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A semianalytical method for simulating mass transport at channel electrodes

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Abstract

A method for simulating electrode reactions in channel flow is developed and efficiently implemented in the symbolic algebra program MapleTM. The steady-state convective diffusion equation for fully developed 2-D laminar (Poiseuille) flow past one or more electrodes in a channel is considered for a charge-transfer electrode reaction between two soluble species. The case where axial diffusion (along the channel, x direction) is neglected and the diffusivities are equal has an exact solution as an infinite series, in which each term is the product of an exponential in x and a confluent hypergeometric function in y (across the channel). The practical implementation consists of evaluating a finite number of terms and numerically evaluating the two parameters in each term. Sturm-Liouville (eigenfunction) theory is used to reliably find the parameters for arbitrary values of the rate constants. Comparison is made with results from a commercial software package that uses a finite-element method.

Key words: channel electrodes, simulations, symbolic algebra, eigenfunctions, Sturm-Liouville, Maple

Introduction

Electrochemical detection is well suited to microfluidic devices [1, 2], and the ready availability of new microfluidic fabrication methods has led to renewed interest in channel electrodes [3], with a consequent need for efficient computational methods. We report here an eigenfunction series method for channel electrodes that may be efficiently implemented by a symbolic algebra program. The application of eigenfunction methods for the solution of convective diffusion equations relevant to electrochemistry has a long history. The solution to the

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Graetz problem, which solves heat transfer to the walls of a tube with laminar flow, was given as an eigenfunction expansion as early as 1883 [4], and an extensive treatment of the electrochemical version was given by Newman [5]. In the context of mass transport in the rectangular channels that we consider here, Moldoveanu and Anderson solved the limiting current case in terms of a series of parabolic cylinder functions [6]. In these cases, the general case of arbitrary rate constants was not attempted, perhaps because a reliable way of locating the eigenvalues was not available. Recently, Schmachtel and Kontturi used eigenfunction methods to numerically solve chronoamperometry currents at the rotating disk electrode [7]. They considered the case of arbitrary rate constants and also showed that the case of quasireversible electrode reactions could be solved as easily as the case of irreversible reactions.

Here we apply the eigenfunction expansion method to 2-D steady-state flow past electrodes in a channel, for the case where axial diffusion (along the channel) is neglected. We derive the exact solution to this case as an infinite series. The practical implementation of this as a numerical method in the symbolic algebra language MapleTM is presented and compared with the more conventional finite-element (FE) method, as implemented in Comsol Multiphysics[®]. It is a mesh-free method and so should give good accuracy at the beginning of the electrode, where there is a step change in boundary conditions and the current density is high. Furthermore, the concentration profile, once determined, can be easily manipulated term by term to find local current densities, average current densities, or collection efficiencies, without significant degradation in accuracy. The accuracy is determined by the number of terms processed, and calculation of additional terms allows the global error to be estimated. An important advantage of the present method is that the whole region above an electrode is solved at one time, so the complexity of the calculation is largely independent of the channel height or width of the electrode.

1. Theory

We consider a solution of the steady-state diffusion-convection problem in a 2-D channel with fully developed laminar (Poiseuille) flow. Key notation is given in Fig. 1 and a full set of symbols are given in the supplementary material, see B. The electrode reaction between two solution species, Eq. (1), has the current density at a particular location at the electrode given by the usual rate law, Eq. (2). The potential at the electrode is fixed, so the rate constants (m s^{-1}) do not vary over the electrode surface. However, we allow the possibility of many electrodes along the wall of the channel, and the potential and rate constants may be different at each. The convective diffusion equation to be solved for each species is Eq. (3). We make the common assumption that the diffusivities of the two species are equal.

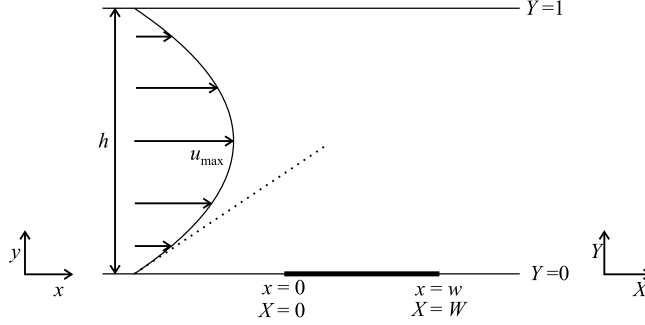


Figure 1: Notation. Flow is from left to right, with one or more embedded electrodes (bold) in the bottom of the channel. Lower case variables are dimensioned, upper case variables are dimensionless. The dotted line is the velocity profile (extending to infinite height) for the L  v  que approximation. The average velocity u_{ave} is $2/3$ of the maximum velocity u_{max} .



$$j(x) = Fv(x) = Fk_{\text{f}}c_{\text{R}}(x, 0) - Fk_{\text{b}}c_{\text{P}}(x, 0) \quad (2)$$

$$0 = D \frac{\partial^2 c_k(x, y)}{\partial y^2} - \frac{4u_{\text{max}}}{h^2} y(h - y) \frac{\partial c_k(x, y)}{\partial x}, \quad k = \text{R, P} \quad (3)$$

Matching of the fluxes at the electrode surface to the reaction rate leads to the boundary conditions, Eq. (4), at the electrode surface. (The convective flux at the walls is zero, so only the diffusive part needs to be considered.) The flux at insulating sections between electrodes and at the top of the channel is zero, Eqs. (5) and (6). The "initial" condition is that the concentrations take the bulk values at a location x_0 upstream of the first electrode, Eq. (7). In the absence of axial diffusion, the solution only propagates downstream, and there is no loss in taking $x_0 = 0$. The measured current density is given by averaging over the electrode surface, Eq. (8).

$$D (\partial c_{\text{R}}(x, y) / \partial y)_{y=0} = -D (\partial c_{\text{P}}(x, y) / \partial y)_{y=0} = v(x) \quad (4)$$

$$(\partial c_{\text{R}}(x, y) / \partial y)_{y=0} = (\partial c_{\text{P}}(x, y) / \partial y)_{y=0} = 0 \quad (5)$$

$$(\partial c_{\text{R}}(x, y) / \partial y)_{y=h} = (\partial c_{\text{P}}(x, y) / \partial y)_{y=h} = 0 \quad (6)$$

$$c_k(x_0, y) = c_k^{\text{b}}, \quad k = \text{R, P} \quad (7)$$

$$j_{\text{ave}} = (FD/w) \int_0^w (\partial c_{\text{R}}(x, y) / \partial y)_{y=0} dx \quad (8)$$

As discussed below, the quasireversible solution including the back reaction can be simply derived from the irreversible solution with apparent rate constant $k = k_{\text{f}} + k_{\text{b}}$, so we need only develop a numerical method for the irreversible

case. We change to dimensionless variables (see Fig. 1): $Y = y/h$, $X = x/h$, $W = w/h$, $C(X, Y) = c_R(x, y)/c_R^b$, $K = hk_f/D$, $J = (h/c_R^b DF)j$ and $A = 4u_{\max}h/D = 6Pe$ where $Pe = u_{\text{ave}}h/D = 2u_{\max}h/3D$ is a Péclet number for mass transfer. The convective diffusion equation and boundary conditions are now:

$$0 = \frac{\partial^2 C(X, Y)}{\partial Y^2} - A Y(1 - Y) \frac{\partial C(X, Y)}{\partial X} \quad (9)$$

$$(\partial C(X, Y)/\partial Y)_{Y=0} = KC(X, 0) \text{ (at electrode)} \quad (10)$$

$$(\partial C(X, Y)/\partial Y)_{Y=0} = 0 \text{ (between electrodes)} \quad (11)$$

$$(\partial C(X, Y)/\partial Y)_{Y=1} = 0 \text{ (top of channel)} \quad (12)$$

$$C(0, Y) = 1 \text{ (upstream)} \quad (13)$$

Writing $C(X, Y) = F(X)G(Y)$ and rearranging gives Eq. (14), which shows that the partial differential equation is separable. The general solution, Eq. (15), is a superposition of products of exponential functions of X and functions of Y that satisfy the differential equation (16), where the primes indicates differentiation with respect to Y .

$$\frac{1}{Y(1 - Y)G(Y)} \frac{d^2 G(Y)}{dY^2} = \frac{A}{F(X)} \frac{dF(X)}{dX} = -b^2 \quad (14)$$

$$C(X, Y) = \sum_{i=1}^{\infty} a_i \exp(-b_i^2 X/A) G_i(Y) \quad (15)$$

$$-G''(Y) = b^2 Y(1 - Y)G(Y) \quad (16)$$

Eq. (16) has an operator $-d^2/dY^2$ operating on $G(Y)$ to give a constant b^2 times a weighting function $Y(1 - Y)$ times $G(Y)$. According to Sturm-Liouville theory [8], such equations have an infinite set of eigenfunction solutions, $G_i(Y)$, which depend on the boundary conditions at the electrode and top channel surfaces. The eigenvalues are the particular values b_i^2 that give valid solutions. As detailed in A, we first narrow the solutions to those that satisfy the zero-flux boundary condition at the top of the channel, Eq. (17). This ensures that the concentration, Eq. (15), satisfies the zero-flux condition, Eq. (12). These solutions $G(Y)$, normalized so that $G(1) = 1$, are given in terms of confluent hypergeometric functions in A.

$$G'(1) = 0 \quad (17)$$

The remaining undetermined constant is b , which is determined by the type of boundary condition at the $Y = 0$ surface, i.e., the electrode surface or an insulating surface between electrodes. Three subcases are considered. The first is the limiting current boundary condition, where the concentration is zero at the electrode surface, Eq. (18). Solving Eq. (18) for b leads to the series of

values in Eq. (19).

$$G(0) = 0 \quad (18)$$

$$b_1^{(\infty)} = 3.82, b_2^{(\infty)} = 11.90, b_3^{(\infty)} = 19.92, \dots \quad (19)$$

$$b_i^{(\infty)} \sim \frac{\pi(i - \frac{1}{2})}{\int_0^1 \sqrt{Y(1-Y)} dY} = 8(i - 1/2) \quad (20)$$

$$8(i - 1) < b_i^{(\infty)} < 8(i - 1/2), \quad i = 1, 2, \dots \quad (21)$$

where the superscript ∞ denotes an infinite rate constant ($K = \infty$). Eq. (20) for the eigenvalues¹ is from Sturm-Liouville theory [8], and although it is an asymptotic formula for large i , closer inspection shows that it works well also for small i : the predicted values $8(i - 1/2)$ are slightly higher than the actual values in Eq. (19). Successive b_i values are in the ranges given in Eq. (21), which means that the numerical solver can reliably find all eigenvalues by searching for one solution of Eq. (18) in each of these ranges.

Consider now the boundary condition for an insulating section of the channel or for zero current at the electrode, where the flux is zero, Eq. (22). Here the eigenvalues are given by Eq. (23).

$$G'(0) = 0 \quad (22)$$

$$b_i^{(0)} = 0, 9.05, 17.15, 25.19, \dots \sim 8(i - 1) \quad (23)$$

The last case is the Robin boundary condition of Eq. (24), where K is a dimensionless rate constant. Here the eigenvalues satisfy the inequalities of Eq. (25).

$$G'(0) - KG(0) = 0 \quad (24)$$

$$8(i - 1) < b_i^{(0)} < b_i^{(K)} < b_i^{(\infty)} < 8(i - 1/2) \quad (25)$$

For all cases, b_i lies between $8(i - 1)$ and $8(i - 1/2)$. (For negative K , a non-physical case, the b_i values lie between $8(i - 1/2)$ and $8i$.)

The coefficients a_i are determined by the "initial" concentration profile at $X = 0$, the upstream edge of the electrode. From Eq. (15), a given initial profile $C(0, Y) = f_0(Y)$ (not necessarily $C(0, Y) = 1$) is a linear combination of the eigenfunctions $G_i(Y)$, and the coefficients can be found using the orthogonality of the eigenfunctions as given in Eq. (26).

$$a_i = \frac{\int_0^1 Y(1 - Y) f_0(Y) G_i(Y) dY}{\int_0^1 Y(1 - Y) G_i(Y)^2 dY} \quad (26)$$

¹We refer to the b_i values as eigenvalues, though strictly these are the square roots of the eigenvalues.

The series form of the concentration, Eq. (15), is easy to manipulate. For example, the dimensionless form of the current density, Eq. (8), averaged over an electrode running from $X = 0$ to $X = W$ gives Eq. (27).

$$J_{\text{ave}} = \frac{1}{W} \int_0^W \left. \frac{\partial C}{\partial Y} \right|_{Y=0} dX \quad (27)$$

(This is also a dimensionless average flux.) It may be calculated term by term as in Eq. (28).

$$J_{\text{ave}} = \frac{A}{W} \sum_{i=1}^{\infty} \frac{a_i}{b_i^2} [1 - \exp(-b_i^2 W/A)] G'_i(0) \quad (28)$$

The quantity $G'_i(0)$ may be evaluated using the differentiation rule Eq. (42).

Aside from the fact that the a_i and b_i values have no simple formula, the treatment is exact to this point. It is implemented as a numerical method by cutting the series expansion off at a finite number of terms, N , and numerically evaluating a_i and b_i for each term.

1.1. Multiple electrodes

The case of multiple electrodes and gaps between them is handled similarly. The solution for the first electrode proceeds as described above, with $f_0(Y) = 1$. This solution at the downstream edge of the electrode is just used as the initial profile that replaces $f_0(Y)$ in the solution of the next "segment". For example, a three-segment configuration might have segment 1 as an electrode between $X = 0$ and $X = 1$, segment 2 as an insulator between $X = 1$ and $X = 2$ with a no-flux boundary condition at $Y = 0$ and then segment 3 as an electrode after $X = 2$. The segment 1 solution $C(1, Y) = f_1(Y)$ is used as the initial profile for segment 2, and the segment 2 solution $C(2, Y) = f_2(Y)$ is used as the initial profile for segment 3.

2. Methods

2.1. Maple

A procedure *chsolve* to implement the above algorithm was written in the commercially available symbolic algebra system MapleTM [9]. The code and examples of its use are available as supplementary material, see B. The procedure takes as inputs: (i) the numerical value of the dimensionless rate constant. As above, "0" indicates the zero flux condition and "infinity" indicates the case of zero concentration at the electrode surface, (ii) the name of a procedure that evaluates the initial concentration profile $f_0(Y)$, (iii) the value of A , and (iv) the number of terms N required in the eigenfunction expansion, Eq. (15). The output is a procedure that evaluates the dimensionless concentration as a function of X and Y , which can then be plotted, differentiated or otherwise manipulated to produce derived quantities.

The case of multiple segments is handled by giving the rate constant as a piecewise function of X . In the single segment case, A can be left as a symbol, and then the output concentration and quantities derived for it can be plotted as a function of A . For the multisegment case, the numerical value of A must be given; this restriction arises from the need to numerically evaluate the integrals in Eq. (26) to find the concentration profile at the beginning of second and subsequent segments.

The limiting factor is the efficient numerical calculation of the integrals in Eq. (26). When the accuracy requested (via the "Digits" variable) is low, Maple works in hardware double precision arithmetic and uses the Numerical Algorithms Group routine "d01akc". For higher accuracy, Maple works in arbitrary precision arithmetic, and uses an adaptive Gaussian quadrature routine "Gquad".

2.2. Comsol

The case of a single electrode under limiting current conditions was also solved using Comsol Multiphysics[®] [10], with the conditions chosen as close as possible to those used in Maple. To effectively non-dimensionalize the problem, the problem was solved in base SI units with the parameters h , w , D and c^b set to unity. The problem was solved for both species using the PARDISO solver, and the A value was changed parametrically to get the solution at different flow rates. The outlet was put 10 electrode widths downstream of the electrode to eliminate the influence of the boundary condition. The outlet boundary condition is given in Eq. (29).

$$D(\partial c_k / \partial x) = 0 \quad (29)$$

To solve for the limiting current case, the rate constant K was set to a high value (10^{10}) to effectively get a concentration of zero at the electrode. The surface concentration was verified post-calculation to be zero. The inlet was put 10 electrode widths from the electrode start and the concentration was set to the boundary inlet concentration, $C = 1$. The absence of axial diffusion was achieved by using anisotropic diffusivities with zero X components. The absence of axial diffusion was verified by checking that the concentration one mesh point upstream of the electrode always is equal to 1.

A mapped mesh following the flow direction was used. A fine mesh was used at the two electrode edges and at the left hand edge at the inlet at the electrode side of the channel. This was set to 0.3% of the dimensionless diffusion layer thickness $\Delta = \delta/h$ estimated using the L  v  que approximation for δ [11] as Eq. (30) with $A = A_{\max}$, where A_{\max} is the highest A value that is evaluated. The mesh is set to grow at a rate of 1.02 out from these points, which ensured that the axial diffusion condition was met and that the desired accuracy was reached at the electrode surface.

$$\Delta = 3^{-1/3} \Gamma(1/3) (W/A)^{1/3} \quad (30)$$

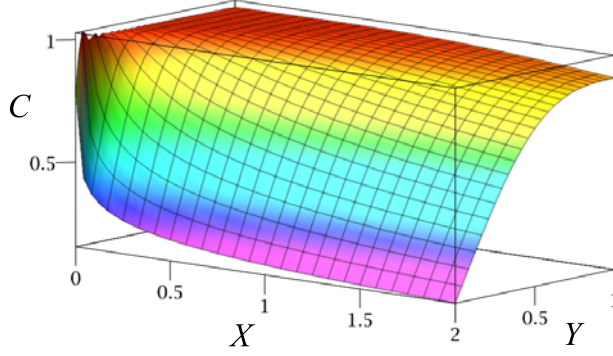


Figure 2: Concentration profile for an irreversible reaction. $K_f = 10$, $A = 100$. Series evaluated to 40 terms. Electrode runs from $X = 0$ to $X = 2$.

3. Results

Examples of the capabilities of this method are given here, with the calculation details given in a Maple worksheet in the supplementary material, see B.

3.1. Irreversible Reaction

The case of $K = K_f = 10$ for $A = 100$ (Péclet number 16.7) is illustrated in Fig. 2. The consumption of the species at the electrode is seen, and its variation along the electrode surface. The increasing thickness of the diffusion layer is also evident, and by $X = 2$, the concentration at the top of the channel is significantly diminished from its initial value of 1. Small ripples in the Y direction close to $X = 0$ are the Gibbs' phenomenon, well known in Fourier theory, which is a special case of the Sturm-Liouville theory applicable here.

The current density J_{ave} for this example agreed with the Comsol result: 2.1815 (Maple, 40 terms) vs 2.1817 (Comsol).

3.2. Flow rate dependence of limiting current

The limiting current density is found from the flux via Eq. (28), for the case of the boundary condition $C(X, 0) = 0$ or Eq. (18). The series in Eq. (28) has numerical values of the a_i and b_i but A and W are still arbitrary, and so the limiting current as a function of flow rate may be readily plotted and compared with the Comsol results as in Fig. 3. For comparison, two approximate relationships are also shown: (i), the limiting current given by the Levich equation [11], Eq. (31), and (ii), the complete consumption or "thin layer" limit [12], Eq. (32).

$$J_{\text{ave}}(\text{Levich}) = \frac{3^{4/3}}{2\Gamma(1/3)} \left(\frac{A}{W} \right)^{1/3} \quad (31)$$

$$J_{\text{ave}}(\text{thin layer}) = A/6 = Pe \quad (32)$$

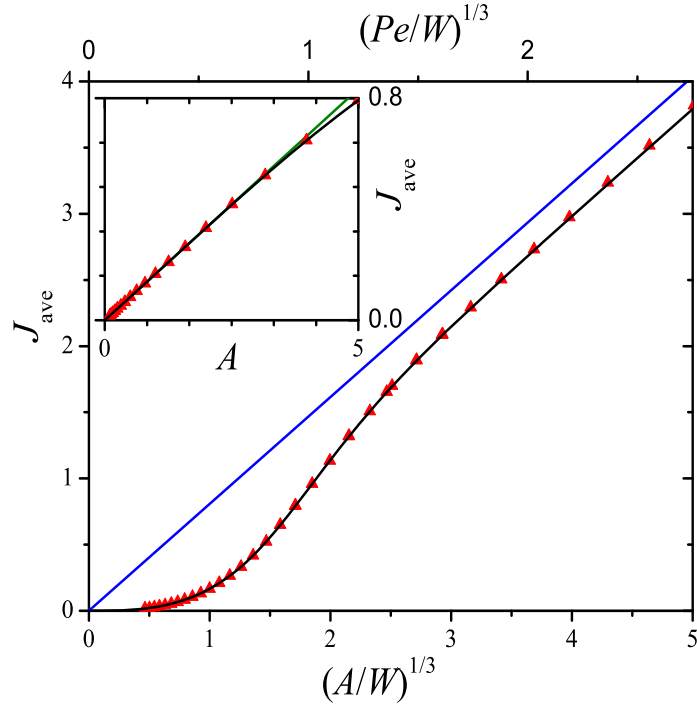


Figure 3: Current density dependence on flow rate. Limiting current ($C = 0$) boundary condition. $A = 6Pe$ is a dimensionless flow rate and W is the dimensionless channel height. Comparison of Maple 40 term eigenfunction solution (black line) and Comsol solution (red triangles). Main figure compares these with the $(A/W)^{1/3}$ dependence of the Levich approximation (blue line, Eq. (31)); inset compares with complete consumption approximation (green line, Eq. (32)). Comsol results and inset data are for $W = 1$.

The Levich equation for limiting current assumes not only the absence of axial diffusion, but also the L  v  que approximation for the velocity profile (see Fig. 1). The L  v  que approximation is valid only when the diffusion layer thickness is small compared to the channel height, i.e., the concentration changes only near the electrode surface. This approximation applies at high flow rates. The current density tends to zero as A tends to zero at fixed W as predicted by Eq. (28). At the lowest flow rates, the reactant is completely consumed before it reaches the downstream edge of the electrode. In this case the total moles reacting per second at the electrode must equal the total moles per second entering the channel, which leads to the thin layer limit of Eq. (32). The behavior and comparison of the curves is further discussed below.

3.3. Quasireversible reactions

Consider now the case of the steady-state current-potential curves where the redox reaction, Eq. (1), is quasireversible. The usual rate law of Eq. (2) is assumed, with the rate constants having the usual Tafel potential dependence. We define a dimensionless product concentration, S , Eq. (33), and nondimensionalize the other quantities similarly to before. We assume the diffusivities are equal and that the product concentration is initially zero.

$$S(X, Y) = c_P(x, y)/c_R^b \quad (33)$$

$$\begin{aligned} -(\partial S(X, Y)/\partial Y)_{Y=0} &= (\partial C(X, Y)/\partial Y)_{Y=0} \\ &= (hk_f/D) C(X, 0) - (hk_b/D) S(X, 0) \\ &= K_f C(X, 0) - K_b S(X, 0) \end{aligned} \quad (34)$$

For the case of equal diffusivities, the principle of unchanging total concentration applies [13], which means that $c_R(x, y) + c_P(x, y) = c_R^b$ everywhere in the channel, or equivalently $S(X, Y) = 1 - C(X, Y)$. Under this condition, it is possible to easily derive the quasireversible solution from the irreversible one [14]. This means that only one mass-transport problem needs to be solved. The quasireversible concentrations are given by Eqs. (35) and (36), where $C_{\text{ir}}^{(K_f+K_b)}$ means the solution to the irreversible problem with rate constant $K_f + K_b$.

$$C(X, Y) = (K_f C_{\text{ir}}^{(K_f+K_b)}(X, Y) + K_b)/(K_f + K_b) \quad (35)$$

$$S(X, Y) = 1 - C(X, Y) \quad (36)$$

That is, the eigenfunction solution is found for the boundary condition of Eq. (24) with $K = K_f + K_b$, and then substituted into Eqs. (35) and (36). Eq. (27) then gives the quasireversible current density. Examples of steady-state current potential curves calculated in this way are given in Fig. 4.

If the product is initially present with concentration c_P^b , then c_R^b is replaced by $c_P^b + c_R^b$ in the definitions of C and S and the revised rule is given by Eq. (37), where $f = c_R^b/(c_P^b + c_R^b)$. An example is given in the supplementary material.

$$C(X, Y) = \frac{C_{\text{ir}}^{(K_f+K_b)}(X, Y) (fK_f - (1-f)K_b) + K_b}{K_f + K_b} \quad (37)$$

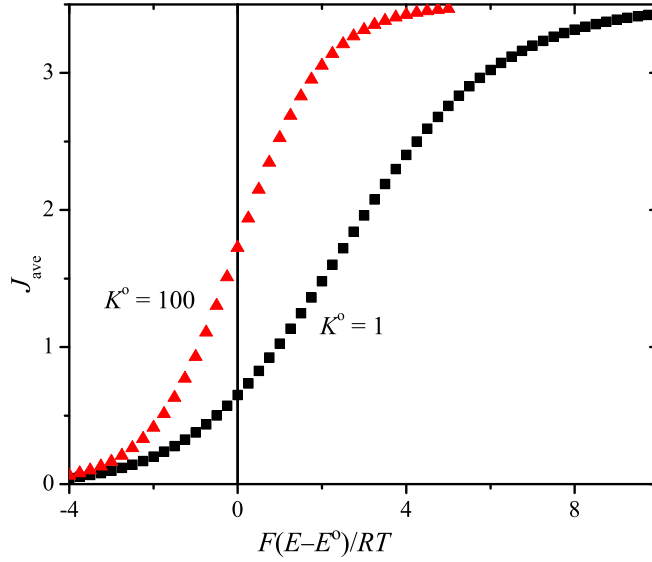


Figure 4: Steady-state current potential curves. Quasireversible reaction, $\beta = 0.5$, $W = 1$, $A = 100$, 40 terms. Curves shown for two values of the dimensionless standard rate constant $K^o = hk^o/D$.

3.4. Collection efficiency

The collection efficiency may be determined by considering flow of reactant solution initially without product past an upstream electrode where the reaction produces product under limiting current conditions. The solution then flows past a gap and then past a downstream electrode that reduces product back to reactant under limiting current conditions. The collection efficiency is calculated as the ratio of the current at the downstream electrode to the current at the upstream electrode.

To implement this, first a two-segment calculation is carried out for the reactant concentration C with boundary condition $K = \infty$ ($C = 0$) for the first segment (upstream electrode) and $K = 0$ (zero-flux) for the second segment (gap between the two electrodes). The product concentration S at the end of the second segment is calculated as $1 - C$ under the assumption that the diffusivities are equal, and this is then used as the initial concentration profile for the calculation of the concentration S for the third segment (second electrode) with boundary condition $K = \infty$ ($S = 0$). Integration of the local current densities over the two electrodes gives the two currents, whose ratio is the collection efficiency. Fig. 5 shows an example where the electrode widths and the gap are all equal and $A = 100$. The collection efficiency here, 0.2955, agrees with the Comsol result, 0.2956. However, it is higher than the value using the standard calculation, 0.2502, which assumes the L  v  que approximation [15]. This is because at this flow rate, a significant amount of the product has diffused across

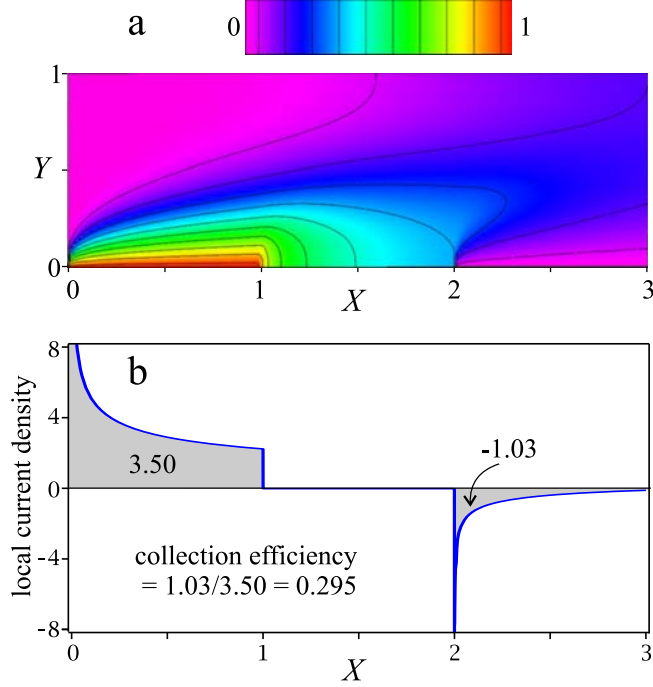


Figure 5: Collection efficiency calculation. (a) Dimensionless concentration of product. Limiting current production at electrode between $X = 0$ and $X = 1$ and limiting current consumption at electrode between $X = 2$ and $X = 3$ (40 term calculation). Contours are at 0.05, 0.15, ..., 0.95. (b) Local dimensionless current density along the channel, and calculation of efficiency from the shaded areas. (Small negative concentrations due to the Gibbs' phenomenon are colored as zero in this plot.)

the channel, and its reflection back enhances the collection efficiency.

4. Discussion

The validity of the method is discussed in two distinct ways. The first (Sec. 4.1) is how accurately the method approximates the exact solution in the absence of axial diffusion. This is estimated both by extending the number of terms evaluated and by comparison with Comsol results, also obtained in the absence of axial diffusion. The second (Sec. 4.2) is a more general assessment of the advantages and disadvantages of the method. The method is useful only when axial diffusion can be neglected, and we show that this is true for wide electrodes at low flow rates. However, since validity of this assumption has been discussed before in the literature [5, 16–18] and the exact regime of validity depends on the accuracy required by the user, a detailed numerical study in the presence and absence of axial diffusion is not attempted.

4.1. Accuracy and convergence

The limiting current case is the most difficult of the cases from a numerical point of view, and so most of the comparisons with Comsol concentrates were done for this case, e.g., in Fig. 3. Comsol's standard triangular mesh leads to unintended "numerical diffusion" in the axial direction, because the mesh edges do not align with the X and Y directions. Use of a rectangular mesh aligned with the X and Y directions solved this problem and led to the agreement shown in Fig. 3. Increasing the Maple calculation from 40 terms to 100 terms makes only a 0.3% difference at the highest flow rate shown on the plot. The three-segment collection efficiency calculation in Sec. 3.4 gives about 3 significant figure agreement with Comsol for 40 terms.

Convergence issues of the eigenfunction method did become significant at higher flow rates than shown in Fig. 3, where the separation from the Levich line increased. Increasing the number of terms is then required to achieve a chosen accuracy. Depending on the accuracy required, the calculation times may become prohibitive, at which point it is simpler to use the Levich formula. The dependence of calculation time on the number of terms did not follow an exact power law, but for 100-300 terms was roughly $t \sim N^{2.4}$. At 300 terms, the deviation from the Levich result decreases with A to 1.7% at $A = 1 \times 10^4$ after which the Levich equation is more accurate. Comsol is known to work well under cases where the Levich equation applies [19, 20]

For the more general case of finite rate constants, the accuracy of the method was investigated over a wide parameter space. A criterion for adequate convergence was taken as less than 0.1% change on increasing the number of terms by 10. It is difficult to prove that this represents absolute convergence, but it enables the trends to be found, and gives reasonable confidence that the results are correct at the 1% level. Parameters investigated were: (i) K from 10^1 to 10^7 by factors of 10, and ∞ , (ii) numbers of terms from 10 to 100 in steps of 10, (iii) A values from 1 to 10^5 in a 1-3-10 sequence. This study led to the following conclusions:

1. Convergence is easier to reach (at a lower number of terms) for lower K values.
2. Convergence is faster at lower A values and/or lower K .
3. For $K \geq 10^5$, the results for 10 or more terms are all within 0.1 % of the $K = \infty$ value.
4. For a given K value, the change from 90 to 100 terms leads to less than 0.1 % change for all A values except for the two largest. The two largest A values only reach this criteria for the two smallest K values.
5. The calculation time is mainly dependent on the number of terms used (and less on the K or A value), but this effect is small enough that 100 terms can be practically calculated as a matter of routine. The calculation time for 100 terms was comparable to the Comsol calculation time.

Although Maple allows for arbitrary precision calculations, the hardware double precision calculations were found to be sufficient for 100 term calcula-

tions, i.e., the accuracy is limited by the number of terms and not the accuracy of the calculation engine.

For multisegment calculations, the calculation time for second and subsequent segments was significantly higher than for the first segment, because of the large number of hypergeometric function evaluations needed in the integrals in the a_i coefficients, Eq. (26). This can be remedied by numerically fitting the concentration profile at the end of a segment to a suitable function, and using that as the initial concentration profile for the next segment. Strictly, this means that the guarantee of higher accuracy with more terms (provided by Sturm-Liouville theory) is invalidated. However, least-squares fitting of the concentration profile at 101 points across the channel to a degree 10 polynomial decreased the calculation time for the second segment to approximately the same time as the first segment without a noticeable change in accuracy (see the collection efficiency calculation in the supplementary material).

4.2. Method assessment

Most analytical solutions for concentrations or currents in channel electrodes have used the L  v  que approximation, and also neglected axial diffusion, e.g., these are standard approximations in calculating collection efficiencies [3, 15, 21]. There has been some consideration of the effects of axial diffusion [5, 16–18], and more recently Amatore and coworkers [12] have mapped out the zone diagram for the various limiting and intermediate cases in terms of the parameters W and Pe . Their analysis explicitly considered consistency with the Levich equation, and noted that this occurs with 5% accuracy for $W \cdot Pe > 15$, defining their zone III. The present work neglects axial diffusion but goes beyond the L  v  que approximation and considers the full velocity profile across the channel. Axial diffusion may be neglected when the time to diffuse axially along the electrode, estimated as w^2/D , is long compared to the time to flow past the electrode, estimated as w/u_{ave} . This leads to $W \cdot Pe \gg 1$, with the exact value dependent on the accuracy required. On the other hand, the L  v  que approximation will apply when the time to diffuse across the channel, estimated as h^2/D , is much greater than the time to flow past it. This leads to the condition $Pe/W \gg 1$. Alternatively, we may require $\Delta = \delta/h = 1.022(W/Pe)^{1/3}$ (Eq. (30)) to be much less than 1, which again leads to $Pe/W \gg 1$. Amatore’s H is our Δ , and in Ref. [12] was found to be less than 0.24 in zone III as expected, since both approximations must apply for the Levich equation to hold.

Validity of the present method requires only $W \cdot Pe \gg 1$. This can be achieved even for low flow rates if W is large, i.e., the electrode is wide enough or the channel height is small enough. Small Pe and large W will violate $Pe/W \gg 1$ and the Levich equation will fail but the present method will not. The limiting current here depends on the ratio Pe/W (Eq. (28), Fig. 3). Therefore, for any given Pe , there is a W above which the method is valid and for any given W , there is a Pe below which the method is valid. That is, we can always find a vertical line on Fig. 3 to the left of which the method works. For example, assume that $W \cdot Pe > 15$ neglects axial diffusion to the accuracy we

require. Then for $Pe = 3$ we need $W > 5$ and so the method is valid to the left of $Pe/W = 3/5$.

The present work indicates that solving for the case of the full parabolic velocity profile across the channel is not significantly more difficult than the L  v  que approximation. Like the semidifferentiation approach of Oldham for planar electrodes [22], the present method first exactly solves the problem across the channel and thereby reduces the problem to solving along the near surface of the channel. It is to be emphasized that the eigenfunction expansion is an exact solution to the problem without axial diffusion, and the only approximation arises from the need to solve for the eigenvalues and coefficients numerically, and to terminate the series after a finite number of terms.

There are standard methods for using eigenfunction expansions that may be used in problems that include axial diffusion, i.e., for elliptic partial differential equations [23], which will be explored in subsequent work. That is, the present confluent hypergeometric functions may be a suitable basis set for the more general case, but the complexity of the method will be significantly greater, and an iterative method may be required.

In terms of a numerical method, the eigenfunction expansion method does not use a mesh and so does not have the complication of creating and validating meshes that FE or finite-difference methods have. Such methods need finer meshes near electrodes and electrode edges. On the other hand, eigenfunction expansion methods are known for slow convergence. Perhaps not surprisingly, we find that the conditions that require a fine, adaptive mesh for FE solution (such as large flow rates), are also the conditions that require more terms for acceptable convergence in our method. Accurate convergence was possible for comparable computational expense as for the FE method, but the present method is algorithmically much simpler and the global error is more easily assessed. An important advantage of the present method is that a whole segment is solved at one time, so the complexity of the calculation is largely independent of the channel height or width of the electrode.

In principle the present method does not require a symbolic algebra system for its implementation. Such systems allow arbitrary precision calculations, but this feature was not found to be necessary here. These systems do have an important advantage in processing the concentration profile into the required measurable quantities, such as average current density or collection efficiency. This processing typically involves differentiation or integration, which is done exactly by simple rules such as the differentiation rule (42), and does not degrade the accuracy of the calculation.

Another advantage of these systems is that the numerical evaluation of the hypergeometric and exponential functions in the solution is deferred until they are needed. In Fig. 2, for example, Maple’s plot routine decides where to evaluate the concentrations, using more points in steeper regions of the plot. The numerical evaluation of these concentrations occurs in the plot routine itself, and not in the construction of the series solution. Therefore, there is no need for evaluate the solution over a fine grid of points just in case they might be required later. This is perhaps seen most clearly in the case of a single electrode,

where the limiting current can be given as a function of an unspecified A , and then this function is used to create Fig. 3.

5. Conclusions

The eigenfunction method developed here is computationally efficient, and is accurate in its domain of validity. It can find concentrations, current densities and derived quantities for any values of the rate constant, and can be used for multiple electrodes in a channel. Although convergence is slower in the same cases where a finite element method would require fine adaptive meshes, there is a distinct advantage in not having to determine and validate a mesh. Implementation in a symbolic algebra system gives flexibility in manipulating the derived quantities without degrading accuracy. Coupled with the advances in computing speed, the advantages of symbolic algebra programs mean that reconsideration of algorithms such as the eigenfunction method demonstrated here can lead to competitive numerical methods with high accuracy that are simple to implement.

6. Conflict of interest

The authors declare no conflict of interest.

7. Acknowledgements

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A. Solution of ODE for $G(Y)$

The differential equation (16) has the general solution Eq. (38) with two arbitrary constants g_1 and g_2 .

$$G(Y) = g_1 G_1(Y) + g_2 G_2(Y) \quad (38)$$

$$G_1(Y) = \exp(bY(1-Y)/2) \times {}_1F_1(1/4 - b/16; 1/2; b(2Y-1)^2/4) \quad (39)$$

$$G_2(Y) = \exp(bY(1-Y)/2) (2Y-1) \times {}_1F_1(3/4 - b/16; 3/2; b(2Y-1)^2/4) \quad (40)$$

Other notations for the confluent hypergeometric functions ${}_1F_1(a; b; z)$ are ${}_1F_1\left(\frac{a}{b}; z\right)$ or $M(a, b, z)$ [24]. It is evident that $G_1(Y)$ is symmetric (even) about $Y = 1/2$ and $G_2(Y)$ is antisymmetric (odd) about this point. Applying the no-flux boundary condition at the top of the channel, $G'(1) = 0$, allows determination of one of the constants, and the other is chosen to scale the functions so that $G(1) = 1$, with the result Eq. (41). This contains the constant b , which is determined from the electrode boundary condition as described in the main text.

$$G(Y) = \frac{G'_2(1)G_1(Y) - G'_1(1)G_2(Y)}{G'_2(1)G_1(1) - G'_1(1)G_2(1)} \quad (41)$$

Derivatives are evaluated using the rule (Ref. [24], Eq. 13.3.15)

$${}_1F_1(c; d; f(Y))' = \frac{c}{d} {}_1F_1(c+1; d+1; f(Y)) f'(Y) \quad (42)$$

According to Sturm-Liouville theory, the eigenfunctions $G_i(Y)$ for different values of b_i that satisfy the boundary conditions are orthogonal with respect to the weight function $Y(1-Y)$:

$$\int_0^1 Y(1-Y)G_i(Y)G_j(Y) dY = 0, \quad i \neq j \quad (43)$$

B. Supplementary material

Supplementary material consists of a table of symbols, a pdf file showing the Maple worksheet that implements the algorithm here and applies it in several examples, a text file with the Maple code for the chsolve procedure, and the Maple worksheet itself. This material can be found, in the online version, at <http://dx.doi.org/10.1016/j.jelechem.XXXX>.

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Symbol	Units	Description
a_i	1	coefficient of term i in eigenfunction expansion.
A	1	dimensionless flow rate = $6Pe$
b	1	separation constant
b_i	1	square root of eigenvalue b_i^2
$b_i^{(0)}$	1	square root of eigenvalue b_i^2 for zero-flux boundary condition
$b_i^{(K)}$	1	square root of eigenvalue b_i^2 for rate constant K
$b_i^{(\infty)}$	1	square root of eigenvalue b_i^2 for $C(X, 0) = 0$ boundary condition
$c_R(x, y), c_P(x, y)$	mol m ⁻³	concentration of reactant R or product P
c_R^b, c_P^b	mol m ⁻³	bulk concentrations of R or P
$C(X, Y)$	1	dimensionless concentration = $c(x, y)/c_R^b$
$C_{ir}^{(K_f+K_b)}(X, Y)$	1	solution $C(X, Y)$ to the irreversible problem with rate constant $K_f + K_b$
D	m ² s ⁻¹	diffusivity
E, E°	V	electrode potential, standard electrode potential
f	1	$f = c_R^b/(c_R^b + c_P^b)$
$f_0(Y)$	1	initial (upstream) dimensionless concentration profile = $C(0, Y)$
F	C mol ⁻¹	Faraday constant
$F(x)$	1	X component of dimensionless concentration, $C(X, Y) = F(X)G(Y)$
$G(x)$	1	Y component of dimensionless concentration, $C(X, Y) = F(X)G(Y)$
h	m	channel height
i	1	index for eigenvalues or terms in eigenfunction expansion
$j(x)$	A m ⁻²	local current density
j_{ave}	A m ⁻²	average current density = current/(electrode area)
$J(x)$	1	dimensionless local current density = $j(x)h/c_R^b DF$
J_{ave}	1	dimensionless current density averaged over electrode area
k°, k_f, k_b	m s ⁻¹	standard, forward, backward rate constants
k	m s ⁻¹	apparent rate constant = $k_f + k_b$
k	1	index for species
K°, K_f, K_b	1	standard, forward, backward dimensionless rate constants = hk°/D , etc.
K	1	dimensionless rate constant, K_f or $K_f + K_b$
N	1	number of terms to evaluate in the eigenfunction expansion
Pe	1	Péclet number = $u_{ave}h/D$
R	J K ⁻¹ mol ⁻¹	Gas constant
$S(X, Y)$	1	dimensionless product concentration = $c_P(x, y)/c_R^b$
T	K	temperature
u_{ave}	m s ⁻¹	average flow velocity
u_{max}	m s ⁻¹	maximum flow velocity = $(3/2)u_{ave}$
$v(x)$	mol m ⁻² s ⁻¹	reaction rate at x
w	m	electrode width (in the x direction)
W	1	dimensionless electrode width = w/h
x	m	direction along channel (in flow direction)
X	1	dimensionless distance along channel = x/h
y	m	direction across channel
Y	1	dimensionless distance across channel = y/h
β	1	symmetry factor
Γ	1	Gamma function
δ	m	diffusion layer thickness in the Lévêque approximation
Δ	1	dimensionless Lévêque diffusion layer thickness = δ/h

This worksheet is Supplementary material for T. Holm, S. Sunde, F. Seland and D.A. Harrington, "A semianalytical method for simulating mass transport at channel electrodes", J. Electroanal. Chem., 2015.
 Execute by entering "enter" on successive execution groups (indicated by the > prompt), or execute the entire worksheet with the "!!!" icon.
 Run the Setup section first, and then the other sections can be run in any order.
 This was produced in Maple 18, but should work in recent earlier versions.

Setup

This section needs to be run before any of the others. It specifies the accuracy required and defines the channel solving routine *chsolve*.

> *restart; with(plots) :*

Find number of hardware digits on this machine. (For a 32-bit machine this will return 15)

> *evalhf(Digits);*

15.

Maple can do calculations utilizing the computer hardware, with accuracy approximately the number of digits above. This is the faster way. Specifying a value for Digits less than this will automatically utilize the hardware option, and give answers approximately accurate to the number of Digits you request below. The floating-point evaluation of the integrals requires a few guard digits, so the Digits you request should be, say, 5 less than the number above. Maple can also work at arbitrary precision, and specifying Digits higher than the above value will give more accuracy, but will run much more slowly. In general, for the eigenfunction methods here, the accuracy is limited by the number of terms chosen in the series, and for most purposes hardware accuracy is sufficient.

> *Digits := 10;*

Digits := 10

Now define the procedure *chsolve* for steady-state solution of a flow channel with no axial diffusion.

chsolve works in non-dimensionalized units. There are two modes:

1. The multisegment mode requires the specification of the boundary conditions at the $Y=0$ surface for successive downstream segments, such as electrode 1, gap, electrode 2, etc.

In this mode, the boundary conditions are specified as a piecewise function for the non-dimensionalized rate constant for the various segments, and a numerical value of the dimensionless flow rate (see below) has to be specified.

2. The single segment mode solves only a single segment (the electrode) of arbitrary length. This mode is detected by presenting only the value of the rate constant (possibly infinity) as the first parameter,

rather than a piecewise function. In this mode a name can be given for dimensionless flow rate. This then allows plots as a function of the dimensionless flow rate to be generated easily.

Parameters:

1. fK is the non-dimensionalized rate constant. For multisegment calculation, it is given as a piecewise function of X , starting at the inlet, which can be at any value of X .

This specifies the boundary conditions at the electrode side ($Y=0$) of the channel. e.g., $X \rightarrow \text{piecewise}(0 \leq X \text{ and } X < 2, 10, 2 \leq X \text{ and } X \leq 3, 0, \text{infinity})$ means $K=10$ at the electrode between $X=0$ and $X=2$,

$K=0$ (zero flux) between 2 and 3 (without an electrode), $K=\text{infinity}$ (concentration zero) for $X \geq 3$ (last number is the

"otherwise" value).

Be careful not to leave out a value, as in $X < 3$, $27, X > 3$, 23 which makes the value at $X=3$ equal to the "otherwise" value, which defaults to zero.

If a simple number K is entered, only a single segment is calculated and this is the K value for $X \geq 0$, with the inlet assumed to be at $X=0$.

2. $f0$ is a function specifying the initial concentration across the channel (Y direction) at the inlet, given as a function of the Y , running from 0 (electrode side) to 1 (top)

e.g., $Y \rightarrow 1$ for flat or $Y \rightarrow 2 \sin(\pi Y)$ for a more interesting profile.

3. Dimensionless flow rate $A = 4v_{\max}h/D$ where v_{\max} is the velocity in the middle of the channel, h is the channel height and D is the diffusivity. For multisegment calculations a number must be given,

but for single segment mode (if the rate fK is a number), a name such as A can be given, and this will be a variable in the output.

4. N is a positive integer specifying the number of terms to calculate in the eigenfunction expansion.

The output is a function (Maple procedure) that takes two arguments representing X and Y and gives the concentration as a (piecewise) function of X (distance along the electrode) and Y (distance away from electrode).

In single segment mode, the returned function is not in piecewise form.

A error message is given if the integrals could not be accurately numerically evaluated. In this case, increasing the setting of Digit may lead to success.

Note that although X and Y are used here to denote along and across the channel respectively, the arguments to fK , $f0$ and the output function can be given any names.

To output a message at the beginning of every segment, set `infolevel[chsolve] := 2` : before running the routine.

```
> chsolve := proc( fK, f0 :: procedure, A :: {numeric, symbol}, N :: posint)
    local b, X, Y, GY, G0, G1, G2, dG1, dG2, dG1at1, dG2at1, den, g1, g2, NormInt, bapprox0, bapprox1, bapproxhalf, bK, a, bc,
    pwise, i, pwfn, Xstart, K, fin, CXY, n, oneseg, intmethod, st;
    oneseg := type( fK, extended_numeric );
    if type( A, symbol ) and not oneseg then error "A must be a number for multisegments" end if;
    if oneseg then pwise := [0, 0, fK]
    elif type( fK, procedure ) and op( 0, fK( X ) ) = piecewise then pwise := convert( fK( X ), 'pwlis' )
    else error "K must be a number, infinity, or a piecewise function"
    end if;
    st := time( ); # start time for CPU clock
    if Digits > floor( evalhf( Digits ) ) then intmethod := '_Gquad' else intmethod := '_d01akc' end if;
    userinfo( 2, chsolve, cat( "Using integration method ", intmethod ) );
    # Solution for G(Y) with G'(1)=0 and G(1)=1
    G1 := Hypergeom( [ 1/4 - (1/16) * b ], [ 1/2 ], (1/4) * b * (-1 + 2 * Y)^2 ) * exp( - (1/2) * b * Y * (-1 + Y) );
```

```

G2 := Hypergeom([3/4-(1/16)*b], [3/2], (1/4)*b*(-1+2*Y)^2*(-1+2*Y)*exp(-(1/2)*b*Y*(-1
+ Y));
dG1 := diff(G1, Y);
dG1at1 := eval(dG1, Y=1);
dG2 := map(simplify, collect(diff(G2, Y), Hypergeom));
dG2at1 := eval(dG2, Y=1);
den := eval(dG2at1*G1-dG1at1*G2, Y=1);
g1 := dG2at1/den;
g2 := -dG1at1/den;
GY := convert(collect((g1*G1+g2*G2), exp), hypergeom);
# Normalization integral
NormInt := Int(Y*(1-Y)*simplify(GY^2, exp), Y=0..1, 'method'=intmethod);
# Various approximations to the b values
bapprox0 := [seq(evalf(8*n), n=1..N)];
bapprox1 := [seq(evalf((n-1)*8), n=1..N)];
bapproxhalf := [seq(evalf((n-1/2)*8), n=1..N)];
# now iterate over the piecewise regions. i=1 is up to the first specified X value - ignore it
pwfn := NULL: # start to assemble the piecewise function
fn := f0; # initial concentration profile
for i from 2 to nops(pwise) by 2 do
    Xstart := pwise[i];
    K := pwise[i+1];
    userinfo(2, chsolve, sprintf("Evaluating segment %d with K = %a at CPU time %.3f s", i/2, K, time() - st));
    if i+2 > nops(pwise) then pwfn := pwfn, X ≥ Xstart else pwfn := pwfn, `and`(X ≥ Xstart, X ≤ pwise[i+2]) end if;
    # Generate the list of b values for this segment
    if K = infinity then
        G0 := eval(GY, Y=0);
        bK := [seq(fsolve(G0, b = bapprox1[n]..bapproxhalf[n]), n=1..N)];
    elif K = 0 then
        bK := [seq(fsolve(eval(diff(GY, Y), Y=0), b = bapprox1[n]..bapproxhalf[n]), n=1..N)];
    elif K > 0 then
        bc := eval(diff(GY, Y), Y=0) - K*(eval(GY, Y=0));
        bK := [seq(fsolve(bc, b = bapprox1[n]..bapproxhalf[n]), n=1..N)];
    else bc := eval(diff(GY, Y), Y=0) - K*(eval(GY, Y=0)); # negative K
        bK := [seq(fsolve(bc, b = bapproxhalf[n]..bapprox0[n]), n=1..N)];
    end if;
    # Generate the list of a values for this segment

```

```

a := map(evalf@unapply(Int(Y* (1 - Y) * fin(Y) * GY, Y=0 ..1,'method'=intmethod) / NormInt, b), bK);
# and now CXY, the concentration for this segment
CXY := add( evalf( collect(exp( - (bK[n])^2 * (X - Xstart) / A) * a[n] * eval(GY, b = bK[n]), exp) ), n = 1 ..N);
if has(CXY, Int) then error "Not all integrals could be evaluated" end if;
if i + 2 ≤ nops(pwise) then fin := unapply(eval(CXY, X=pwise[i + 2]), Y) end if; # find profile for next segment
pwfn := pwfn, CXY;
end do;
userinfo(2, chsolve, sprintf("Completing calculation at CPU time %.3f s", time( ) - st));
if oneseg then
    unapply(CXY, X, Y);
else
    unapply(piecewise(pwfn), X, Y);
end if;
end proc:

```

[Set infolevel to 2 or higher to print out information messages.

[> infolevel[chsolve] := 2 :

▼ Concentration profile for an irreversible reaction

This generates Fig. 2.

Run chsolve in single segment mode with nondimensionalized forward rate constant $K=10$ (evaluating 40 terms), and $A = 100$.

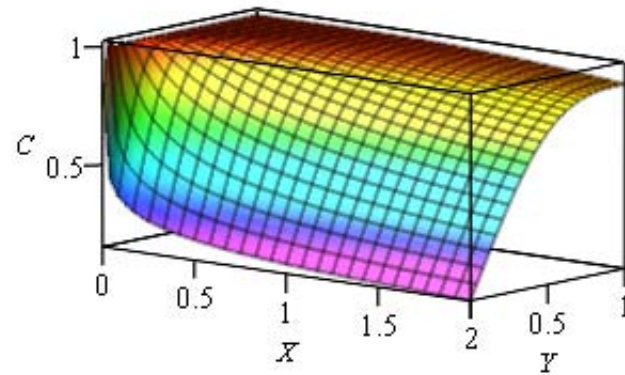
```
> C := chsolve(10, Y ↦ 1, 100, 40) :
```

```
chsolve: Using integration method _d01akc
```

```
chsolve: Evaluating segment 1 with K = 10 at CPU time 0.078 s
```

```
chsolve: Completing calculation at CPU time 9.750 s
```

```
> plot3d(C(X, Y), X=0..2, Y=0..1, orientation = [ -50, 80 ], scaling = constrained, shading = zhue, thickness = 2, tickmarks = [6, 4, 3], labels = [X, Y, 'C'] );
```



Calculate the dimensionless current density

$$> \frac{\text{int}\left(\text{eval}\left(\frac{\partial}{\partial Y} C(X, Y), Y=0\right), X=0..2\right)}{2};$$

2.181490264

> unassign('C'); #clean up for later

Limiting current as a function of flow rate

Run chsolve in single segment mode with infinite rate constant (evaluating 40 terms). Leave A unspecified so that the current can be plotted as a function of A .

```
> A := 'A': #forget any previous value A may have had
```

```
  C := chsolve(infinity, Y ↦ 1, A, 40) :
```

```
chsolve: Using integration method _d01akc
```

```
chsolve: Evaluating segment 1 with K = infinity at CPU time 0.016 s
```

```
chsolve: Completing calculation at CPU time 7.831 s
```

The current density is a function of electrode width W and A in the combination A/W . This is the same as the current for $W=1$ as a function of A .

```
> Ilim := int( eval( ( ∂ / ∂ Y ) C(X, Y), Y=0 ), X=0..1 ) :
```

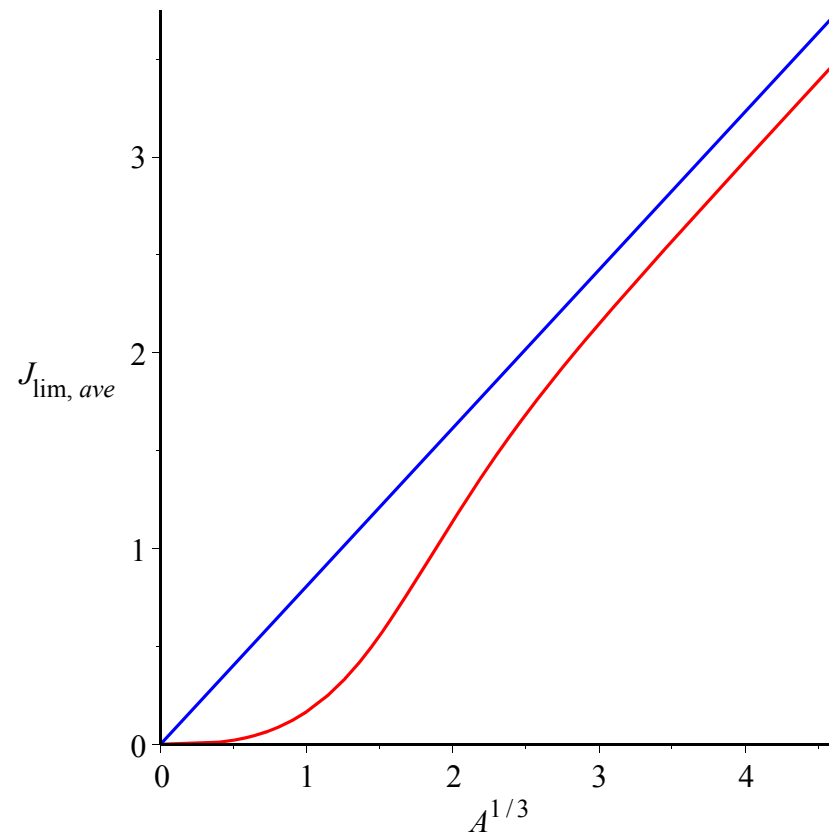
For comparison, the Levich result using the Leveque approximation is

```
> IlimLev := ( 3 4/3 A 1/3 ) / ( 2 Γ( 1/3 ) ) :
```

Plot the limiting current vs $A^{\frac{1}{3}}$ by using a parametric plot with A as parameter. The blue curve is the Levich result using the Leveque approximation.

```
> p1 := plot( [ [ A 1/3, Ilim, A=0..100 ], colour=red ] ) :
```

```
  p2 := plot( [ [ A 1/3, IlimLev, A=0..100 ], colour=blue ] ) : display( p1, p2, labels = [ A 1/3, Jlim, ave ] )
```



```
> unassign('p1','IlimLev','p2','Ilim','C','J');
```

▼ A multisegment example

A = 100. Electrode between $X=0$ and $X=1$ with nondimensionalized rate constant $K=10$, then a gap (no-flux boundary condition, $K=0$) to $X=3$, then a second electrode at limiting current ($K=\text{infinity}$).

Note that we do not need to define the end of the last segment - it goes to wherever we want to calculate it to.

```
> fK := x → piecewise(x ≥ 0 and x < 1, 10, x ≥ 1 and x ≤ 3, 0, infinity);
```

```
fK := x → piecewise(0 ≤ x and x < 1, 10, 1 ≤ x and x ≤ 3, 0, ∞)
```

```
> C := chsolve(fK, Y ↦ 1, 100, 40) :
```

```
chsolve: Using integration method _d01akc
```

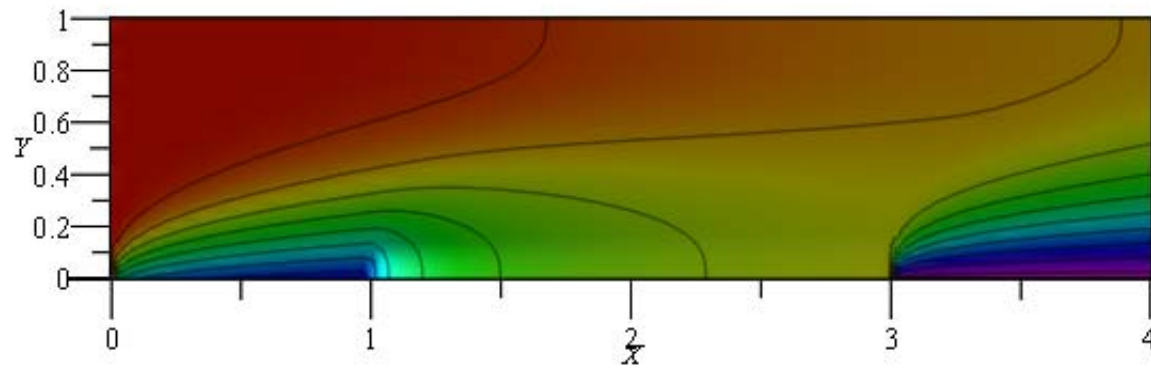
```
chsolve: Evaluating segment 1 with K = 10 at CPU time 0.016 s
```

```
chsolve: Evaluating segment 2 with K = 0 at CPU time 9.735 s
```

```
chsolve: Evaluating segment 3 with K = infinity at CPU time 80.481 s
```

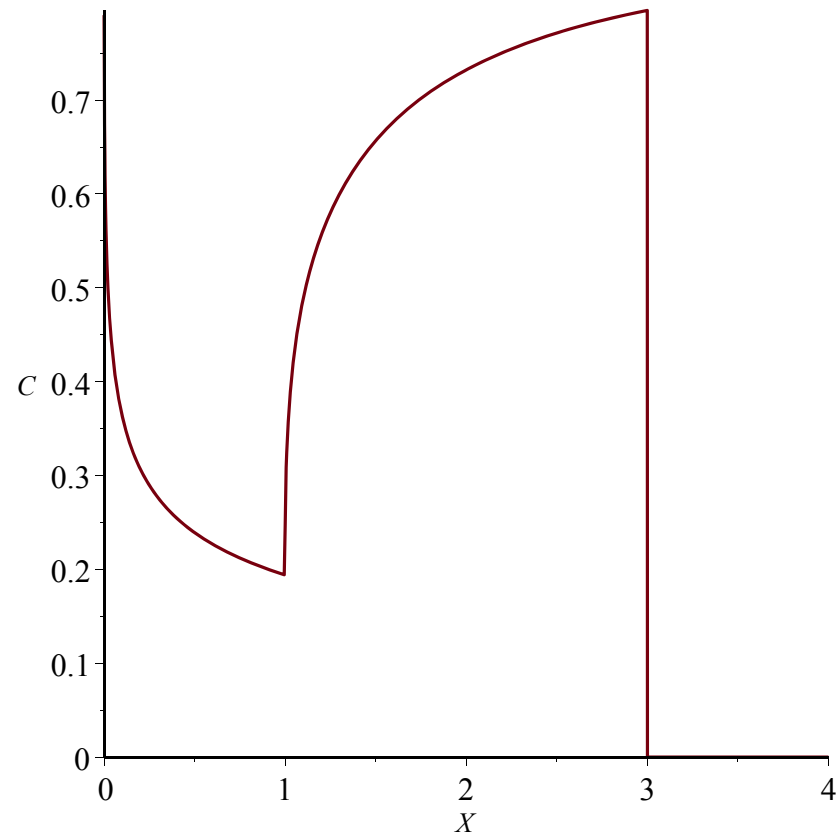
```
chsolve: Completing calculation at CPU time 147.421 s
```

```
> plot3d(C(X, Y), X=0..4, Y=0..1, axes=boxed, orientation=[-90, 0], scaling=constrained, style=surfacecontour, shading=zhue, grid=[120, 30], lightmodel=none);
```



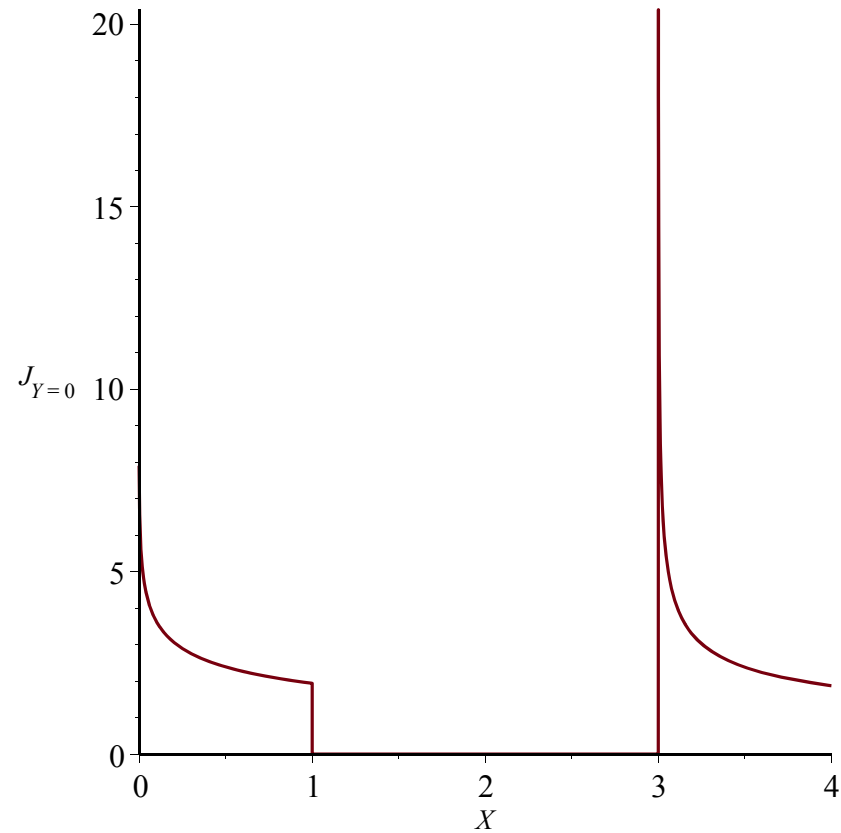
Plot of the concentration along $Y=0$ as a function of X .

```
> plot(C(X, 0), X=0..4, labels=[X, C]);
```



Now plot the dimensionless current density (which is also the dimensionless flux) at $Y=0$ as a function of X . $D[2](C)$ means differentiate C with respect to the second variable (here Y), and then $(X,0)$ means evaluate it at $Y=0$ (and any X).

> `plot(D[2](C)(X, 0), X=0..4, labels=[X, $J_{Y=0}$]);`



Integrate to find to total current at each of the two electrodes

```
> evalf(Int(D[2](C)(X, 0), X=0..1)); evalf(Int(D[2](C)(X, 0), X=3..4));
```

2.649842130

2.845540912

```
> unassign('C', 'fK', 'J');
```


Collection efficiency calculation

Collection efficiency calculation. Start with only reactant (nondimensionalized concentration denoted by C) in solution. Then limiting current production of product of concentration S at electrode 1, then a gap, then limiting current removal of S at electrode 2. Electrode 1 ends at $X1$, gap ends at $X2$ and electrode 2 ends at $X3$.

```
> A := 100.; X1 := 1; X2 := 2; X3 := 3; Terms := 40;
```

```
A := 100.
```

```
X1 := 1
```

```
X2 := 2
```

```
X3 := 3
```

```
Terms := 40
```

Start by calculating the concentration C for the first two segments, i.e., electrode 1 and the gap. Rate constant for segment 1 is infinity (concentration $C = 0$) and for segment 2 is zero (no-flux condition)

```
> fK := x → piecewise(x ≥ 0 and x ≤ X1, infinity, 0);  
C12 := chsolve(fK, Y ↦ 1, A, Terms) :
```

```
fK := x → piecewise(0 ≤ x and x ≤ X1, ∞, 0)
```

```
chsolve: Using integration method _d01akc
```

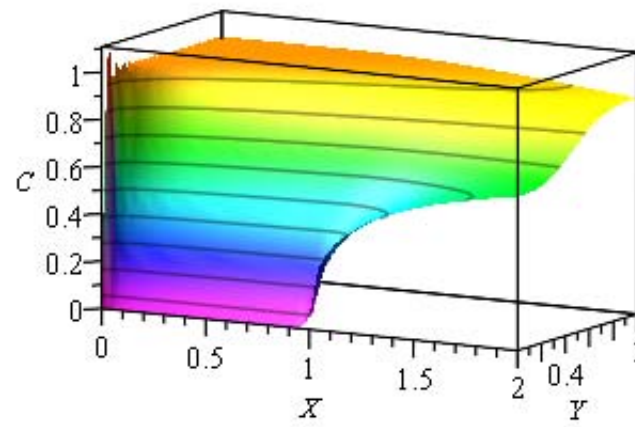
```
chsolve: Evaluating segment 1 with K = infinity at CPU time 0.031 s
```

```
chsolve: Evaluating segment 2 with K = 0 at CPU time 8.050 s
```

```
chsolve: Completing calculation at CPU time 80.325 s
```

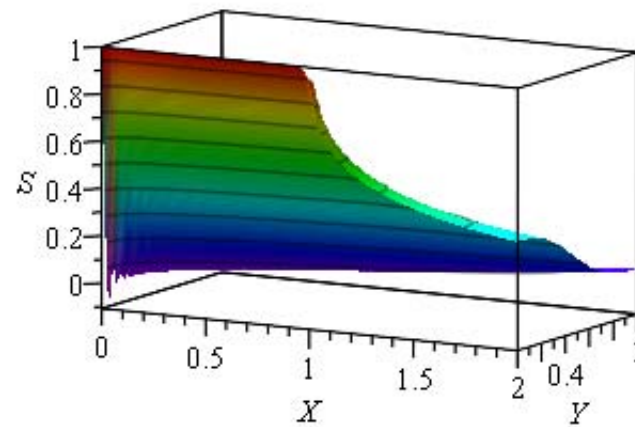
Plot the concentration for the first two segments

```
> plot3d(C12(X, Y), X=0..X2, Y=0..1, axes = boxed, orientation = [-60, 80], scaling = constrained, style = surfacecontour, shading = zhue, labels = [X, Y, C]);
```



For equal diffusivities, the concentration S is just $1-C$. Plot of concentration S for the first two segments is therefore

```
> p12 := plot3d(1 - C12(X, Y), X=0..X2, Y=0..1, axes=boxed, orientation=[-60, 80], scaling=constrained, style
= surfacecontour, shading=zhue) : display(p12, labels=[X, Y, S]);
```



For electrode 2 we will calculate the concentration S , not C , so we first calculate the concentration profile as a function of Y at the end of the second segment, so we can use it as the inlet profile for electrode 2.

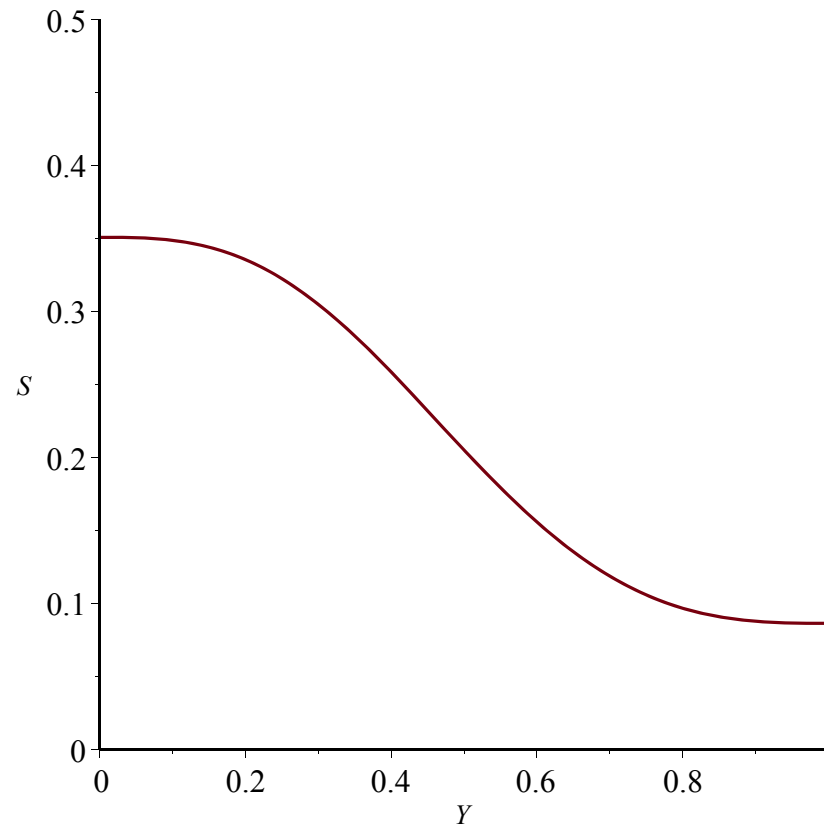
Make a function for the concentration S at $X2$.

```
> f2 := Y → 1 - C12(X2, Y);
```

$$f2 := Y \rightarrow 1 - C12(X2, Y)$$

A plot of $f2$ across the channel shows that for low flow rates (small A) the concentration may be non-zero at the top of the channel

```
> plot(f2(Y), Y=0..1, S=0..0.5);
```



Now calculate the limiting current removal of the species with concentration S at electrode 2.

```
> S3 := chsolve( $x \rightarrow \text{piecewise}(x \geq X2, \text{infinity})$ , f2, A, Terms) :
```

```
chsolve: Using integration method _d01akc
```

```
chsolve: Evaluating segment 1 with K = infinity at CPU time 0.016 s
```

```
chsolve: Completing calculation at CPU time 67.736 s
```

For large A the above can be a slow calculation, which can be speeded up by "digitizing" $f2$, which otherwise contains a large number of hypergeometric function calls, called multiple times in evaluating the integrals. For example, fit the values of this function at 101 points

to a degree 10 polynomial

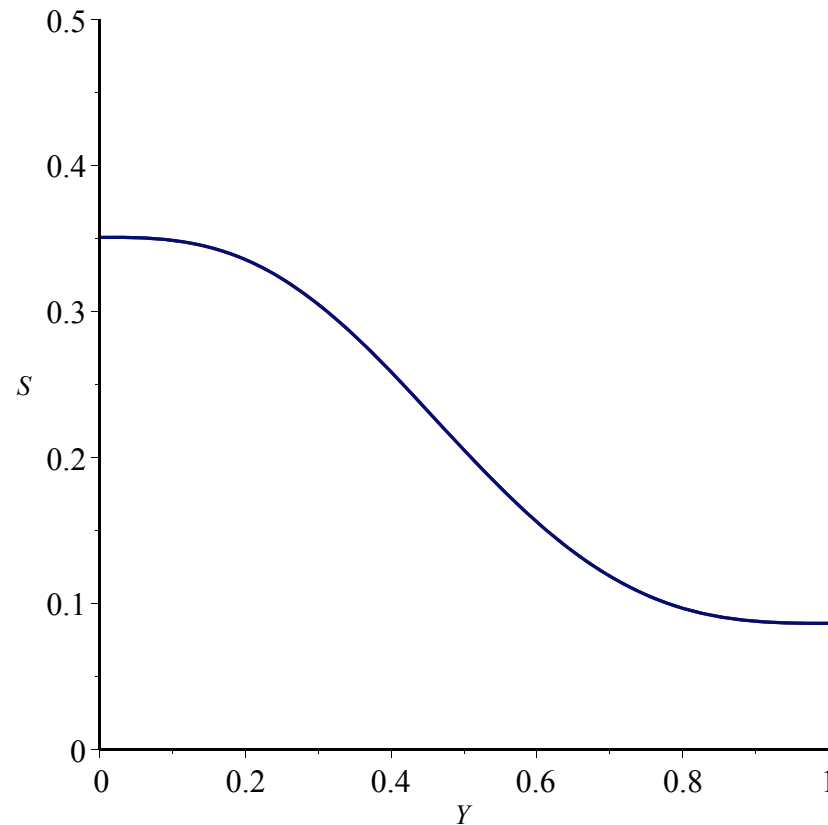
```
> Npts := 100 : ptsx := Vector( [ seq(  $\frac{y}{\text{evalf}(Npts)}$ , y = 0 .. Npts ) ] ) : ptsy := Vector( [ seq(  $f2\left(\frac{y}{Npts}\right)$ , y = 0 .. Npts ) ] ) :
```

```
poly := Statistics:-PolynomialFit(10, ptsx, ptsy, Y) :  
f2num := unapply(poly, Y);
```

```
f2num := Y →  $0.35076306058932977 - 0.0007295694864722106 Y + 0.030359870791725488 Y^2 - 2.696279913451493 Y^3$   
 $+ 5.466781527848835 Y^4 - 21.77687142388346 Y^5 + 74.29381125320275 Y^6 - 126.53498843259962 Y^7$   
 $+ 113.52306213396496 Y^8 - 52.540859493750034 Y^9 + 9.971197107777435 Y^{10}$ 
```

This simpler function is indistinguishable from the original data when plotted (below are two plots on top of each other).

```
> plot( [ f2(Y), f2num(Y) ], Y = 0 .. 1, S = 0 .. 0.5);
```



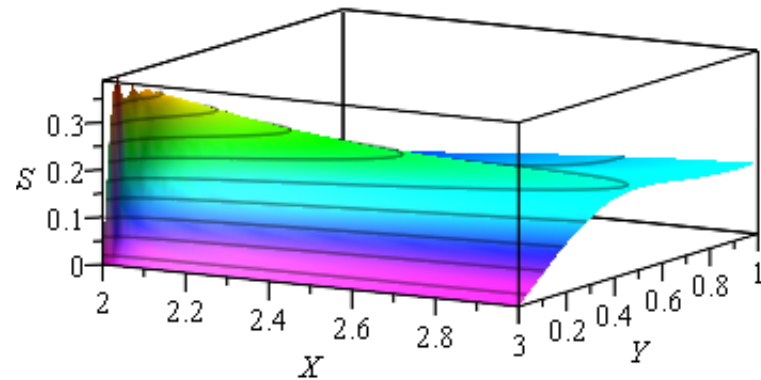
Chsolve now evaluates faster, but it is now hard to show that the error will diminish as the number of terms increases.

```
> S3num := chsolve(x→piecewise(x ≥ X2, infinity), f2num, A, Terms) :
chsolve: Using integration method _d01akc
chsolve: Evaluating segment 1 with K = infinity at CPU time 0.016 s
chsolve: Completing calculation at CPU time 8.065 s
```

Returning to the original concentration S at the second electrode S_3 ,

```
> p3 := plot3d(S3(X, Y), X=X2..X3, Y=0..1, axes=boxed, orientation=[-60, 80], scaling=constrained, style=surfacecontour,
```

```
shading = zhue) : display(p3, labels = [X, Y, S]);
```

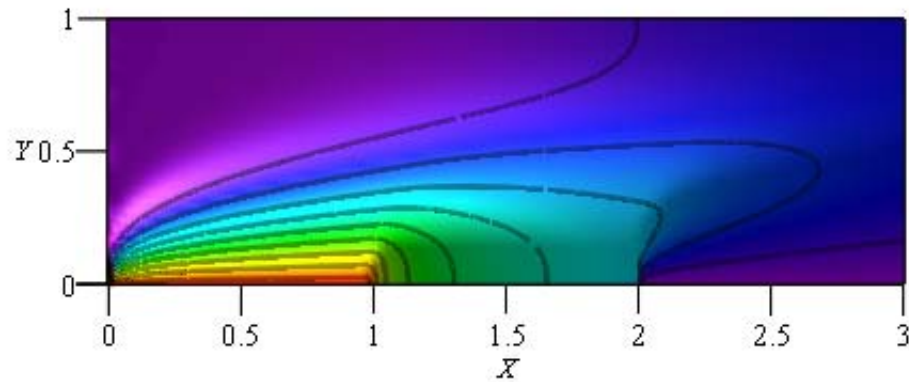


Now we stitch the concentration S in the three segments together into a single piecewise function: between 0 and X_2 we have $1-C12$ and between X_2 and X_3 we have S_3

```
> S := (X, Y) → simplify(piecewise(0 ≤ X and X ≤ X2, 1 - C12(X, Y), X > X2, S3(X, Y)), piecewise) :
```

So that now it is easy to plot the concentration S for all three segments.

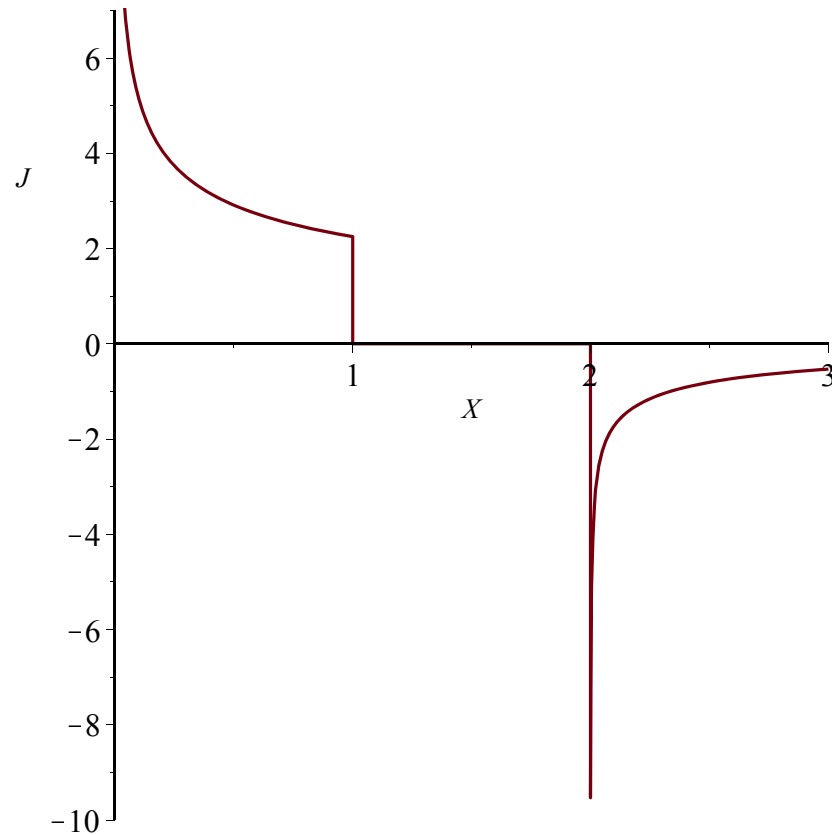
```
> plot3d(S(X, Y), X=0..X3, Y=0..1, axes = boxed, orientation = [-90, 0], scaling = constrained, style = surfacecontour, shading = zhue, thickness = 3, tickmarks = [6, 4, 3], labels = [X, Y, " "], grid = [120, 30], lightmodel = none)
```



Work out the current density at $Y=0$ as a function of position along the channel.

> $J := -\text{eval}(\text{diff}(S(X, Y), Y), Y=0) :$

> $\text{plot}(J, X=0..X3, \text{labels} = [X, J]) ;$



Integrate the current density over the two electrodes and then find their ratio, which is the collection efficiency.

```
> I1 := evalf(int(J, X=0..X1));
  I2 := evalf(int(J, X=X2..X3));
  `Collection Efficiency` := -  $\frac{I2}{I1}$ ;
```

$I1 := 3.501587202$

$I2 := -1.034546271$

Collection Efficiency := 0.2954506660

For comparison, the collection efficiency assuming the Leveque approximation (to which ours should tend at large A) may be calculated as given in C.M.A Brett and A.M.C.F. Oliveira-Brett, Hydrodynamic Electrodes, in Comprehensive Chemical Kinetics, Eds. C.H. Bamford and R.G. Compton, Elsevier, Amsterdam, 1986, v 26, p. 355.

$$> \alpha := \frac{X2}{X1} - 1; \beta := \frac{X3}{X1} - \frac{X2}{X1};$$

$$\alpha := 1$$

$$\beta := 1$$

$$> F := \theta \rightarrow \frac{3^{\frac{1}{2}}}{4 \cdot \pi} \cdot \ln \left(\frac{\left(1 + \theta^{\frac{1}{3}}\right)^3}{1 + \theta} \right) + \frac{3}{2 \cdot \pi} \cdot \arctan \left(\frac{2 \cdot \theta^{\frac{1}{3}} - 1}{3^{\frac{1}{2}}} \right) + \frac{1}{4};$$

$$F := \theta \rightarrow \frac{1}{4} \frac{\sqrt{3} \ln \left(\frac{(1 + \theta^{1/3})^3}{1 + \theta} \right)}{\pi} + \frac{3}{2} \frac{\arctan \left(\frac{1}{3} (2 \theta^{1/3} - 1) \sqrt{3} \right)}{\pi} + \frac{1}{4}$$

$$> \text{'Leveque Collection Efficiency'} := 1 - F \left(\frac{\alpha}{\beta} \right) + \beta^{\frac{2}{3}} \cdot (1 - F(\alpha)) - (1 + \alpha + \beta)^{\frac{2}{3}} \cdot \left(1 - F \left(\frac{\alpha}{\beta} \cdot (1 + \alpha + \beta) \right) \right);$$

$$\text{Leveque Collection Efficiency} := 1 - \frac{\sqrt{3} \ln(2)}{\pi} - 3^{2/3} \left(\frac{3}{4} - \frac{1}{4} \frac{\sqrt{3} \ln \left(\frac{1}{4} (1 + 3^{1/3})^3 \right)}{\pi} - \frac{3}{2} \frac{\arctan \left(\frac{1}{3} (2 \cdot 3^{1/3} - 1) \sqrt{3} \right)}{\pi} \right)$$

$$> \text{evalf}(\text{'Leveque Collection Efficiency'});$$

$$0.2502095250$$

$$> \text{unassign}('A', 'X1', 'X2', 'X3', 'C12', 'f2', 'S3', 'S', 'I1', 'I2', 'J', 'N', 'Terms', 'N0', '\alpha', '\beta', 'F', 'p12', 'p3', 'fK', 'Npts', 'ptsx', 'ptsy', 'poly', 'S3num', 'f2num', \\ \text{'Collection Efficiency'}, \text{'Leveque Collection Efficiency'});$$

Steady-state current vs potential for a quasireversible reaction - no product initially

Used for Fig. 4. Start with only reactant (nondimensionalized concentration denoted by C) in solution. Reference rate constants and potentials to E^0 (strictly to the formal potential). $K0$ = standard nondimensionalized rate constant. Let $e = F(E - E^0)/RT$. Illustrate the method at a single potential, and then later run it in a loop to generate the current vs potential curve.

```
> e := 1.; K0 := 1; β := 0.5; A := 100; Terms := 40;
```

```
e := 1.
```

```
K0 := 1
```

```
β := 0.5
```

```
A := 100
```

```
Terms := 40
```

```
> Kf := K0·exp((1 - β)·e); Kb := K0·exp(-β·e); K := Kf + Kb;
```

```
Kf := 1.648721271
```

```
Kb := 0.6065306597
```

```
K := 2.255251931
```

Start by calculating the concentration profile for the irreversible case, but with rate constant $K = Kf + Kb$

```
> Cir := chsolve(K, Y ↦ 1, A, Terms) :
```

```
chsolve: Using integration method _d01akc
```

```
chsolve: Evaluating segment 1 with K = 2.255251931 at CPU time 0.016 s
```

```
chsolve: Completing calculation at CPU time 8.783 s
```

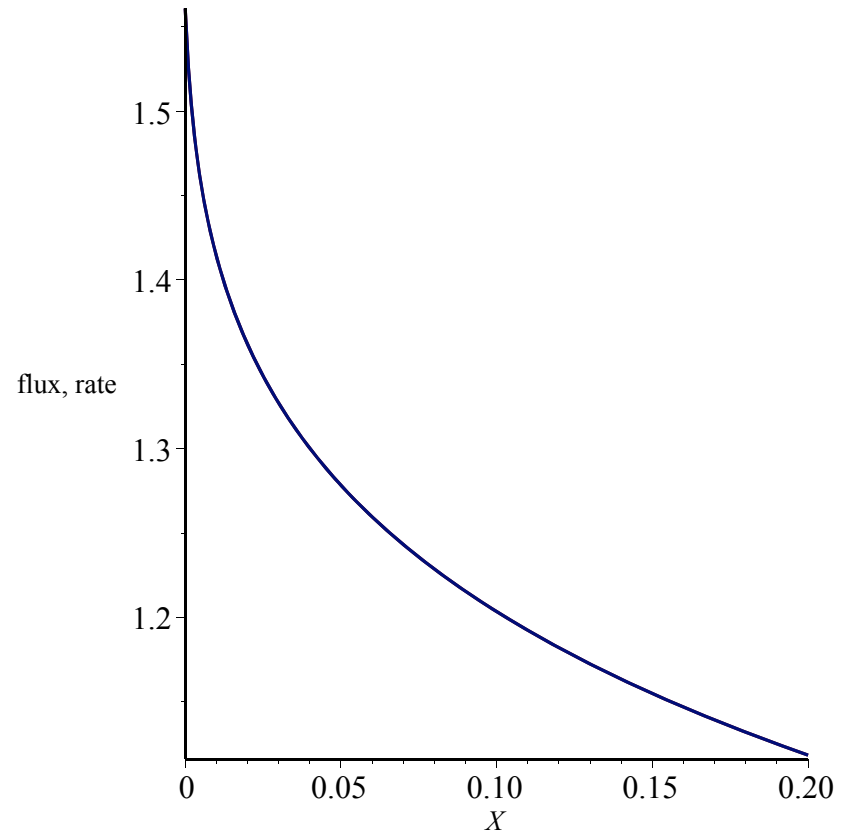
The quasireversible concentration may be found by the rule:

```
> CQ := (X, Y) →  $\frac{Cir(X, Y) \cdot Kf + Kb}{K}$ ;
```

$$CQ := (X, Y) \rightarrow \frac{Cir(X, Y) Kf + Kb}{K}$$

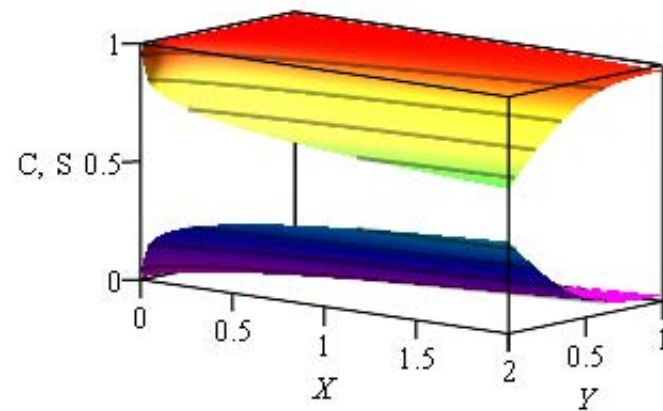
The product concentration is $1 - CQ$. Check that the electrode boundary condition holds by plotting the flux and the rate expression, which should be equal. The two plots are on top of each other.

```
> plot( [ eval(  $\frac{\partial}{\partial Y} CQ(X, Y), Y=0$  ), Kf·CQ(X, 0) - Kb·(1 - CQ(X, 0)) ], X=0 ..0.2, labels = [X, "flux, rate"] );
```



Plot the two concentration profiles together.

```
> plot3d( [CQ(X, Y), 1 - CQ(X, Y) ], X=0..0.2, Y=0..0.1, orientation = [ -50, 80 ], view = [ DEFAULT, DEFAULT, 0..1 ], scaling
= constrained, style = surfacecontour, shading = zhue, thickness = 2, tickmarks = [ 6, 4, 3 ], labels = [ X, Y, "C, S" ] );
```



Now put it in a loop to calculate the steady-state current potential curve. Choose electrode width $W=1$ to integrate over to get the total current. ei and ef are the initial and final potentials (units of RT/F) and de is the potential increment. Choose the parameters

> $K0 := 10.$; $\beta := 0.5$; $A := 100.$; $Terms := 40$; $W := 1.$;
 $ei := -4.$; $ef := 8.$; $de := 1$;

$K0 := 10.$

$\beta := 0.5$

```

A := 100.
Terms := 40
W := 1.
ei := -4.
ef := 8.
de := 1

```

And loop around. Setting infolevel[chsolve] to 1 suppresses information messages from chsolve. forget(hypergeom) clears out memory used for remembering the results of hypergeom calls.

```

> infolevel[chsolve] := 1 :
  IQ := NULL : E := NULL :
  for e from ei to ef by de do
    print(e);
    Kf := K0·exp( (1 - β) · e ); Kb := K0·exp( -β · e ); K := Kf + Kb;
    Cir := chsolve(K, Y ↦ 1, A, Terms);
    CQ := (X, Y) →  $\frac{Cir(X, Y) \cdot Kf + Kb}{K}$ ;
    IQ := IQ, evalf(int(eval(diff(CQ(X, Y), Y), Y=0), X=0 .. W));
    E := E, e;
    forget(hypergeom);
  end do;
  E := [E] : IQ := [IQ] :
  infolevel[chsolve] := 2 :

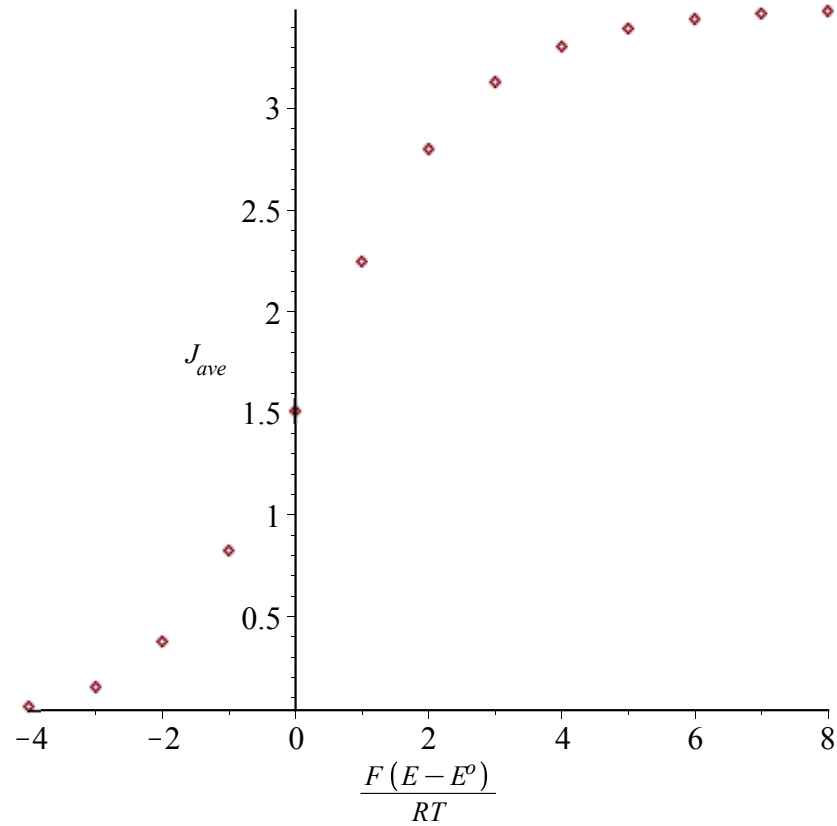
```

```

-4.
-3.
-2.
-1.
0.
1.
2.
3.
4.
5.
6.

```

```
> plot(E, IQ, style=point, labels = [  $\frac{F(E - E^0)}{RT}$ ,  $J_{ave}$  ] );
```



```
> unassign('E','IQ','e','ei','ef','de','β','W','A','K0','Kf','Kb','K','Cir','CQ','Terms','J');
```

7.
8.

Steady-state current vs potential for a quasireversible reaction - with product initially

Let $C = c/(c^b + s^b)$ and $S = s/(c^b + s^b)$, where c^b and s^b are bulk concentrations. Let $f = c^b/(c^b + s^b)$ be the fraction of the initial concentration that is reactant. $K_{eq} = \exp(F(E_{rev} - E^0)/RT) = s^b/c^b$ (Nernst equation). Let $E = \eta F/RT$. Let v_{eq} be the exchange rate, so $v_{eq} = k_{feq} \cdot c^b = k_{beq} \cdot s^b$ or $V'_{eq} = K_{feq} \cdot c^b = K_{beq} \cdot s^b$ or $V_{eq} = V'_{eq}/(c^b + s^b) = K_{feq} \cdot f = K_{beq} \cdot (1-f)$

> $A := 100.; E := -3.; f := 0.6; V_{eq} := 1; \beta := 0.5; Terms := 40;$

$A := 100.$

$E := -3.$

$f := 0.6$

$V_{eq} := 1$

$\beta := 0.5$

$Terms := 40$

> $K_{eq} := \frac{(1-f)}{f}; K_{feq} := \frac{V_{eq}}{f}; K_f := K_{feq} \cdot \exp((1-\beta) \cdot E); K_{beq} := \frac{V_{eq}}{1-f}; K_b := K_{beq} \cdot \exp(-\beta \cdot E); K := K_f + K_b;$

$K_{eq} := 0.6666666667$

$K_{feq} := 1.6666666667$

$K_f := 0.3718836002$

$K_{beq} := 2.500000000$

$K_b := 11.20422268$

$K := 11.57610628$

Solve with the irreversible Robin boundary condition with $K = K_f + K_b$

> $Cir := chsolve(K, Y \mapsto 1, A, Terms) :$

$chsolve$: Using integration method `_d01akc`

$chsolve$: Evaluating segment 1 with $K = 11.57610628$ at CPU time 0.000 s

$chsolve$: Completing calculation at CPU time 9.781 s

The irreversible concentration can be converted to the quasireversible concentration by the following rule.

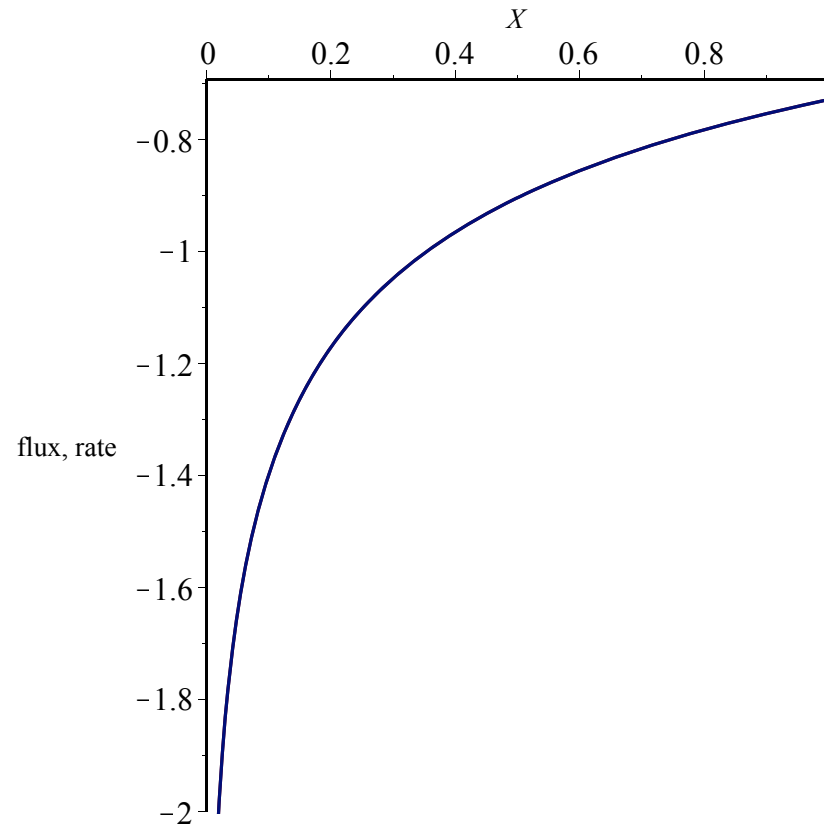
> $CQ := (X, Y) \rightarrow \frac{Cir(X, Y) \cdot (f \cdot K_f - (1-f) \cdot K_b) + K_b}{K};$

$CQ := (X, Y) \rightarrow \frac{Cir(X, Y) (f K_f - (1-f) K_b) + K_b}{K}$

The product concentration is $SQ = 1 - CQ$. The quasireversible current density calculated from the flux should agree with that from the

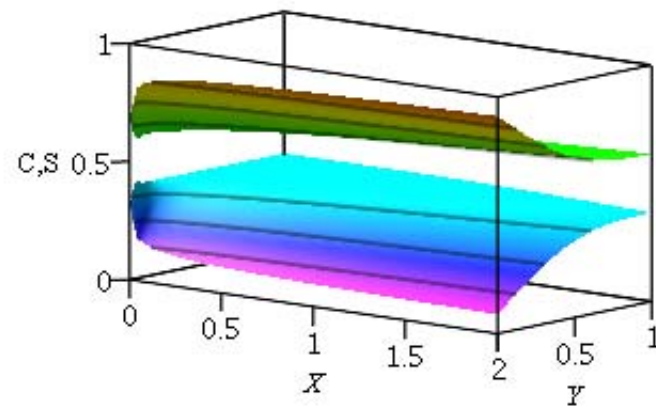
rate expression. The two plots are on top of each other.

```
> plot( [ eval(  $\frac{\partial}{\partial Y} CQ(X, Y), Y=0$  ),  $K_f \cdot CQ(X, 0) - K_b \cdot (1 - CQ(X, 0))$  ], X=0..1, labels = [X, "flux, rate"] );
```



Plot the reactant and product concentrations

```
> plot3d( [CQ(X, Y), 1 - CQ(X, Y)], X=0..2, Y=0..1, orientation = [ -50, 80 ], view = [DEFAULT, DEFAULT, 0..1], scaling
= constrained, style = surfacecontour, shading = zhue, thickness = 2, font = [Times, normal, 10], tickmarks = [6, 4, 3], labels
= [X, Y, "C,S"] );
```



Now work out the steady-state current potential curve. Choose parameters on the next line.

> $V_{eq} := 1; f := 0.6; \beta := 0.5; A := 100; W := 1; Terms := 40;$
 $e_i := -6; e_f := 6; d_e := 1;$

$V_{eq} := 1$

$f := 0.6$

$\beta := 0.5$

```

A := 100
W := 1
Terms := 40
ei := -6
ef := 6
de := 1

```

And loop around. Setting infolevel[chsolve] to 1 suppresses information messages from chsolve. forget(hypergeom) clears out memory used for remembering the results of hypergeom calls.

```

> infolevel[chsolve] := 1 :
  Keq := (1-f)/f; Kfeq := Veq/f; Kbeq := Veq/(1-f);
  IQ := NULL : E := NULL :
  for e from ei to ef by de do
    print(e);
    Kf := Kfeq*exp((1-beta)*e); Kb := Kbeq*exp(-beta*e); K := Kf + Kb;
    Cir := chsolve(K, Y -> 1, A, Terms);
    CQ := (X, Y) -> (Cir(X, Y) * (f*Kf - (1-f)*Kb) + Kb) / K;
    IQ := IQ, evalf(int(eval(diff(CQ(X, Y), Y), Y=0), X=0 .. W));
    E := E, e;
    forget(hypergeom);
  end do;
  E := [E] : IQ := [IQ] :
  infolevel[chsolve] := 2 :

```

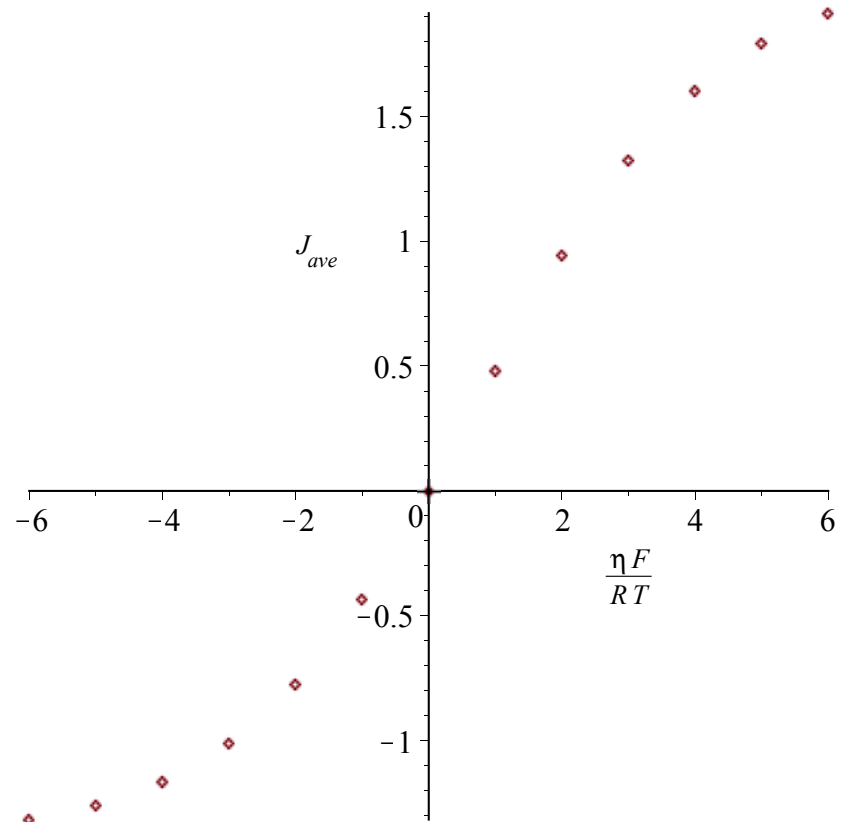
```

Keq := 0.6666666667
Kfeq := 1.666666667
Kbeq := 2.500000000
-6
-5
-4
-3
-2
-1

```

```
> plot(E, IQ, style=point, labels = [  $\frac{\eta F}{R T}, J_{ave}$  ] );
```

0
1
2
3
4
5
6



```
> unassign('Keq','Kb','f','A','Cir','E','Kbeq','ef','CQ','W','Kf','Veq','IQ','K','Terms','beta','Kfeq','ei','de','J');
```