta_A \mathbf{A} \cdot \boldsymbol{\tau}_0 \cong -(H_1 H_2)^{-1} \zeta_W J_A (\mathbf{A} \times \boldsymbol{\Theta}_A) \cdot (\mathbf{V}_W \times \mathbf{S}) \\
f_{A4} &\cong \zeta_W (Q_W + K_W)
\end{aligned}$$

These expressions are also limiting expressions for f_{A1E} . This implies that there are instances for which $f_{A1E} \rightarrow f_{A4}$. Figure S4 displays the joint probability density of the ratio f_{A1E}/f_{A4} and R_A from the Monte Carlo calculations carried out using inputs distributed as in Table S3. The following results have been obtained:

(1) $f_{A1E} > f_{A4}$ always, but there are limiting processes in which the two become arbitrarily close. The red-toned pixels at $f_{A1E}/f_{A4} \cong 1$ are examples of this behavior. Then, the much simpler A1E model performs as well as model A4. But there are also conditions for which $f_{A1E} \gg f_{A4}$. About 15% of all Monte Carlo samples fell off the scale of figure S4, with $f_{A1E}/f_{A4} > 31.6$.

(2) The tendency for $f_{A1E} \cong f_{A4}$ intensifies when the system is under either air- or water-barrier control, as exemplified by the two swooping red-toned curves converging either to $(R_A, f_{A1E}/f_{A4}) = (0,1)$ or $(1,1)$. However, $R_A \cong 0$ or 1 is no guarantee for $f_{A1E} \cong f_{A4}$. Significant probability density is found when $R_A \cong 0$ or 1 at larger values of f_{A1E}/f_{A4} .

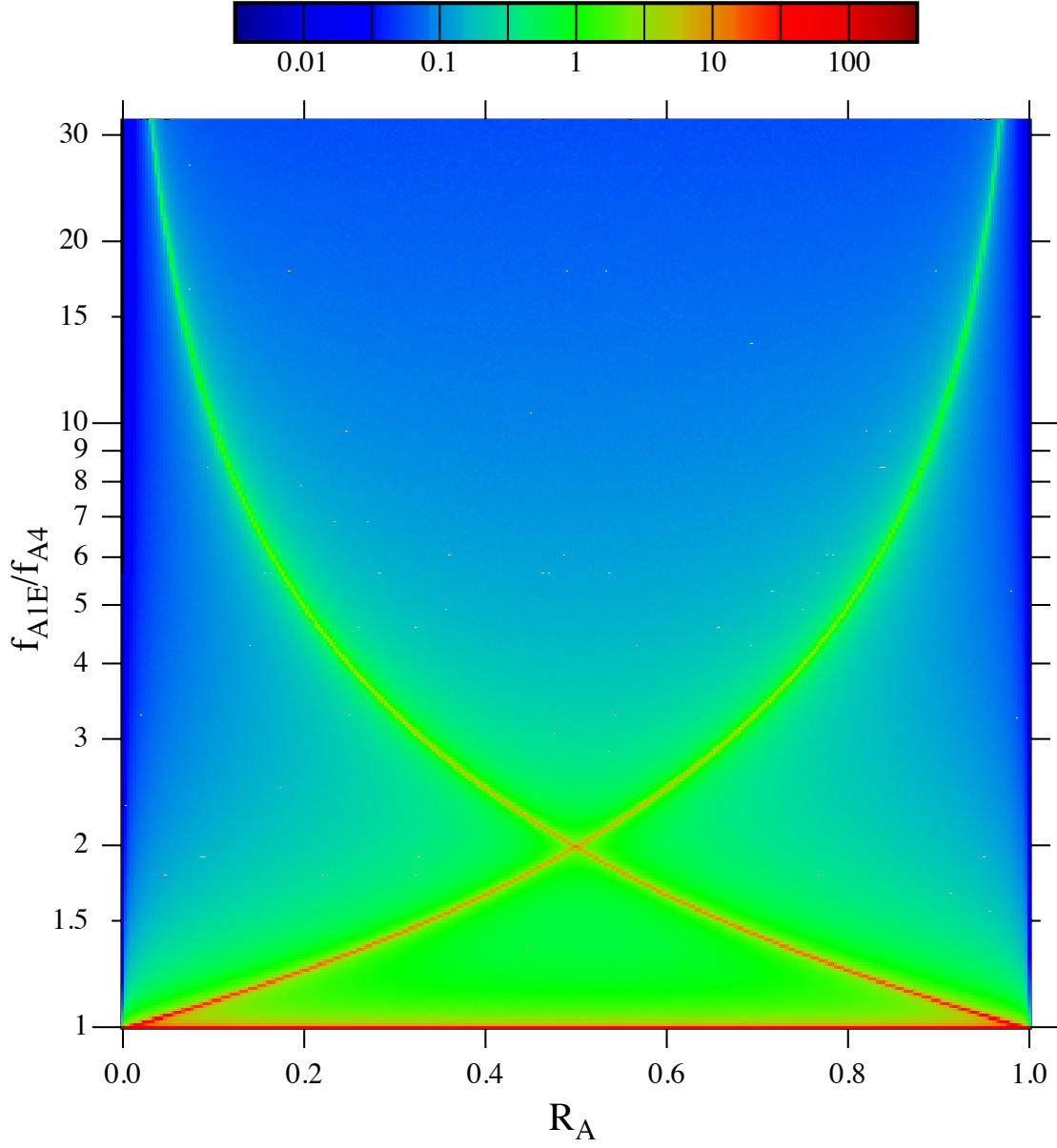


Figure S4. Joint probability density of model instances with the indicated values of R_A and f_{A1E}/f_{A4} .

Figure S5 displays the joint distribution of the ratio f_{A3}/f_{A4} and R_A in the Monte Carlo runs. We find $f_{A3} < f_{A4}$ always, but with many instances of $f_{A3}/f_{A4} \cong 1$. Similar calculations, not shown, indicate that $f_{A2} < f_{A3} < f_{A4} < f_{A1E}$ always, with the possibility that any two of the four can become arbitrarily close.

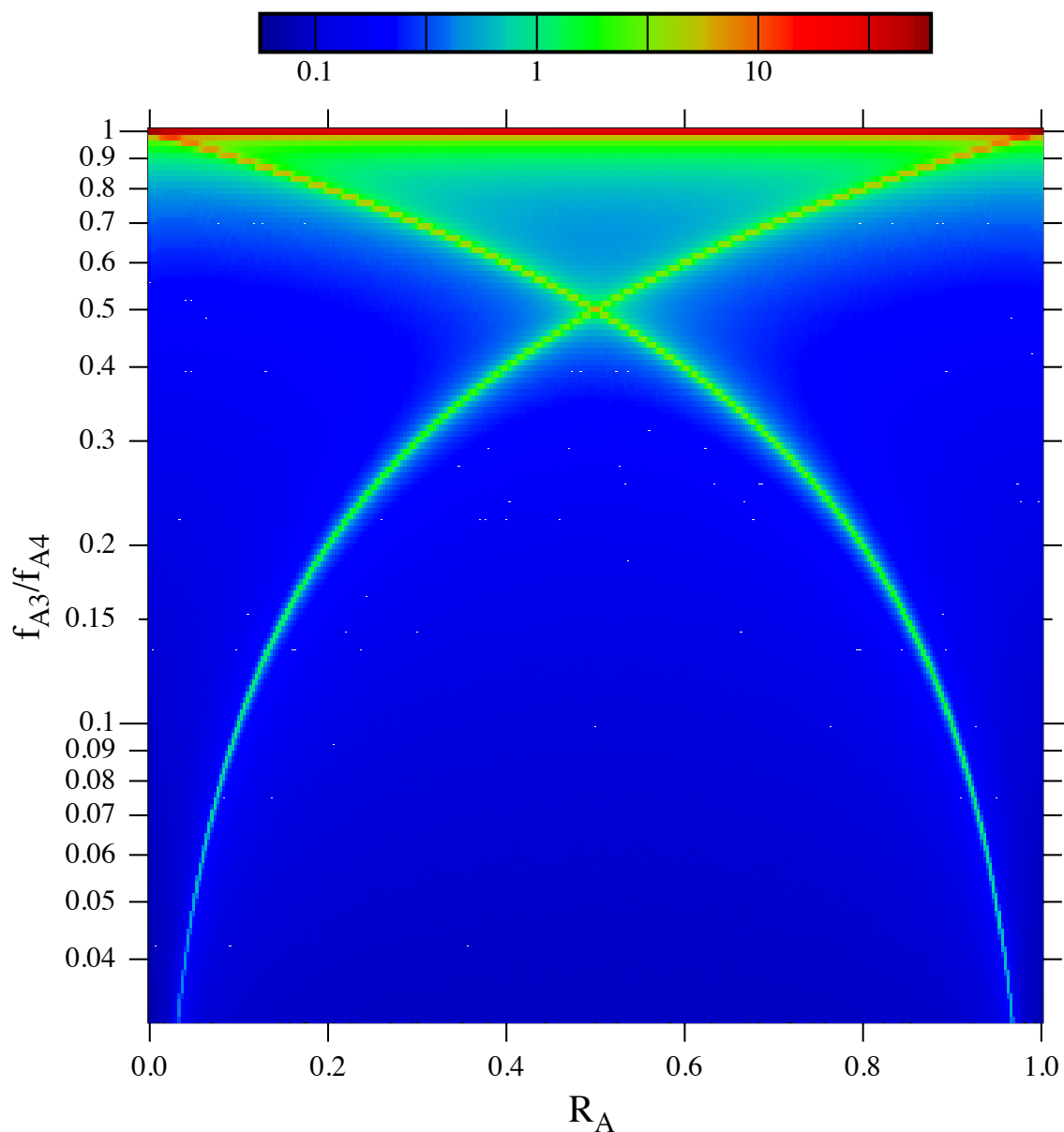


Figure S5. Joint probability of model instances with the indicated values of R_A and f_{A3}/f_{A4} .

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