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# Rules to transform concentrations and currents for irreversible reactions to those of quasireversible reactions

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## Abstract

Transformation rules are given that take the concentration or current expressions for the simple irreversible electron-transfer reaction  $R \rightarrow P + e^-$  and convert them to the corresponding quantities for the quasireversible reaction. They apply for many standard electrochemical mass-transport cases, including simple diffusion and convection-diffusion for the rotating disk or channel flow, provided that the diffusivities of the two species are equal. The forward rate constant is replaced by the sum of the forward and reverse rate constants, the result is scaled and then a constant added. Rules are also given for some cases where the diffusivities are unequal. As an application, a new solution of the concentration profile for a channel electrode within the Lévêque approximation neglecting axial diffusion is given.

*Key words:* diffusion, convection, mass-transport, irreversible, quasireversible

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## Introduction

Electrochemists have devised a wide variety of configurations to study the heterogeneous redox reaction (1) between solution species, e.g., semiinfinite 1-D diffusion, spherical diffusion, finite length diffusion, rotating disk electrode, rotating ring electrode, channel and tube electrodes. Conversely, when a new electrode configuration is devised, a known redox couple is frequently used for calibration and comparison with theory. There is a large literature describing analytical solutions for the current density and solution concentration profile for the benchmark conditions, in which R and P have bulk concentrations  $c_R^b$  and  $c_P^b$  respectively, there is no adsorption and the diffusivities are independent of concentration. Nonetheless, finding exact analytical solutions is difficult and

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a wide variety of approximation schemes have been used.



The quasireversible case, in which the forward and backward rates are both considered, requires solution of two coupled mass transport problems for the two solution species R and P, and leads to complicated expressions for the concentrations and current. It is evident that the equations for the irreversible case, in which only the forward reaction occurs, can be readily found from the quasireversible equations by setting the backward rate constant to zero. I show here that the converse, going from the equations for the irreversible case to the equations for the quasireversible case is surprisingly easy in many cases, provided the diffusivities are assumed equal. In the special case that there is no product initially present in the bulk, the concentration of R may be obtained by replacing  $k_f$  by  $k_f + k_b$ , scaling by  $k_f / (k_f + k_b)$ , and adding  $k_b c_{\text{R}}^{\text{b}} / (k_f + k_b)$ . The significance of this is that the irreversible problem is inevitably easier to solve than the quasireversible case, and so may be used as a bridge to the quasireversible case.

Although it is easy to verify validity of this transformation for simple cases, it is harder to establish the exact types of problems for which it holds. This work shows that simple transformations apply whenever the mass transport equations are linear in the concentration and the concentration always appears in a derivative. This covers a wide class of problems that includes all those mentioned in the introductory sentence. The key assumption is that the diffusivities of R and P are equal, an assumption that is common in analyzing experimental data and leads to only small errors in determining the rate constant. It has been known for a long time that this assumption implies that the sum of the reactant and product concentrations are constant, at least for steady-state systems with diffusion only. For simple systems, the sum is often derived or used without further comment, e.g., [1–3]. Oldham and Feldberg [4] extended this to multispecies systems including cases where migration, natural convection and some homogeneous reactions were present, and Kottke and Fedorov [5] included forced convection.

Recently, Schmachtel and Kontturi [6] used the constant total concentration property to show that the same eigenfunction method could be used to solve quasireversible potential step transients for finite-length diffusion as was used to solve irreversible transients. Their work comes closest to the present work, since they noted that the quasireversible case was a transformed version of the irreversible case with different eigenvalues. Here the general rule is formulated and shown to cover a wide variety of convective diffusion systems, though we consider only supported systems and neglect migration. The use of a transformation rule is proposed here as a simple way to find new analytical solutions. It can also be used to simplify numerical simulations of quasireversible systems.

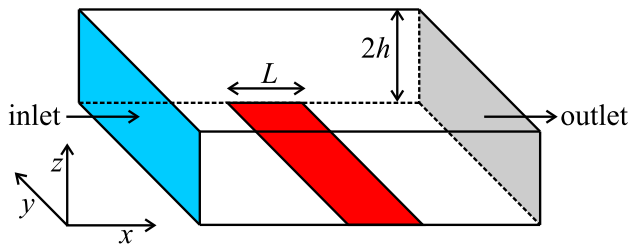


Figure 1: Example coordinates and boundaries. Channel electrode (red) in the side of a rectangular channel. Arrows indicate the flow direction.

## 1. Theory

### 1.1. Notation

The concentrations of R and P,  $c_R$  and  $c_P$ , have second subscripts ir and qr to indicate irreversible or quasireversible; in generic equations that apply to either type of reaction the second subscript is omitted. Superscript s means at the electrode surface and b means the bulk concentration specified at another boundary; unsuperscripted means in the solution. The current densities  $j$  and surface concentrations  $c_R^s$  or  $c_P^s$  are local values that in general vary across the electrode surface, and  $j$  must be integrated over the surface to get the measured current. If  $j$  is constant across the surface as is the case for uniformly accessible electrodes, then the measured current density is equal to  $j$ . The concentrations in the solution depend on 1, 2 or 3 spatial variables, depending on the dimensionality of the problem, and also on time, if a transient problem rather than a steady-state problem is considered. Where a specific coordinate system is used, the coordinate normal to the electrode surface into the solution is denoted by  $z$ . The channel electrode (Fig. 1) provides a non-trivial example of the requirements that are discussed below.

### 1.2. Assumptions

1. The mass-transport (partial) differential equations governing the concentrations of R and P satisfy three conditions: (i) they are linear, (ii) the concentration is present only in derivatives, and (iii) they are the same for R and P.

The general term in such a differential equation is some function of the coordinates times a partial derivative of concentration with respect to some of the coordinates. The notation is awkward if specified in the most general form that allows for different coordinate systems and dimensionalities. Therefore, the following deals with the specific case of convective diffusion for incompressible flow, which covers the majority of cases of interest, but this not intended to be limit the generality of the following discussion. For this case, the concentrations of R and P are governed by Eqs. (2) and (3), which includes the possibility of diffusion alone (fluid velocity  $\mathbf{v} = 0$ ).

Condition (iii) requires that the diffusivities of R and P must be equal.

$$\partial c_{\text{R}}/\partial t = D\nabla^2 c_{\text{R}} - \mathbf{v} \cdot \nabla c_{\text{R}} \quad (2)$$

$$\partial c_{\text{P}}/\partial t = D\nabla^2 c_{\text{P}} - \mathbf{v} \cdot \nabla c_{\text{P}} \quad (3)$$

Extension to incompressible fluids is not possible because the additional term  $c\nabla \cdot \mathbf{v}$  depends on the concentration and not its derivative (condition ii). On the other hand, the channel electrode with axial diffusion term  $D\partial^2 c/\partial x^2$  neglected is no longer strictly of the above form but satisfies the three conditions and is acceptable. Both steady-state ( $\partial c/\partial t = 0$ ) and time-dependent situations are included.

2. *The surface reaction rate  $v$  ( $\text{mol m}^{-2} \text{s}^{-1}$ ) is first order in concentrations of R and P: irreversible rate  $v = k_{\text{f}}c_{\text{R,ir}}^{\text{s}}$ ; quasireversible rate  $v = k_{\text{f}}c_{\text{R,qr}}^{\text{s}} - k_{\text{b}}c_{\text{P,qr}}^{\text{s}}$ .*
3. *The fluxes of R and P at the electrode surface are given by Fick's first law. This implies boundary conditions at the electrode surface:*

$$-\mathbf{n} \cdot D\nabla c_{\text{P}} = \mathbf{n} \cdot D\nabla c_{\text{R}} = v \quad (4)$$

where  $\mathbf{n}$  is a unit vector normal to the electrode surface into the solution. (All normal derivatives  $\mathbf{n} \cdot \nabla$  in this paper are understood to be at a boundary surface.) For convective systems, the no-slip boundary conditions means the convective component is zero at the electrode surface and so only the diffusive flux appears here. The key property is that the the concentration appears as a derivative. This means for example that migration is excluded.

4. *At boundary surfaces other than the electrode, there is a zero-gradient boundary condition (Eq. (5)), and/or a fixed-concentration boundary condition, where the concentrations have constant values  $c^{\text{b}}$  or  $s^{\text{b}}$  appropriate to the bulk solution (Eq. (6)).*

$$\mathbf{n} \cdot \nabla c_{\text{R}} = \mathbf{n} \cdot \nabla c_{\text{P}} = 0 \quad (5)$$

$$c_{\text{R}} = c_{\text{R}}^{\text{b}}, \quad c_{\text{P}} = c_{\text{P}}^{\text{b}} \quad (6)$$

For example, on the insulating surfaces in the channel electrode (uncolored regions in Fig. 1), the fluxes of R and P and therefore the gradients in their concentrations are zero. For the inlet of the channel electrode (blue), so long as the inlet surface is far enough upstream of the electrode for back diffusion to be negligible, then  $(\partial c_{\text{R}}/\partial x)|_{x=x_{\text{inlet}}} = (\partial c_{\text{P}}/\partial x)|_{x=x_{\text{inlet}}} = 0$ , i.e., the concentration gradient is zero even though the convective-diffusive flux is nonzero. Under the same assumption, the inlet concentrations may be fixed at their bulk values,  $c_{\text{R}}|_{x=x_{\text{inlet}}} = c_{\text{R}}^{\text{b}}$  and  $c_{\text{P}}|_{x=x_{\text{inlet}}} = c_{\text{P}}^{\text{b}}$ . Other examples of constant concentration are semiinfinite 1-D diffusion or convective diffusion at the rotating disk electrode, for which the concentrations are fixed at their bulk values at the boundary  $z = \infty$ .

This assumption only requires specification of these types of boundary

conditions at enough boundaries to ensure a unique solution. For example, for the channel electrode in the  $x$  direction the derivative is second order and so two conditions are required; if these are taken as fixing the value of the concentration and flux at the inlet, then no condition needs to be specified at the outlet. Since the irreversible and quasireversible solutions are assumed to exist, sufficient and consistent boundary conditions of these types must exist to make each case a well-posed problem.

5. *For time-dependent problems, the initial conditions are that the concentrations are constant everywhere at their bulk values  $c_R^b$  or  $c_P^b$ .*
6. *The rate constants are fixed, i.e., are independent of time (potentiostatic conditions).*

This covers the case of steady-state voltammetry, and also the case of chronoamperometry experiments in which the potential is constant after the step.

### 1.3. Transformation rules

Consider a solution  $c_{ir}$  of the irreversible problem with the rate constant  $k_f$ , and local current density  $j_{ir}$  at a particular location on the electrode surface. The notation  $[\dots]_{k_f \rightarrow k_f + k_b}$  is introduced to mean replace  $k_f$  by  $k_f + k_b$  in the expression enclosed in the square brackets. Then under the assumptions discussed above, the concentrations and current density for the quasireversible case with forward and backward rate constants  $k_f$  and  $k_b$  are obtained from the irreversible solutions by using the following transformation rules:

$$c_{R,qr} = \frac{k_f c_R^b - k_b c_P^b}{(k_f + k_b) c_R^b} [c_{R,ir}]_{k_f \rightarrow k_f + k_b} + \frac{k_b (c_R^b + c_P^b)}{k_f + k_b} \quad (7)$$

$$c_{P,qr} = c_R^b + c_P^b - c_{R,qr} \quad (8)$$

$$j_{qr} = (k_f c_R^b - k_b c_P^b) \left[ \frac{j_{ir}}{k_f c_R^b} \right]_{k_f \rightarrow k_f + k_b} \quad (9)$$

The case where P is initially absent follows by setting  $c_P^b = 0$ . These transformations are written for the concentrations in the solution or at the surface and the local current densities. However, averaging both sides of these equations over the electrode surface shows that they also apply for the average surface concentrations and the average or measured current densities.

### 1.4. Derivation

Rule (8) is a statement about the constancy of the sum  $c_{P,qr} + c_{R,qr}$ . To show this, the two governing equations (2) and (3) are added, as are the zero-gradient boundary conditions (5), and fixed-concentration boundary conditions (6). The electrode boundary conditions  $-\mathbf{n} \cdot D \nabla c_{P,qr} = v$  and  $\mathbf{n} \cdot D \nabla c_{R,qr} = v$  are subtracted, giving a zero-gradient boundary condition  $\nabla (c_{P,qr} + c_{R,qr}) = 0$ . The result is a linear boundary-value problem for  $c_{P,qr} + c_{R,qr}$  with all boundary conditions either zero-gradient or  $c_{P,qr} + c_{R,qr} = c_P^b + c_R^b$ . The solution is that

$c_{\text{P,qr}} + c_{\text{R,qr}} = c_{\text{P}}^{\text{b}} + c_{\text{R}}^{\text{b}}$  everywhere, which establishes rule (8). Using this result, the electrode boundary condition for the reactant can be rewritten as Eq. (10):

$$\begin{aligned} \mathbf{n} \cdot D\nabla c_{\text{R,qr}} &= k_{\text{f}} c_{\text{R,qr}}^{\text{s}} - k_{\text{b}} (c_{\text{R}}^{\text{b}} + c_{\text{P}}^{\text{b}} - c_{\text{R,qr}}^{\text{s}}) \\ &= (k_{\text{f}} + k_{\text{b}}) c_{\text{R,qr}}^{\text{s}} - k_{\text{b}} (c_{\text{R}}^{\text{b}} + c_{\text{P}}^{\text{b}}) \end{aligned} \quad (10)$$

The irreversible solution  $c_{\text{R,ir}}$  is assumed to exist, and the quasireversible solution  $c_{\text{R,qr}}$  needs to be found in terms of it. The governing equations and boundary conditions are the same for these two quantities, with the exception of the electrode boundary condition, which for the quasireversible case is now Eq. (10), and for the irreversible case is Eq. (11):

$$\mathbf{n} \cdot D\nabla c_{\text{R,ir}} = k_{\text{f}} c_{\text{R,ir}}^{\text{s}} \quad (11)$$

Now the irreversible solution applies for any value of the rate constant, so replacement of  $k_{\text{f}}$  by the sum of the quasireversible rate constants  $k_{\text{f}} + k_{\text{b}}$  gives a solution  $[c_{\text{R,ir}}]_{k_{\text{f}} \rightarrow k_{\text{f}} + k_{\text{b}}}$  to the irreversible problem; the motivation for this is comparison of Eqs. (10) and (11). The governing equation and zero-gradient boundary conditions are linear and contain only derivatives, so scaling by a constant and adding a second constant gives another solution that satisfies these requirements, though not necessarily the fixed-concentration boundary condition or the electrode boundary condition. With two adjustable constants, it should be possible to satisfy the two remaining boundary conditions, even for the quasireversible case. Therefore, the conjecture is that

$$c_{\text{R,qr}} = a [c_{\text{R,ir}}]_{k_{\text{f}} \rightarrow k_{\text{f}} + k_{\text{b}}} + b \quad (12)$$

Substitution into the left-hand side of Eq. (10) gives

$$\mathbf{n} \cdot D\nabla c_{\text{R,qr}} = \mathbf{n} \cdot D\nabla \left( a [c_{\text{R,ir}}]_{k_{\text{f}} \rightarrow k_{\text{f}} + k_{\text{b}}} + b \right) = a \left( \mathbf{n} \cdot D\nabla [c_{\text{R,ir}}]_{k_{\text{f}} \rightarrow k_{\text{f}} + k_{\text{b}}} \right) \quad (13)$$

$$= a (k_{\text{f}} + k_{\text{b}}) c_{\text{R,ir}} = a (k_{\text{f}} + k_{\text{b}}) (c_{\text{R,qr}} - b) / a \quad (14)$$

$$= (k_{\text{f}} + k_{\text{b}}) c_{\text{R,qr}} - b (k_{\text{f}} + k_{\text{b}}) \quad (15)$$

and agreement with Eq. (10) requires  $b = k_{\text{b}} (c_{\text{R}}^{\text{b}} + c_{\text{P}}^{\text{b}}) / (k_{\text{f}} + k_{\text{b}})$ . The constant  $a$  is then found by requiring  $c_{\text{R,qr}} = c_{\text{R}}^{\text{b}}$  at the boundaries where  $c_{\text{R,ir}} = c_{\text{R}}^{\text{b}}$  (and hence  $[c_{\text{R,ir}}]_{k_{\text{f}} \rightarrow k_{\text{f}} + k_{\text{b}}} = c_{\text{R}}^{\text{b}}$ ):

$$c_{\text{R}}^{\text{b}} = a c_{\text{R}}^{\text{b}} + k_{\text{b}} (c_{\text{R}}^{\text{b}} + c_{\text{P}}^{\text{b}}) / (k_{\text{f}} + k_{\text{b}}) \quad (16)$$

$$a = \frac{k_{\text{f}} c_{\text{R}}^{\text{b}} - k_{\text{b}} c_{\text{P}}^{\text{b}}}{(k_{\text{f}} + k_{\text{b}}) c_{\text{R}}^{\text{b}}} \quad (17)$$

Therefore the governing equation (2) and all boundary conditions are satisfied, which establishes rule (7).

To derive the current density rule (9), the relationship between current density and flux,  $j = F\mathbf{n} \cdot D\nabla c$ , is used together with Eq. (13):

$$\begin{aligned}
j_{\text{qr}} &= F\mathbf{n} \cdot D\nabla c_{\text{R,qr}} = Fa \left( \mathbf{n} \cdot D\nabla [c_{\text{R,ir}}]_{k_{\text{f}} \rightarrow k_{\text{f}} + k_{\text{b}}} \right) \\
&= \frac{k_{\text{f}}c_{\text{R}}^{\text{b}} - k_{\text{b}}c_{\text{P}}^{\text{b}}}{(k_{\text{f}} + k_{\text{b}})c_{\text{R}}^{\text{b}}} [j_{\text{ir}}]_{k_{\text{f}} \rightarrow k_{\text{f}} + k_{\text{b}}} \\
&= (k_{\text{f}}c_{\text{R}}^{\text{b}} - k_{\text{b}}c_{\text{P}}^{\text{b}}) \left[ \frac{j_{\text{ir}}}{k_{\text{f}}c_{\text{R}}^{\text{b}}} \right]_{k_{\text{f}} \rightarrow k_{\text{f}} + k_{\text{b}}} \tag{18}
\end{aligned}$$

### 1.5. Unequal diffusivities

The assumption of equal diffusivities is common in electrochemistry, but it is of interest to extend these results to non-equal diffusivities. The ability to do this depends on finding changes of variables that eliminate the explicit diffusivities in both governing equations and the boundary conditions. That is, the classes of systems for which transformations can be found will be more restrictive than for equal diffusivities, and in general different rules will be required for different geometries. An exhaustive analysis will not be attempted here, but two examples are given to illustrate the method. The case of steady-state diffusing systems (no convection) is chosen because it involves no further restriction on geometry, and the transient 1-D semiinfinite diffusion case is given as a restricted-geometry case that finds widespread use.

#### 1.5.1. Steady-state diffusing systems

Kottke and Fedorov [5] showed that for steady-state with diffusion only, the sum of diffusivity-weighted concentrations was constant, Eq. (19), and this quantity has often been invoked in solving electrochemical problems, e.g., [6, 7].

$$D_{\text{R}}c_{\text{R}} + D_{\text{P}}c_{\text{P}} = D_{\text{R}}c_{\text{R}}^{\text{b}} + D_{\text{P}}c_{\text{P}}^{\text{b}} \tag{19}$$

For steady state without convection, changing variables to  $C_{\text{R}} = D_{\text{R}}c_{\text{R}}$ ,  $C_{\text{P}} = D_{\text{P}}c_{\text{P}}$ ,  $C_{\text{R}}^{\text{b}} = D_{\text{R}}c_{\text{R}}^{\text{b}}$ ,  $C_{\text{P}}^{\text{b}} = D_{\text{P}}c_{\text{P}}^{\text{b}}$ ,  $K_{\text{f}} = k_{\text{f}}/D_{\text{R}}$ ,  $K_{\text{b}} = k_{\text{b}}/D_{\text{P}}$ , converts the governing equations (2) and (3) and boundary/initial conditions (4), (5) and (6) to

$$0 = \nabla^2 C_{\text{R}}, \quad 0 = \nabla^2 C_{\text{P}} \tag{20}$$

$$\mathbf{n} \cdot \nabla C_{\text{P}} = \mathbf{n} \cdot \nabla C_{\text{R}} = 0 \tag{21}$$

$$C_{\text{R}} = C_{\text{R}}^{\text{b}}, \quad C_{\text{P}} = C_{\text{P}}^{\text{b}} \tag{22}$$

$$-\mathbf{n} \cdot \nabla C_{\text{P,qr}} = \mathbf{n} \cdot \nabla C_{\text{R,qr}} = K_{\text{f}}C_{\text{R,qr}} - K_{\text{b}}C_{\text{P,qr}} \tag{23}$$

$$\mathbf{n} \cdot \nabla C_{\text{R,ir}} = K_{\text{f}}C_{\text{R,ir}} \tag{24}$$

These equations are found from the original ones by the substitutions  $D \rightarrow 1$ ,  $c_{\text{R}} \rightarrow C_{\text{R}}$ ,  $c_{\text{P}} \rightarrow C_{\text{P}}$ ,  $c_{\text{R}}^{\text{b}} \rightarrow C_{\text{R}}^{\text{b}}$ ,  $c_{\text{P}}^{\text{b}} \rightarrow C_{\text{P}}^{\text{b}}$ ,  $k_{\text{f}} \rightarrow k_{\text{f}}/D_{\text{R}}$ ,  $k_{\text{b}} \rightarrow k_{\text{b}}/D_{\text{P}}$ , and



applying these same substitutions to the transformation rules (7) - (9) gives the rules for this case:

$$c_{R,qf} = \frac{k_f c_R^b - k_b c_P^b}{(k_f + k_b D_R/D_P) c_R^b} [c_{R,ir}]_{k_f \rightarrow k_f + k_b (D_R/D_P)} + \frac{(k_b/D_P) (D_R c_R^b + D_P c_P^b)}{k_f + k_b D_R/D_P} \quad (25)$$

$$c_{P,qf} = (D_R c_R^b + D_P c_P^b - D_R c_{R,qf}) / D_P \quad (26)$$

$$j_{qf} = (k_f c_R^b - k_b c_P^b) \left[ \frac{j_{ir}}{k_f c_R^b} \right]_{k_f \rightarrow k_f + k_b (D_R/D_P)} \quad (27)$$

### 1.5.2. Time-dependent 1-D semiinfinite diffusion to a planar electrode

As usual, the planar electrode is assumed to be at  $z = 0$  and the concentration takes its bulk value at  $z = \infty$ . Following a change of variables known for a long time [8], the  $z$  axis is transformed differently for the two species  $Z_R = z/D_R^{1/2}$ ,  $Z_P = z/D_P^{1/2}$ , and the new variables for the concentrations and rate constants are  $C_R = D_R^{1/2} c_R$ ,  $C_P = D_P^{1/2} c_P$ ,  $C_R^b = D_R^{1/2} c_R^b$ ,  $C_P^b = D_P^{1/2} c_P^b$ ,  $K_f = k_f/D_R^{1/2}$ , and  $K_b = k_b/D_P^{1/2}$ . In these variables, the new governing equations (28) have the same boundary/initial conditions as above, Eqs. (21) - (24).

$$\partial C_R / \partial t = \partial^2 C_R / \partial Z_R^2, \quad \partial C_P / \partial t = \partial^2 C_P / \partial Z_P^2 \quad (28)$$

Although the transformations of the  $z$  coordinate are different for the two species, the boundaries are at the same location in the new coordinates ( $Z_R = Z_P = 0$  and  $Z_R = Z_P = \infty$ ). However, the different transformations mean that the equivalent of Eq. (19) now relates different physical locations in the solution via a well-known relationship ([9], Eq. (136)), which is expressed here as a substitution rule that will be used to find  $c_{P,qf}$  from  $c_{R,qf}$ .

$$D_R^{1/2} [c_{R,qf}]_{z \rightarrow z(D_R/D_P)^{1/2}} + D_P^{1/2} c_{P,qf} = D_R^{1/2} c_R^b + D_P^{1/2} c_P^b \quad (29)$$

Following the same procedure as the previous case, the substitutions  $D \rightarrow 1$ ,  $c_R \rightarrow C_R$ ,  $c_P \rightarrow C_P$ ,  $c_R^b \rightarrow C_R^b$ ,  $c_P^b \rightarrow C_P^b$ ,  $k_f \rightarrow k_f/D_R^{1/2}$ , and  $k_b \rightarrow k_b/D_P^{1/2}$  transform the original system to the new system, and so are used, together with Eq. (29), to find the transformation rules for this case:

$$c_{R,qf} = \frac{k_f c_R^b - k_b c_P^b}{(k_f + k_b (D_R/D_P)^{1/2}) c_R^b} [c_{R,ir}]_{k_f \rightarrow k_f + k_b (D_R^{1/2}/D_P^{1/2})} + \frac{(k_b/D_P^{1/2}) (D_R^{1/2} c_R^b + D_P^{1/2} c_P^b)}{(k_f + k_b (D_R/D_P)^{1/2})} \quad (30)$$

$$c_{P,qf} = c_R^b + c_P^b - [c_{R,qf}]_{z \rightarrow z(D_R/D_P)^{1/2}} \quad (31)$$

$$j_{qf} = (k_f c_R^b - k_b c_P^b) \left[ \frac{j_{ir}}{k_f c_R^b} \right]_{k_f \rightarrow k_f + k_b (D_R^{1/2}/D_P^{1/2})} \quad (32)$$

## 2. Examples

### 2.1. Chronoamperometry current density for semiinfinite 1-D diffusion to a planar electrode

This time-dependent example has only diffusive mass transport, and the expressions are classic results in electrochemistry [10, 11]. Assuming equal diffusivities, the irreversible current is converted to the quasireversible current by rule (9):

$$j_{\text{ir}} = Fk_{\text{f}}c_{\text{R}}^{\text{b}} \operatorname{erfc} \left( k_{\text{f}} (t/D)^{1/2} \right) \exp \left( k_{\text{f}}^2 t/D \right) \quad (33)$$

$$j_{\text{qr}} = F \left( k_{\text{f}}c_{\text{R}}^{\text{b}} - k_{\text{b}}c_{\text{P}}^{\text{b}} \right) \times \operatorname{erfc} \left( (k_{\text{f}} + k_{\text{b}}) (t/D)^{1/2} \right) \exp \left( (k_{\text{f}} + k_{\text{b}})^2 t/D \right) \quad (34)$$

For unequal diffusivities, the rule (32) converts Eq. (33) with  $D = D_{\text{R}}$  to

$$j_{\text{qr}} = F \left( k_{\text{f}}c_{\text{R}}^{\text{b}} - k_{\text{b}}c_{\text{P}}^{\text{b}} \right) \times \operatorname{erfc} \left( Qt^{1/2} \right) \exp \left( Q^2 t \right) \quad (35)$$

where  $Q = k_{\text{f}}/D_{\text{R}}^{1/2} + k_{\text{b}}/D_{\text{P}}^{1/2}$ .

### 2.2. Koutecky-Levich steady-state current density at the rotating disk

$$j_{\text{ir}} = \frac{FDk_{\text{f}}c_{\text{R}}^{\text{b}}}{\delta k_{\text{f}} + D} \quad (36)$$

$$j_{\text{qr}} = \frac{FD \left( k_{\text{f}}c_{\text{R}}^{\text{b}} - k_{\text{b}}c_{\text{P}}^{\text{b}} \right)}{\delta \left( k_{\text{f}} + k_{\text{b}} \right) + D} \quad (37)$$

where  $\delta = 1.6117\nu^{1/6}\omega^{-1/2}D^{1/3}$  is the diffusion layer thickness,  $\nu$  is the kinematic velocity and  $\omega$  is the angular velocity. This example involves steady-state convective diffusion, making the usual approximation that the velocity component normal to the electrode is approximated by the first nonzero (quadratic) term.

The quasireversible Koutecky-Levich equation is not common in the literature, though Greef et al [12] show how to derive it through use of the diffusion layer concept, which bypasses the necessity to calculate the concentration profile. Their result assumes equal diffusivities, though the result for different diffusivities is known [13, 14]. This result can be confirmed explicitly using the analytical form of the steady-state concentration in terms of the incomplete gamma function [14]. Application of the transformation rules (7) and (8) leads to quasireversible concentrations that can be verified as solutions of the rotating disk steady-state convective diffusion equation. Subsequent calculation of the flux verifies the quasireversible current expression (37).

### 2.3. Steady-state 2-D concentration profile for flow past a channel electrode

The rules have intrinsic interest based on their simplicity and ability to relate known literature results, as in the above two examples. However, here they are used to generate new results. The electrode is not uniformly accessible in this case. The concentration for the irreversible reaction at a 2-D channel electrode has been given by Tolmachev, Scherson, Wang and Palencsar [15–17] under the assumption that axial diffusion is neglected. The quasireversible current was given much earlier by Matsuda [18], who bypassed calculation of the concentration. A calculation of the quasireversible concentrations by Klatt and Blaedel [19] was shown by Tolmachev et al [15] to be incorrect.

The quasireversible concentrations are derived here in the Appendix using the transformation rules, and appear to be new results. This example emphasizes that although the irreversible solution is rather complicated, requiring convolution integrals and special functions for its expression, the quasireversible solution is not much more complicated. It requires only modification of a composite constant ( $\sigma$ ), and then scaling and addition of the constant to the irreversible solution. In the context of this work, it is interesting that Tolmachev et al [15] showed that the product and reactant concentration profiles obey equivalent governing equations and boundary conditions without the assumption of equal diffusivities, but did not couple the two concentrations with the kinetics.

### 3. Discussion

The typical mass-transport equations of electrochemistry are the diffusion equation and various convective-diffusion equations. These equations are linear, and typically involve only derivatives of the concentration. This allows the scaling and addition operations here to work. The simplicity of the rules reflects the fact that for equal diffusivities the mass-transport of the two species is the same, in the sense that a change of variables converts them to the same governing equation with the same boundary/initial conditions. The complexity of the equations for the quasireversible case is not significantly different from the complexity in the irreversible case, as is shown nicely by the channel example 2.3. In effect, the quasireversible solutions are simply “dressed up” versions of the irreversible solutions.

It is perhaps not surprising that the substitution  $k_f \rightarrow k_f + k_b$  appears in the transformation since  $k_f + k_b$  is a common measure of the overall rate, but it is interesting that the rate constants in the quasireversible case are not all in the  $k_f + k_b$  combination. The current transformation rule (9) reveals that the bulk concentrations appear solely in the combination  $F(k_f c_R^b - k_b c_P^b)$ , the kinetic current density, which is an interesting universality seen in all three rule sets. It is clear that in general

$$j = F(k_f c_R^s - k_b c_P^s) \quad (38)$$

$$= F(k_f c_R^b (c_R^s/c_R^b) - k_b c_P^b (c_P^s/c_P^b)) \quad (39)$$

where the functions  $c_{\text{R}}^{\text{s}}/c_{\text{R}}^{\text{b}}$  and  $c_{\text{P}}^{\text{s}}/c_{\text{P}}^{\text{b}}$  must separately tend to zero at the reversible potential, but it is less obvious that the current density can be written as product of the kinetic current density and a single function.

The rules here relate irreversible reactions to quasireversible reactions over many convective diffusion situations. Other relationships may be found in the literature, for example relating band and hemicylinder electrodes [20], rotating ring to rotating disk [21], or relating tube, channel and rotating ring/disk electrodes [16, 22]. These types of relationships typically rely on changes of variables that show that seemingly disparate situations are actually equivalent, and do not easily generalize. Relations that are more general are known, typically for diffusion only and especially for reversible and/or steady state conditions. Notable is Oldham's pan-voltammetric relationship for any type of time variation or reversibility conditions [14] with diffusion only. A universal relationship for diffusing reversible systems was found that relates current normalized by limiting current to potential for multipotential waveforms when the diffusivities are equal [1]. In terms of quasireversible systems, Bond et al [23] studied diffusion to the inlaid disk electrode at steady-state from reversible to irreversible kinetics. That work relates to the present work insofar as a rule to transform the irreversible case to the quasireversible case was given. A similar rule was given for the extension of this to inlaid planar electrodes of any geometry [24]. Most recently, Molina et al [25] have given an accurate but approximate framework for analyzing steady-states curves across different geometries that applies for diffusion and quasireversible conditions, with the equal diffusivity assumption.

The transformation from an irreversible solution to a quasireversible solution enables the apparently simpler mathematics of the irreversible case to extend to the more complicated quasireversible case. Since the reversible case is the limit of the quasireversible case as the rate constants  $k_{\text{f}}$  and  $k_{\text{b}}$  become large while their ratio remains constant, it should be possible to proceed to the analytical solution of the reversible case, provided the limit can be evaluated.

The transformations depends only on linear mass-transport, so an approximate convective diffusion equation works as well as an exact one, so long as it is linear and has only derivatives of concentration. This is exhibited in examples 2.2 and 2.3, where approximate quadratic and linear velocity profiles replace the exact profiles. If the exact solutions for the irreversible cases were known, then the method would still apply. In fact, the equations given in example 2.2 would still apply, but the diffusion layer thickness would have a different value.

Although the focus here is on analytical solutions, it is evident that the transformation can still be applied if only tabulated (or fitted) numerical solutions are available in terms of a non-dimensionalized parameter that included  $k_{\text{f}}$ , similarly to the classical Nicholson and Shain methodology used for cyclic voltammetry [26]. One simply solves the irreversible case for apparent forward rate constant  $k_{\text{f}} + k_{\text{b}}$  and applies the transformation to get the quasireversible solution.

Although time-dependent transient cases are covered, this is only when the rate constants do not depend on time (assumption 6). Since the rate constants depend on potential, this precludes time-varying potentials, such as in linear

sweep voltammetry. This assumption may be too restrictive, and it may be possible to develop transformations for linear sweep or cyclic voltammetry, but it is clear that time dependence introduces an additional parameter describing the speed of the change, so that the transformation rule will be more complicated. As an illustration of the difficulty, the substitution  $k_f \rightarrow k_f + k_b$  for constant  $k$  replaces a constant with a constant, but for linear-sweep voltammetry replaces an exponential with a function similar to cosh. In general, a change in functional form of partial differential equation makes a very large change in the solution, and so we cannot expect as simple a rule to apply. On the other hand, an additional speed parameter is not required for a sequence of potential steps, and an extension to that case may be simpler.

The change of variables used for steady state diffusion with unequal diffusivities (Sec. 1.5.1) was geometry independent because it did not change the independent variables. The case of transient 1-D semiinfinite diffusion to a planar electrode exemplifies the restrictions that geometry plays. The change of variables there does not work for 1-D cylindrical or spherical diffusion because the location of the electrode at non-zero radius  $r_s$  would move differently for the two species. Appropriate changes of variable are known for many cases of interest, and so can be used to generate transformation rules for specific geometries.

#### 4. Conclusions

For the common assumption of equal diffusivities of the two species, the transformation rules presented here allow easy conversion of analytical solutions for irreversible reactions to the corresponding analytical solutions for quasireversible reactions, for a wide variety of geometries and hydrodynamic conditions. Some transformation rules are also given for cases with unequal diffusivities, but these are less general and different rules are needed for different geometries or hydrodynamics. These rules give a surprising and elegant link between known literature and textbook results, which show that the apparently more complicated quasireversible case is not really more difficult than the irreversible case. Furthermore, new experimental arrangements in microfluidic electrochemistry, microelectrodes, or nanoelectrochemistry are continually being developed, and the present theory aids in the use of these methods, particularly in the calibration stage where standard redox couples are used for validation.

The theory is applied here to give a new result for channel electrodes. The main change is simply the reinterpretation of a kinetic parameter  $\sigma$ , and so extension to other cases where the irreversible analytical case is known is expected to be simple. The theory also enables simplification of the effort involved in numerical computer simulations, since only one concentration needs to be solved for, and the other can be found from the transformation.

Development of similar transformation rules under relaxed assumptions should prove useful in a variety of additional classes of problems in electrochemistry.

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### A. Steady-state 2-D concentration profile for flow past a channel electrode

This corresponds to the geometry of Fig. 1 with the channel width (in the  $y$  direction) infinitely large so that it reduces to a 2-D problem. I start with the concentration for the irreversible case given by Tolmachev et al. [15–17], and the interested reader may refer to those works for the derivation and additional commentary. The problem is solved within the Lévêque approximation, with the flow velocity approximated as proportional to  $z$ ,  $v_z = 2v_0z/h$ , where  $2v_0$  is the velocity in the centre of the channel in this approximation. Axial diffusion (parallel to the channel in the  $x$  direction) is neglected, and under these assumptions the convective diffusion equation is Eq. (40). Because axial diffusion is neglected, the solution only propagates downstream and the inlet may be chosen at the upstream edge of the electrode, which may be taken as  $x = 0$ . In the Lévêque view, the diffusive processes take place close to the electrode and therefore it is assumed that extending the linear velocity profile to  $z = \infty$  is an acceptable approximation. Therefore the boundary conditions (4) and (41) apply.

Tolmachev et al defined the non-dimensional concentration  $\theta(X, Z)$  (Eq. 42), with  $X = x/L$  and  $Z = (2v_0h^2/DL)^{1/3}z/h$ . (The symbols are slightly different here for consistency with the rest of the paper;  $Z$  is used for  $Y$  [15, 16] or  $\xi$  [17] and  $z$  is used for  $y$ .) The irreversible concentration above the electrode ( $0 < x < L, 0 < z < 2h$ ) is given by a convolution integral, Eq. (43). To evaluate it, the function  $\theta(X, 0)$  (Eq. (44)) is required, where the exponential integral and incomplete gamma functions are defined by  $\text{Ei}(a, z) = \int_1^\infty \exp(-zt)/t^a dt$  and  $\Gamma(a, z) = \int_z^\infty t^{a-1} \exp(-t) dt$ ,  $\Gamma(z)$  is the gamma function and the other symbols

are defined in Eqs. (45) - (47).

$$0 = D (\partial^2 c_i(x, z) / \partial z^2) - (2v_0 z / h) (\partial c_i(x, z) / \partial x), \quad i = \text{R, P} \quad (40)$$

$$c_i(x, \infty) = c_i(0, z) = c_i^b, \quad i = \text{R, P} \quad (41)$$

$$c_{\text{R,ir}}(x, z) = c_{\text{R}}^b (1 - \theta(X, Z)) \quad (42)$$

$$\begin{aligned} \theta(X, Z) &= \frac{\sigma^{1/3}}{\Gamma(1/3)} \int_0^X [1 - \theta(X_1, 0)] \\ &\quad \times (X - X_1)^{-2/3} \exp\left(-\frac{Z^3}{9(X - X_1)}\right) dX_1, \end{aligned} \quad (43)$$

$$\begin{aligned} \theta(X, 0) &= 1 - \exp(-\chi) \left[ 1 - \frac{(-\chi)^{1/3} \Gamma(2/3) + \chi \text{Ei}(1/3, -\chi)}{\chi^{1/3} \Gamma(2/3)} \right. \\ &\quad \left. - \frac{(-\chi)^{2/3} (-\Gamma(1/3) + \Gamma(1/3, -\chi))}{\chi^{2/3} \Gamma(1/3)} \right] \end{aligned} \quad (44)$$

$$\chi = \sigma X \quad (45)$$

$$\sigma = \alpha^3 (k_{\text{f}}^3 / D^2) (hL / 2v_0) \quad (46)$$

$$\alpha = 3^{-1/3} \Gamma(1/3) / \Gamma(2/3) \quad (47)$$

(Eq. (43) corrects a typo in Eq. (18) of Ref. [16] by writing  $\Gamma(1/3)$  rather than  $\Gamma(2/3)$ .) The solution for the region downstream of the electrode is the same except that the upper limit of the integral in (43) is 1. Although  $\theta(X, 0)$  in Eq. (44) is real, not all its components are, and for this reason I propose that the equivalent form Eq. (48) in terms of the explicitly real Whittaker functions  $M_{1/3, 1/6}(\chi)$  and  $M_{1/6, 1/3}(\chi)$  [27] may be preferable for numerical work.

$$\theta(X, 0) = 1 - \exp(-\chi) + 3 \exp(-\chi/2) \left[ \frac{M_{1/3, 1/6}(\chi)}{\chi^{1/3} \Gamma(1/3)} - \frac{M_{1/6, 1/3}(\chi)}{2\chi^{1/6} \Gamma(2/3)} \right] \quad (48)$$

To derive the quasireversible solution, the transformation rule (7) is applied to Tolmachev's irreversible solution.

$$c_{\text{qr}}(x, z) = \frac{k_{\text{f}} c_{\text{R}}^b - k_{\text{b}} c_{\text{P}}^b}{k_{\text{f}} + k_{\text{b}}} (1 - \theta(X, Z)) + \frac{k_{\text{b}} (c_{\text{R}}^b + c_{\text{P}}^b)}{k_{\text{f}} + k_{\text{b}}} \quad (49)$$

$$\sigma_{\text{qr}} = \alpha^3 ((k_{\text{f}} + k_{\text{b}})^3 / D^2) (hL / 2v_0) \quad (50)$$

where  $\theta(X, Z)$  is the same complicated expression but with  $\sigma$  replaced by  $\sigma_{\text{qr}}$  given in Eq. (50). The concentration of P then follows immediately from Eq. (8). It may be verified that the quasireversible concentrations  $c_{\text{R,qr}}$  and  $c_{\text{P,qr}}$  thus found satisfy the convective diffusion equation (40) with the appropriate boundary conditions by using the properties of  $\theta(X, Y)$ , namely that it satisfies  $(\partial^2 \theta / \partial Z^2) = Z (\partial \theta / \partial X)$ ,  $\theta(0, Z) = \theta(X, \infty) = 0$  and  $(\partial \theta / \partial Z)_{Z=0} = \sigma_{\text{qr}}^{1/3} (\theta(X, 0) - 1) / \alpha$ .

## References

- [1] A. Molina, J. Gonzalez, M.C. Henstridge, R.G. Compton, Voltammetry of electrochemically reversible systems at electrodes of any geometry: a general, explicit analytical characterization, *J. Phys. Chem. C* 115 (2011) 4054.
- [2] I. Streeter, R.G. Compton, Steady state voltammetry at non-uniformly accessible electrodes: a study of Tafel plots for microdisc and tubular flow electrodes in the reversible and irreversible limits of electron transfer, *Phys. Chem. Chem. Phys.* 9 (2007) 862.
- [3] E. Kjeang, B. Roesch, J. McKechnie, D.A. Harrington, N. Djilali, D. Sinton, Integrated electrochemical velocimetry for microfluidic devices, *Microfluid. Nanofluid.* 3 (2007) 403.
- [4] K.B. Oldham, S.W. Feldberg, Principle of unchanging total concentration and its implications for modeling unsupported transient voltammetry, *J. Phys. Chem. B* 103 (1999) 1699.
- [5] P.A. Kottke, A.G. Fedorov, Generalized principles of unchanging total concentration, *J. Phys. Chem. B* 109 (2005) 16811.
- [6] S. Schmachtel, K. Kontturi, Transient solutions of potential steps at the rotating disc electrode with steady state initial concentration profiles for one electron transfer reactions, *Electrochim. Acta* 56 (2011) 6812.
- [7] L. Rajendron, M.V. Sangaranarayanan, Diffusion at ultramicro disk electrodes: chronoamperometric current for steady-state  $Ec'$  reaction using scattering analogue techniques, *J. Phys. Chem. B.* 103 (1999) 1518.
- [8] J. Koutecky, J. Koryta, The general theory of polarographic kinetic currents, *Electrochim. Acta* 3 (1961) 338.
- [9] K.B. Oldham, C.G. Zoski in: C.H. Bamford, R.G. Compton, *Comprehensive Chemical Kinetics*, Elsevier, Amsterdam, 1986, v. 26., Ch. 2., p. 79.
- [10] P. Delahay, Unified theory of polarographic waves, *J. Am. Chem. Soc.* 75 (1953) 1430.
- [11] D.D. Macdonald, *Transient Techniques of Electrochemistry*, Plenum, NY, 1977.
- [12] R. Greef, R. Peat, L.M. Peter, D. Pletcher, J. Robinson, *Instrumental Methods in Electrochemistry*, Ellis-Horwood, Chichester, U.K., 1985.
- [13] Y.V. Pleskov, V.Y. Filinovskii, *The Rotating Disc Electrode*, Consultants Bureau, N.Y., 1976.
- [14] J.B. Oldham, J.C. Myland, A.M. Bond, *Electrochemical Science and Technology: Fundamentals and Applications*, Wiley, Chichester, U.K., 2012.



- [15] Y.V.Tolmachev, Z. Wang, D.A. Scherson, Theoretical aspects of laminar flow in a channel-type electrochemical cell as applied to *in situ* attenuated total reflection-infrared spectroscopy, *J. Electrochem. Soc.* 143 (1996) 3160.
- [16] Y.V.Tolmachev, Z. Wang, D.A. Scherson, *In situ* spectroscopy in the presence of convective flow under steady-state conditions: a unified mathematical formalism, *J. Electrochem. Soc.* 143 (1996) 3539.
- [17] D.A. Scherson, Y.V. Tolmachev, Z. Wang, A. Palencsar, Extensions of the Koutecky–Levich equation to channel electrodes, *Electrochem. Solid State Lett.* 11 (2008) F1.
- [18] H. Matsuda, Zur theorie der stationären strom-spannungs-kurven von redox-elektrodenreactionen in hydrodynamischer voltammetrie. II. laminare rohr-und kanal strömungen, *J. Electroanal. Chem.* 15 (1967) 325.
- [19] L.N. Klatt, W.J. Blaedel, Quasi-reversible and irreversible charge transfer at the tubular electrode, *Anal. Chem.* 39 (1967) 1065.
- [20] C.A. Amatore, B. Fosset, M.R. Deakin, R.M. Wightman, Electrochemical kinetics at microelectrodes part III: equivalency between band and hemicylinder electrodes, *J. Electroanal. Chem.* 225 (1987) 33.
- [21] H. Matsuda, Theory of stationary current-voltage curves of redox-electrode reactions in hydrodynamic voltammetry VI: ring electrodes, *J. Electroanal. Chem.* 35 (1972) 77.
- [22] P.R. Unwin, R.G. Compton, The relationship between mass transport to channel and rotating disk electrodes, *J. Electroanal. Chem.* 245 (1988) 287.
- [23] A.M. Bond, K.B. Oldham, C.G. Zoski, Theory of electrochemical processes at an inlaid disc microelectrode under steady-state conditions, *J. Electroanal. Chem.* 245 (1988) 71.
- [24] L. Xiaoping, L. Juntao, C. Chuansin, The general characteristics of microelectrodes of any planar geometry under steady-state conditions, *J. Electroanal. Chem.* 295 (1990) 15.
- [25] A. Molina, J. Gonzalez, E.O. Barnes, R.G. Compton, Simple analytical equations for the current-potential curves at microelectrodes: a universal approach, *J. Phys. Chem. C* 118 (2014) 346.
- [26] R.S. Nicholson, I. Shain, Theory of stationary electrode polarography: single scan and cyclic methods applied to reversible, irreversible, and kinetic systems, *Anal. Chem.* 36 (1964) 706.
- [27] F.V. Olver, D.W. Lozier, R.F. Boisvert, C.W. Clark, (Eds.), *NIST Handbook of Mathematical Functions*, NIST and Cambridge University Press, NY, 2010, Sec. 13.14. Online version at <http://dlmf.nist.gov/>.