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# Laplace Transform Methods for Transient Diffusion; or, Some Good Questions from Ralph White

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Motivated by years of correspondence with Prof. Ralph White, I discuss two unconventional ways to solve diffusion problems with Laplace transforms. A method to derive error-function series, alternatives to Fourier series that converge rapidly and avoid the Gibbs phenomenon at short times, is illustrated by example. It is shown how Mittag-Leffler partial-fractions expansions can facilitate derivations of Fourier-series solutions from the same starting point. Several basic problems pertinent to electrochemical transport are analyzed, culminating in the development of a modified Cottrell equation applicable to thin films of unsupported electrolytic solutions sandwiched between planar electrodes.

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Every few months for as long as I can remember I have received an e-mail out of the blue from Ralph White with a technical question. Cases in point:

- From 2013: “Professor Monroe, Please show me how (using maple?) to take the limit of your Eq. 20 to get the similarity solution. Thank you.”
- From 2014: “I need your help again if you have the time. Please send me your derivations of Eqs. 21 and 22 of your dendrite paper. Thank you.”
- From 2015: “Chuck, please show me how to go from your Eqs. 21 a to 21 b with  $n = 1$ . Maple yields the correct solution, but I would like to know how to obtain the solution by hand.”

And so on, in a bursty correspondence that traces back to November 2005, when I was in my first position as a professional academic. The topics have varied—engineering mathematics, electrochemical thermodynamics, transport theory—but Ralph’s ask is always the same: explain! Each query has posed a unique, intellectually profitable, and sometimes tough scientific communication challenge for me. In a few (luckily, a very few) cases our discussions have revealed my past mistakes. In many more others, Ralph’s brain teasers have helped me clarify, formalize, or extend methods I previously understood intuitively.

I cannot quote the text of Prof. White’s first message—the e-mail account that received it at Imperial College London is long gone. I do have a copy of my response in a file here at Oxford, however. Dusting it off, and gathering it together with the other bits and pieces of this illuminating exchange over the last 18 years, I find that many of Ralph’s queries dealt with the analysis of transient diffusion problems. Often the tricks I needed were similar. And, although Carslaw and Jaeger<sup>1</sup> and Bird, Stewart and Lightfoot<sup>2</sup> both present results apparently derived by related strategies, I do not know literature sources that cover the methods directly. So I am putting some of my answers to Ralph forward in this essay, which will provide a few worked examples relevant to electrochemical transport modelling.

Numerical approaches to mass-transport problems have become increasingly dominant, but a place still remains for analytical techniques. Electrochemical applications often involve instantaneous changes in applied current or voltage, and thus boundary conditions, which induce rapid and then gradual composition variations that may be difficult to capture numerically. The electrical signatures of these mass-transfer processes can be understood by asymptotic analysis. Formulas that describe asymptotic regimes, for example at short

times after a current pulse initiates, or during long-time relaxations of voltage at open circuit, aid the interpretation of experiments. Standard laboratory techniques for physical property measurement almost universally rely on asymptotic formulas. Analytical results also have utility within computational models. As well as providing exact formulas useful for testing numerical algorithms, they can be incorporated into more complicated multiscale simulations to reduce calculation time.

Below I illustrate two techniques for solving simple diffusion problems analytically. Both leverage the idea that Laplace transformation turns transient partial differential equations into ordinary differential equations, which are often more easily solved. I demonstrate two ways to manipulate Laplace transformed functions that facilitate their return to the time domain. First, series expansion around an infinite value of the Laplace variable produces error-function series in the time domain, which are smoother and converge more rapidly than Fourier series at short times. These series often involve a less familiar class of special function called integrated complementary error functions, which I briefly describe and show how to compute more efficiently. Second, Mittag-Leffler expansion—series expansion about the poles of a complex function—allows direct derivations of Fourier series from Laplace transforms, providing a useful alternative to the more familiar separation of variables technique. I close the paper with a new physical example, deriving a corrected Cottrell equation applicable to thin-film electrolytic media such as battery separators.

## The Meltdown Problem

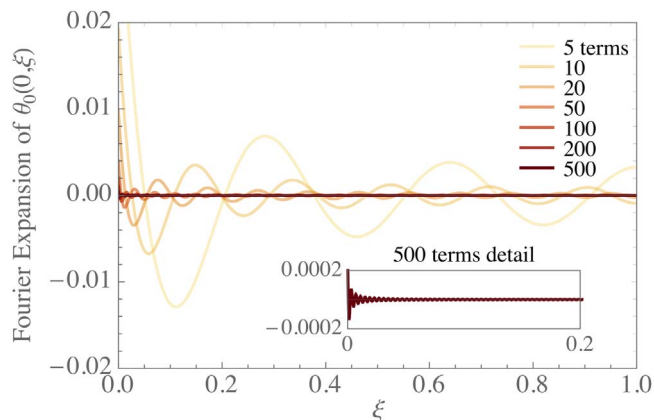
Ralph’s first question concerned the “nuclear meltdown problem”. That year I had coauthored a pedagogical paper for *Chemical Engineering Education* with my (and Ralph’s—two and a half decades prior) doctoral advisor Prof. John Newman,<sup>3</sup> in which we discussed transient heat transfer through a slab, the far face of which is a thermal insulator, and the near face of which receives heat energy at constant rate. Phrased dimensionlessly in terms of time  $\tau$ , position  $\xi$ , and temperature  $\theta_0(\tau, \xi)$ , the governing equation (GE) is

$$\text{GE: } \frac{\partial \theta_0}{\partial \tau} = \frac{\partial^2 \theta_0}{\partial \xi^2}, \quad [1]$$

the boundary conditions (BCi and BCii) are

$$\text{BCi: } \left. \frac{\partial \theta_0}{\partial \xi} \right|_{\tau,0} = -1 \quad \text{and} \quad \text{BCii: } \left. \frac{\partial \theta_0}{\partial \xi} \right|_{\tau,1} = 0, \quad [2]$$

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**Figure 1.** Illustration of slow short-time convergence of Fourier series and the Gibbs phenomenon. Plot of  $\theta_0$  from Eq. 4 with respect to position  $\xi$  at time  $\tau = 0$ , with the sum truncated after various numbers of terms. The boundary conditions stipulate a slope at  $\xi = 0$  that opposes the uniform initial condition, which induces spatially oscillatory behavior in the Fourier series. (Inset) Adding harmonics increases the wavenumber and decreases the amplitude of oscillations near  $\xi = 0$  at zero time, but never eliminates them altogether.

and the initial condition (IC) is

$$\text{IC: } \theta_0(0, \xi) = 0. \quad [3]$$

The problem has relevance to this journal's readership because it relates closely to a basic problem in electrolyte transport, as we shall see in the next section.

For the meltdown problem, separation of variables yields a Fourier-series solution, namely

$$\theta_0(\tau, \xi) = \tau + \frac{1}{2}\xi^2 - \xi + \frac{1}{3} - \frac{2}{\pi^2} \sum_{k=1}^{\infty} \frac{1}{k^2} e^{-k^2\pi^2\tau} \cos(k\pi\xi), \quad [4]$$

a form of which can be found in the classic *Conduction of Heat in Solids*, Section 3.8, Eq. 3.<sup>1</sup> The Appendix provides details of the derivation.

Fourier expansions work well at long times, requiring few terms for accuracy. But when  $\tau$  nears zero the series from Eq. 4 requires many terms and also exhibits the Gibbs phenomenon—the oscillatory overshoot behavior of Fourier series at jump discontinuities, or near boundaries when initial conditions do not satisfy the boundary conditions. Figure 1 presents  $\theta_0(0, \xi)$  using truncated sums from Eq. 4 to illustrate these issues.

One of the essential exercises from the first edition of *Transport Phenomena* provides a way to avoid the difficulties with Fourier series that Fig. 1 exhibits. Problem 11.F<sup>2</sup> lays out a similarity transformation for the meltdown problem, under the assumption that the diffusion boundary-layer thickness is very small. This leads to the result

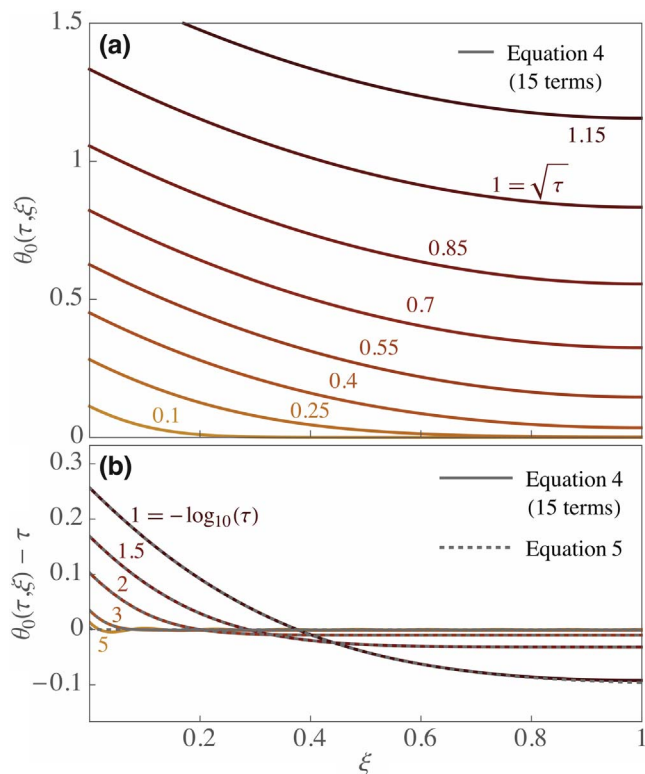
$$\lim_{2\sqrt{\tau} \ll 1} \theta_0(\tau, \xi) = 2\sqrt{\tau} \operatorname{erfc}\left(\frac{\xi}{2\sqrt{\tau}}\right), \quad [5]$$

wherein

$$\operatorname{erfc}(z) = \int_z^{\infty} \operatorname{erfc}(u) du \quad [6]$$

defines the first integrated complementary error function. White and Subramanian provide a guide for obtaining short-time asymptotic results like this with Maple symbolic mathematics software.<sup>4</sup>

Figure 2 shows the Fourier-series solution from Eq. 4 (keeping 15 terms in the sum) alongside Bird, Stewart, and Lightfoot's self-



**Figure 2.** Two canonical solutions of the meltdown problem. (a) Plot of the Fourier series for  $\theta_0(\tau, \xi)$  at various  $\sqrt{\tau}$  values. (b) Comparison of the 15-term Fourier expansion with Bird, Stewart, and Lightfoot's self-similar solution at small  $\tau$ . Note that the  $\sqrt{\tau} = 0.1$  curve in panel (a) equals the  $-\log_{10}(\tau) = 2$  curve in panel (b).

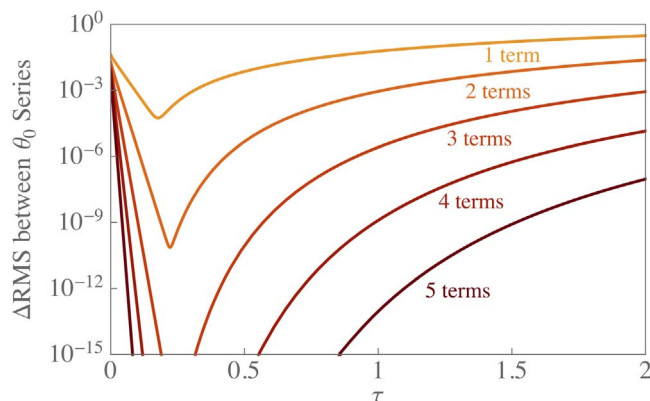
similar solution from Eq. 5. Whereas the Fourier-series result clearly exhibits the Gibbs phenomenon at  $\tau = 10^{-5}$ , the similarity solution does not oscillate and matches the slope demanded by the inner boundary condition. The similarity solution also works surprisingly well at times between  $\tau = 10^{-3}$  and  $\tau = 10^{-1.5} \approx 0.03$ , but by  $\tau = 0.1$ , the two solutions begin to differ. Although not shown on the figure, this deviation grows as  $\tau$  continues to rise.

Since it derives from the same governing equations, the short-time solution 5 expresses a limiting behavior of solution 4. My main concern in 2005 was to develop a clearer understanding of how this was true. In particular, was it possible to derive a solution with the same accuracy across timescales as Eq. 4, the form of which allowed a straightforward limit to be taken to reveal Eq. 5? Ralph's 2013 question from the preamble specifically asks for this limit process.

Of course Prof. Newman already had thought of the same question, knew that a direct connection between the two solutions could indeed be found, and taught me the relevant derivation. He showed me that by solving the Laplace transformed governing system, one could develop an answer in terms of an infinite series of error functions, rather than the trigonometric functions that arise when solving by separation of variables. Thus, with only scarce detail of our workings, Newman and I stated the result

$$\theta_0(\tau, \xi) = 2\sqrt{\tau} \sum_{k=0}^{\infty} \left[ \operatorname{erfc}\left(\frac{2k + \xi}{2\sqrt{\tau}}\right) + \operatorname{erfc}\left(\frac{2k + 2 - \xi}{2\sqrt{\tau}}\right) \right], \quad [7]$$

which can also be found—without derivation—in Carslaw and Jaeger (Section 3.8, Eq. 4).<sup>1</sup> This formula both matches the Fourier series when plotted and reduces to Eq. 5 in the limit where  $2\sqrt{\tau} \ll 1$ . An error-function series even has key practical benefits,



**Figure 3.** Equivalence of Fourier series and error-function series expansions. Plot of the root-mean-square difference  $\Delta\text{RMS}$  (over  $\xi$  from 0 to 1) between the Fourier series of  $\theta_0$  from Eq. 4 and the error-function series from Eq. 7 as a function of time  $\tau$ , with varying numbers of terms in the two expansions.

because it apparently converges pointwise, as do its derivatives, and does not succumb to the Gibbs phenomenon at short times.

The gist of Ralph's first message to me was: How does one derive an error-function series like this? Explain! Since the methodology has served me in good stead numerous times over the years, I will lay out the details here.

### Error-function Series from Laplace Transforms

Let  $\bar{\theta}_0(\xi) = \mathcal{L}\{\theta_0(\tau, \xi)\}$  represent the Laplace transform of  $\theta_0(\tau, \xi)$  with respect to  $\tau$ . The definition of the Laplace transformation operator  $\mathcal{L}\{\}$  can be applied to partial derivatives to show that  $\mathcal{L}\{\partial\theta_0/\partial\xi\} = d\bar{\theta}_0/d\xi$  and  $\mathcal{L}\{\partial\theta_0/\partial\tau\} = s\bar{\theta}_0(\xi) - \theta_0(0, \xi)$ . After being transformed, Eqs. 1 through 3 reduce to the ordinary system

$$\text{GE: } \frac{d^2\bar{\theta}_0}{d\xi^2} - s\bar{\theta}_0 = 0 \quad [8]$$

$$\text{BCi: } \left. \frac{d\bar{\theta}_0}{d\xi} \right|_0 = -\frac{1}{s} \quad \text{BCii: } \left. \frac{d\bar{\theta}_0}{d\xi} \right|_1 = 0, \quad [9]$$

which is solved by

$$\bar{\theta}_0(\xi) = \frac{\cosh[(1 - \xi)\sqrt{s}]}{s^{3/2} \sinh(\sqrt{s})}, \quad [10]$$

as detailed in the Appendix. Once rearranged properly, this function can produce a series whose term-by-term inversion yields Eq. 7. These rearrangements comprise the method I intend to illustrate.

Our first step hinges on knowing how a certain class of Laplace transformations looks, and on recognizing this form within Eq. 10. We observe that hyperbolic functions are sums of exponentials and note that many Laplace transforms involving exponentials are well known. Also, we see a natural-number power of  $\sqrt{s}$  in the denominator. In Abramowitz and Stegun's excellent tables,<sup>5</sup> we find both of these features in the transform pair

$$\mathcal{L}^{-1}\left\{\frac{e^{-a\sqrt{s}}}{s^{3/2}}\right\} = 2\sqrt{\tau} \operatorname{erfc}\left(\frac{a}{2\sqrt{\tau}}\right) \quad \text{for } a \geq 0; \quad [11]$$

since we know how to invert  $e^{-a\sqrt{s}}/s^{3/2}$ , we first recast Eq. 10 as a sum of convolutions with it. This can be done by breaking up the hyperbolic cosine into its constituent exponential terms, and then distributing out  $(1 - \xi)$  when necessary to isolate an exponential of a negative multiple of  $\sqrt{s}$ . The less compact form of Eq. 10 we shoot for is

$$\bar{\theta}_0(\xi) = \frac{e^{-\xi\sqrt{s}}}{s^{3/2}} \cdot \frac{e^{\sqrt{s}}}{2 \sinh(\sqrt{s})} + \frac{e^{-(1-\xi)\sqrt{s}}}{s^{3/2}} \cdot \frac{1}{2 \sinh(\sqrt{s})}, \quad [12]$$

in which each term on the right is a convolution with the form  $e^{-a\sqrt{s}}/s^{3/2}$ , with  $a \geq 0$ .

The second step of analysis forms  $\bar{\theta}_0$  into an infinite series by analyzing the remaining factors in the convolved pairs of terms. Using the definition of hyperbolic sine in terms of exponentials, one finds that

$$\frac{e^{\sqrt{s}}}{2 \sinh(\sqrt{s})} = \frac{e^{\sqrt{s}}}{e^{\sqrt{s}} - e^{-\sqrt{s}}} = \frac{1}{1 - e^{-2\sqrt{s}}} \quad \text{and} \quad [13]$$

$$\frac{1}{2 \sinh(\sqrt{s})} = \frac{1}{e^{\sqrt{s}} - e^{-\sqrt{s}}} = \frac{e^{-\sqrt{s}}}{1 - e^{-2\sqrt{s}}}. \quad [14]$$

Noting that short times in the  $\tau$  domain correspond to large values of  $s$  in the Laplace domain, we seek expressions of these functions that capture their behavior in the neighborhood of very large  $s$ . Letting  $x = e^{-\sqrt{s}}$ , the large- $s$  regime corresponds to  $x$  near zero. We recognize functions amenable to Maclaurin expansion,

$$\frac{1}{1 - x^2} = \sum_{k=0}^{\infty} x^{2k} \quad \text{and} \quad \frac{x}{1 - x^2} = \sum_{k=0}^{\infty} x^{2k+1}. \quad [15]$$

Thus Eq. 12 can be stated equivalently in a large- $s$  expansion as

$$\bar{\theta}_0(\xi) = \sum_{k=0}^{\infty} \frac{e^{-(2k+\xi)\sqrt{s}}}{s^{3/2}} + \sum_{k=0}^{\infty} \frac{e^{-(2k+2-\xi)\sqrt{s}}}{s^{3/2}}, \quad [16]$$

in which both summands have the form of the transform whose inverse we know, from Eq. 11. Exploiting the linearity of the  $\mathcal{L}^{-1}\{\}$  operator, this inverts term by term to produce Carslaw and Jaeger's—and my and Newman's—error-function series for  $\theta_0(\tau, \xi)$ , Eq. 7.

Figure 3 plots the square root of the integral from  $\xi = 0$  to 1 of the squared difference between the expansions of  $\theta_0(\tau, \xi)$  by Fourier series (Eq. 4) and by error-function series (Eq. 7). As expected, the root-mean-square difference between the two expansions decreases as their numbers of terms increase. Truncated series agree well at moderate times, with the mean-square differences reaching minima near  $\tau = 1/4$  (i.e.,  $2\sqrt{\tau} = 1$ ). At shorter times the difference between the expansions rises because the truncated Fourier series becomes inaccurate; at longer times it rises because the truncated error-function series does. Significantly, an error-function series with just five terms, which avoids the Gibbs phenomenon and achieves accuracy at short times, works nearly as well as the Fourier series expansion up to  $\tau = 1$ . At  $\tau = 2$  the error-function series matches the Fourier series within seven significant digits—about the same as the extent to which the Fourier series itself deviates from its long-time asymptotic limit.

### Current Step through an Electrolyte Slab

Electrochemical engineering provides many practically significant diffusion problems related to the meltdown problem. One example is the transient distribution of molar salt concentration  $c$  induced by applying a constant current density  $i$  to an initially equilibrated slab of a redox-active binary electrolytic solution sandwiched between identical planar electrodes separated by distance  $L$ . A summary of physical assumptions and parameters which frame this transport problem follows.

We suppose that a formula unit of the dissolved salt contains a single cation, with equivalent charge  $z_+$  and formula-unit stoichiometry  $\nu_+$ , and a single anion, with charge  $z_-$  and stoichiometry  $\nu_-$ , which together satisfy  $z_+\nu_+ + z_-\nu_- = 0$  because salt formula units balance charge. We adopt a local electroneutrality approximation, so

that the cation concentration at position  $x$  within the electrolyte slab at any time  $t$  is  $\nu_+c(t, x)$ , the anion concentration is  $\nu_-c(t, x)$ , and the current density is constant with respect to position,  $i(t)$  only. The electrolyte is sufficiently dilute that the solvent is in great excess, solution density is independent of salt concentration, and solvent flux determines the rate of convection. We take salt flux in the solution to be parametrized by a Fickian diffusivity  $D$  and cation transference number  $t_+$ , both constant, and let  $c_\infty$  represent the equilibrium bulk concentration of salt.

At the electrodes, we allow that ions from the salt participate in a general interfacial half-reaction with cation stoichiometry  $s_+$  and anion stoichiometry  $s_-$ , such that the number  $n$  of electrons the electrode supplies in a reaction step is  $n = -(s_+z_+ + s_-z_-)$ . Note that  $s_k$  is zero when ion  $k$  does not participate in the interfacial reaction. Otherwise, our sign convention follows Newman's:<sup>6</sup> if species  $k$  is a reactant in a half-reaction written as a reduction,  $s_k$  is negative, and when species  $k$  is a product,  $s_k$  is positive. For example, if the electrolyte were from a lithium-ion battery, the half-reaction at both electrodes would be single-electron reduction of lithium cations, for which  $z_+ = 1$ ,  $s_+ = -1$ ,  $s_- = 0$ , and  $n = 1$ ; if the electrolyte were from a typical alkaline battery, the half-reaction would be two-electron oxidation of hydroxide anions, for which  $z_- = -1$ ,  $s_+ = 0$ ,  $s_- = 2$ , and  $n = 2$ . Because solvent molecules are not involved in the interfacial reaction, the solvent flux at the interfaces is zero.

Taking these experimental conditions and physical assumptions into account, the transport problem is

$$\text{GE: } \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}, \quad [17]$$

which follows from the salt material balance because  $t_+$  is constant and there is no convection. GE is subject to boundary conditions

$$\begin{aligned} \text{BCi: } -\frac{s_+i}{nF} &= -\nu_+D \frac{\partial c}{\partial x} \Big|_{x=0} + \frac{t_+i}{Fz_+} \quad \text{and} \\ \text{BCii: } -\frac{s_+i}{nF} &= -\nu_+D \frac{\partial c}{\partial x} \Big|_{x=L} + \frac{t_+i}{Fz_+}, \end{aligned} \quad [18]$$

derived by equating the interfacial reaction rate driven by the applied current to the solution-phase flux law that describes cation diffusion and migration at both faces of the slab. Last, the initial condition

$$\text{IC: } c(0, x) = c_\infty \quad [19]$$

expresses that the electrolyte starts in a uniform state.

By recasting Eqs. 17 through 19 in terms of unitless variables

$$\tau = \frac{Dt}{L^2}, \quad \xi = \frac{x}{L}, \quad \text{and} \quad \theta_1 = \frac{DFz_+\nu_+(c - c_\infty)}{i \left( \frac{s_+z_+}{s_+z_+ + s_-z_-} - t_+ \right) L}, \quad [20]$$

the transient concentration  $\theta_1(\tau, \xi)$  of an initially equilibrated slab of redox-active binary electrolytic solution to a step change in current is seen to satisfy the dimensionless equation system

$$\text{GE: } \frac{\partial \theta_1}{\partial \tau} = \frac{\partial^2 \theta_1}{\partial \xi^2} \quad [21]$$

$$\text{BCi: } \frac{\partial \theta_1}{\partial \xi} \Big|_{\xi=0} = -1 \quad \text{BCii: } \frac{\partial \theta_1}{\partial \xi} \Big|_{\xi=1} = -1 \quad [22]$$

$$\text{IC: } \theta_1(0, \xi) = 0. \quad [23]$$

Prof. White's 2014 question from the preamble was asking for derivations of two different solutions of this problem.

To get an error-function series, the method laid out in the "Error-function series from Laplace transforms" section can be implemented again, taking account of the different boundary conditions. In Laplace space, we have

$$\text{GE: } \frac{d^2 \bar{\theta}_1}{d\xi^2} - s \bar{\theta}_1 = 0, \quad [24]$$

$$\text{BCi: } \frac{d\bar{\theta}_1}{d\xi} \Big|_0 = -\frac{1}{s}, \quad \text{and} \quad \text{BCii: } \frac{d\bar{\theta}_1}{d\xi} \Big|_1 = -\frac{1}{s}. \quad [25]$$

This can be solved directly, or we can use the result from the prior section, as promised. One can exploit the principle of superposition to show that the function

$$\bar{\theta}_1(\xi) = \bar{\theta}_0(\xi) - \bar{\theta}_0(1 - \xi), \quad [26]$$

defined in terms of the Laplace transformed solution of the meltdown problem,  $\bar{\theta}_0(\xi)$ , satisfies Eqs. 24 and 25; the boundary conditions can be verified by observing that

$$\begin{aligned} \frac{d\bar{\theta}_1}{d\xi} &= \frac{d\bar{\theta}_0(u)}{du} \Big|_{\xi} - \frac{d\bar{\theta}_0(u)}{du} \Big|_{1-\xi} \frac{d(1-\xi)}{d\xi} \\ &= \frac{d\bar{\theta}_0}{d\xi} \Big|_{\xi} + \frac{d\bar{\theta}_0}{d\xi} \Big|_{1-\xi}. \end{aligned} \quad [27]$$

The application of several hyperbolic identities (see the Appendix) allows  $\bar{\theta}_1$  to be written compactly as

$$\bar{\theta}_1(\xi) = \frac{\sinh \left[ \left( \frac{1}{2} - \xi \right) \sqrt{s} \right]}{s^{3/2} \cosh \left( \frac{1}{2} \sqrt{s} \right)}, \quad [28]$$

which the Maclaurin expansion process from the prior section proves equivalent to

$$\bar{\theta}_1(\xi) = \frac{e^{-\xi\sqrt{s}}}{s^{3/2}} + \sum_{k=1}^{\infty} (-1)^k \left[ \frac{e^{-(k-\xi)\sqrt{s}}}{s^{3/2}} + \frac{e^{-(k+\xi)\sqrt{s}}}{s^{3/2}} \right]. \quad [29]$$

Laplace inversion of this sum term by term produces

$$\begin{aligned} \theta_1(\tau, \xi) &= 2\sqrt{\tau} \left\{ \text{i!erfc} \left( \frac{\xi}{2\sqrt{\tau}} \right) \right. \\ &\quad \left. + \sum_{k=1}^{\infty} (-1)^k \left[ \text{i!erfc} \left( \frac{k-\xi}{2\sqrt{\tau}} \right) + \text{i!erfc} \left( \frac{k+\xi}{2\sqrt{\tau}} \right) \right] \right\}, \end{aligned} \quad [30]$$

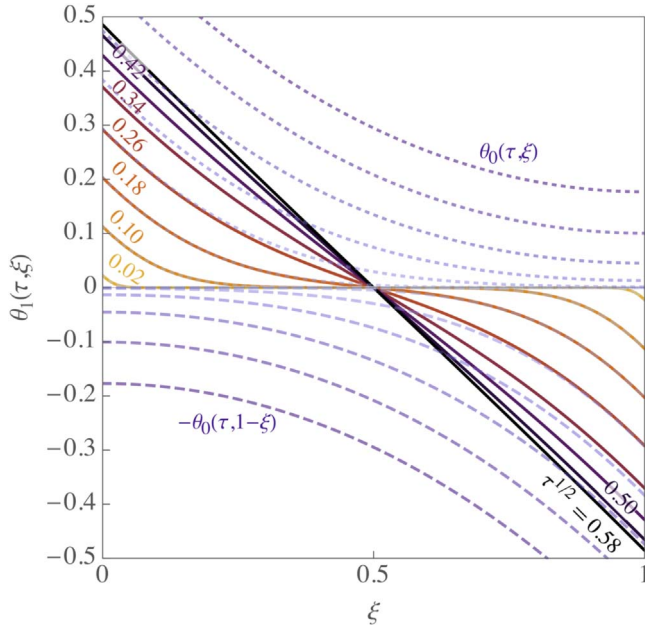
the desired error-function series. This is Eq. 22 of Monroe and Newman,<sup>7</sup> as Prof. White requested in 2014.

Plots of Eq. 30 at various times are presented in Fig. 4. As mandated by the boundary conditions from Eq. 22, the slopes of the concentration distribution at the inner and outer boundaries equate, and are constant at all times. The constant-current step problem appears to reach its steady state faster than the meltdown problem attains its long-time behavior, with the transient change in profiles diminishing substantially after  $\sqrt{\tau} = 1/2$ .

To emphasize the connection with the meltdown problem, Fig. 4 also shows the functions  $\theta_0(\tau, \xi)$  and  $-\theta_0(\tau, 1 - \xi)$  whose Laplace transforms were superposed in Eq. 26. The steady accumulation terms characteristic of the earlier problem cancel out between these two functions, yielding a transient that averages to zero at all times.

### Fourier Series from Laplace Transforms

We should check Eq. 30 against a more typical answer to the constant-current step problem. We could start over, and attack the



**Figure 4.** Concentration response to a current step. (Warm colors, solid lines) Position dependence of the error-function series expansion of  $\theta_1(\tau, \xi)$  at several values of the square root of dimensionless time. The series was truncated after five terms in the sum from Eq. 30. (Cool colors, dashed lines) Position dependences of  $\theta_0(\tau, \xi)$  (shorter dashes) and  $-\theta_0(\tau, 1 - \xi)$  (longer dashes) at the same times. By the principle of superposition, these two functions add up to  $\theta_1$ .

system of Eqs. 21 through 23 with separation of variables, but an alternative approach to inverting the Laplace transform is worth discussing. Inspection of Eq. 28 shows that  $\bar{\theta}_1(\xi)$  is a meromorphic function: it is complex differentiable with respect to  $s$  everywhere excepting a countable set of isolated points (poles). Laplace transforms that arise from physical problems—particularly diffusion problems—often have this character.

Mittag-Leffler's partial fractions theorem helps to recast unpleasant looking, but nevertheless meromorphic, Laplace transforms in more easily invertible forms. The main implication of the theorem—proved very clearly by Spiegel et al. (see Ref. 8, problem 7.33)—is that if  $f(s)$  is any meromorphic complex function analytic at  $s = 0$ , with a countable number of simple poles  $s_k$  ordered such that  $|s_{k+1}| \geq |s_k|$ , and if  $\text{Res}\{f(s_k)\}$  stands for the residue of  $f(s)$  at  $s_k$ , defined as

$$\text{Res}\{f(s_k)\} = \lim_{s \rightarrow s_k} (s - s_k) f(s), \quad [31]$$

then the infinite sum

$$f(s) = f(0) + \sum_{k=1}^{\infty} \frac{\text{Res}\{f(s_k)\}}{s_k} + \sum_{k=1}^{\infty} \frac{\text{Res}\{f(s_k)\}}{s - s_k} \quad [32]$$

provides an exact series expansion of  $f(s)$ . Moreover, by taking a limit of both sides, one can see that

$$\lim_{s \rightarrow \infty} f(s) = f(0) + \sum_{k=1}^{\infty} \frac{\text{Res}\{f(s_k)\}}{s_k} \quad [33]$$

connects the large- $s$  limit of  $f(s)$  to the first two terms on the right of the expansion.

For example, the function  $\bar{\theta}_1(\xi)$  from Eq. 28 affords a simple pole at  $s = 0$ . Because the hyperbolic cosine in its denominator goes to zero at imaginary half-odd-integer multiples of  $\pi$ ,  $\bar{\theta}_1(\xi)$  also has simple poles when

$$s_k = -\pi^2(2k - 1)^2 \quad [34]$$

for all positive integers  $k$ . It satisfies all of the conditions needed to implement a Mittag-Leffler expansion, except analyticity at  $s = 0$  (because  $\bar{\theta}_1(\xi)$  has a pole there). We observe the limiting behavior

$$\lim_{s \rightarrow 0} s \bar{\theta}_1(\xi) = \frac{1}{2} - \xi, \quad [35]$$

which is worth computing anyway because the final value theorem (cf. Varma and Morbidelli, Chapter 8.2.7<sup>9</sup>) tells us it is the steady-state (long-time asymptotic) solution of the problem. Forming the function  $g(s)$  by removing the pole at zero, as

$$g(s) = \bar{\theta}_1(\xi) - \frac{\frac{1}{2} - \xi}{s}, \quad [36]$$

defines a meromorphic function analytic at  $s = 0$ , and consequently amenable to Mittag-Leffler expansion.

At pole  $s_k$ , the residue of our newly defined function  $g(s)$  is

$$\text{Res}\{g(s_k)\} = \lim_{s \rightarrow s_k} \frac{(s - s_k) \sinh\left(\frac{1}{2}\sqrt{s}\right) \cosh(\xi\sqrt{s})}{s^{3/2} \cosh\left(\frac{1}{2}\sqrt{s}\right)}, \quad [37]$$

which has been simplified with the hyperbolic identity  $\sinh(A + B) = \sinh(A) \cosh(B) + \cosh(A) \sinh(B)$ . One can facilitate taking the limit by introducing a variable  $\omega$  such that  $\frac{1}{2}\sqrt{s} = \frac{1}{2}\sqrt{s_k} + \omega$ . As detailed in the Appendix, liberal application of hyperbolic identities for  $\sinh(A + B)$  and  $\cosh(A + B)$  simplifies Eq. 37 all the way down to

$$\begin{aligned} \text{Res}\{g(s_k)\} &= \lim_{\omega \rightarrow 0} 4\omega \sqrt{s_k} g(s_k + 4\omega \sqrt{s_k}) \\ &= \frac{4 \cosh(\xi \sqrt{s_k})}{s_k}, \end{aligned} \quad [38]$$

after which one can insert Eq. 34, use that  $\cosh(jx) = \cos(x)$ , where  $j$  is the imaginary unit, and immediately write the Mittag-Leffler expansion of  $g(s)$  via Eq. 32 as

$$\begin{aligned} g(s) &= g(0) + \sum_{k=1}^{\infty} \frac{4 \cos[(2k - 1)\pi\xi]}{(2k - 1)^4 \pi^4} \\ &\quad - \sum_{k=1}^{\infty} \frac{4 \cos[(2k - 1)\pi\xi]}{(2k - 1)^2 \pi^2 [s + \pi^2(2k - 1)^2]}, \end{aligned} \quad [39]$$

an easily invertible Laplace transform.

The first two terms on the right of Eq. 39 are independent of  $s$ . Despite their rather complicated forms, the relationship from Eq. 33 requires that they exactly cancel out, because  $\lim_{s \rightarrow \infty} \bar{\theta}_1(\xi) = 0$ . Indeed,  $g(0)$  is a removable singularity of  $g(s)$ ,

$$g(0) = \lim_{s \rightarrow 0} \left[ \bar{\theta}_1(\xi) - \frac{\frac{1}{2} - \xi}{s} \right] = -\frac{4\xi^3 - 6\xi^2 + 1}{24}, \quad [40]$$

dependent only on  $\xi$ , and it can be shown that

$$\sum_{k=1}^{\infty} \frac{4 \cos[(2k - 1)\pi\xi]}{(2k - 1)^4 \pi^4} = -g(0), \quad [41]$$

that is, the sum over all residues of  $g(s)$  divided by the corresponding pole locations is just the Fourier series expansion of  $-g(0)$ . Observe also that  $g(0)$  is a function of  $\xi$  compatible with the basis functions  $\cos[(2k - 1)\pi\xi]$ : it averages to zero over  $0 \leq \xi \leq 1$  and has zero slope at both of the interval's ends, and consequently does not

succumb to the Gibbs phenomenon. Although we have evaluated the two lead terms in the expansion of  $g(s)$  here for completeness, one generally does not need to work out such terms when using Mittag-Leffler expansion to invert a Laplace transform, because they usually cancel each other out. In the unusual case where the transform inverts to a time-domain function containing a unit impulse at zero, the Bromwich integral representation of the inverse Laplace transform (see Hildebrand, Chapter 11.2<sup>10</sup>) shows that  $g(s)$  will have a nonzero limit at infinity. Equation 33 still helps to simplify calculations in these cases.

Thus, recalling that  $\bar{\theta}_1(\xi) = \frac{1}{s}(\frac{1}{2} - \xi) + g(s)$ , the transform pair  $\mathcal{L}^{-1}\{1/(s+a)\} = e^{-at}$  enables term-by-term inversion to produce

$$\theta_1(\tau, \xi) = \frac{1}{2} - \xi - \frac{4}{\pi^2} \sum_{k=1}^{\infty} \frac{\cos[(2k-1)\pi\xi] e^{-\pi^2(2k-1)^2\tau}}{(2k-1)^2}. \quad [42]$$

This is the other result Ralph asked for in 2014—Eq. 21 of the “dendrite paper” he mentioned.<sup>7</sup>

### Integrated Integrated Error Functions, etc.

Many mass-transfer problems lead to an ordinary differential equation that elementary transport classes do not usually cover in its general form. The error function differential equation is defined for integer  $n$  as

$$\frac{d^2y}{dz^2} + 2z \frac{dy}{dz} - 2ny = 0, \quad [43]$$

and has solutions involving repeated integrals of complementary error functions when  $n \geq 1$ . This equation comes up when analyzing boundary-layer problems amenable to similarity transformations. Taylor dispersion (see Levich, Chapter 2.21<sup>11</sup>) is an example of the  $n = -1$  case; examples where  $n = 0$  include what is commonly called “Stokes’s first problem”—the impulsive motion of a flat plate through a viscous fluid (analyzed in article 334a of Lamb’s *Hydrodynamics*<sup>12</sup>)—as well as the diffusion-layer penetration problem; the meltdown problem is a typical example where  $n = 1$ . The “Eq. 21a” Ralph asked about in his 2015 query states that when  $n \geq 0$ , Eq. 43 is solved generally by

$$y(z) = Ai^n \operatorname{erfc}(z) + Bi^n \operatorname{erfc}(-z), \quad [44]$$

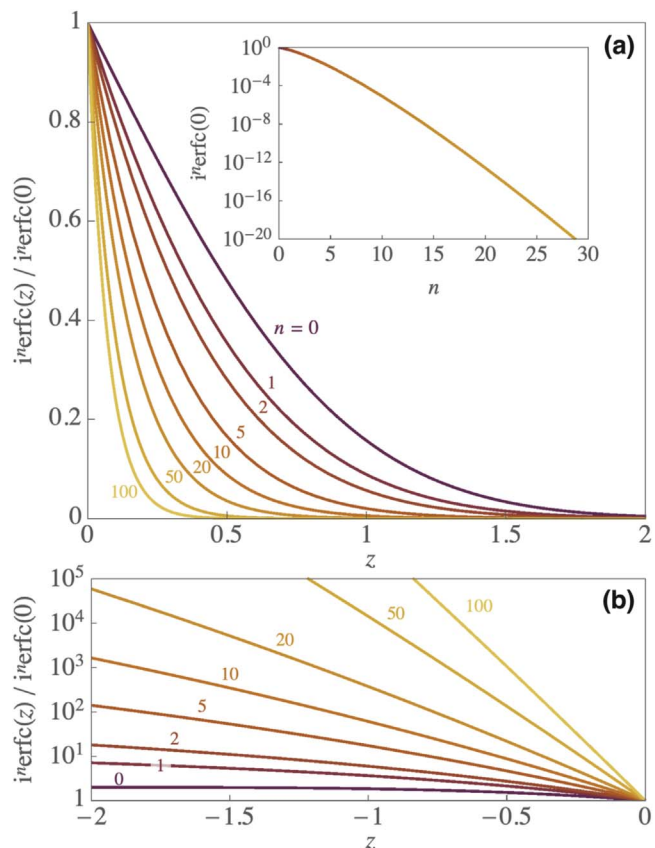
where  $A$  and  $B$  are arbitrary constants and  $i^n \operatorname{erfc}(z)$  is the  $n$ th integrated complementary error function.

We have already seen the first integrated complementary error function; the action that defines it can be repeated indefinitely. One defines the  $n$ th integrated complementary error function  $i^n \operatorname{erfc}(z)$  by integrating  $\operatorname{erfc}(z)$  from  $z$  to infinity  $n$  times. The definition can be stated inductively, a process that also extends  $i^n \operatorname{erfc}(z)$  to integer  $n \geq -1$ , by letting

$$\begin{aligned} i^{-1} \operatorname{erfc}(z) &= \frac{2}{\sqrt{\pi}} e^{-z^2} \quad \text{and} \\ i^n \operatorname{erfc}(z) &= \int_z^{\infty} i^{n-1} \operatorname{erfc}(z) dz \quad ; \quad n = 0, 1, 2, \dots \end{aligned} \quad [45]$$

Note that this definition has it that  $i^0 \operatorname{erfc}(z)$  is just  $\operatorname{erfc}(z)$ , the standard complementary error function. Setting  $n = 1$  here consequently reproduces the definition of  $i^1 \operatorname{erfc}(z)$  in Eq. 6.

Repeated integration is not practical for numerical calculations. But the error function differential equation is useful because  $n$ th integrated complementary error functions can be computed at any complex  $z$  without performing a string of integrals. For integer  $n \geq 1$  they obey an algebraic recurrence relation



**Figure 5.** The family of integrated complementary error functions. (a, main panel) Plots of  $i^n \operatorname{erfc}(z)/i^n \operatorname{erfc}(0)$  from  $z = 0$  to 2 at a range of  $n$  values, calculated at higher  $n$  with recurrence relation 46. The functions decrease super-exponentially with  $z$  at all  $n$ . (a, inset) Values of  $i^n \operatorname{erfc}(0)$  from Eq. 48. These decrease rapidly as  $n$  rises. (b) Normalized functions  $i^n \operatorname{erfc}(-z)/i^n \operatorname{erfc}(0)$  rise exponentially as the argument grows more negative.

$$i^n \operatorname{erfc}(z) = -\frac{z}{n} i^{n-1} \operatorname{erfc}(z) + \frac{1}{2n} i^{n-2} \operatorname{erfc}(z), \quad [46]$$

reported by Abramowitz and Stegun.<sup>5</sup> This shows, for example, that

$$i^1 \operatorname{erfc}(z) = -z \operatorname{erfc}(z) + \frac{1}{\sqrt{\pi}} e^{-z^2}, \quad [47]$$

which can also be proved by integrating  $z e^{-z^2}$  with a  $u$ -substitution and equating this closed-form result to the integral of  $z e^{-z^2}$  by parts. Recurrence relation 46 is the “Eq. 21b” mentioned in Ralph’s 2015 question, and Eq. 47 gives the case where  $n = 1$ .

Bearing in mind how  $i^{-1} \operatorname{erfc}(z)$  and  $i^0 \operatorname{erfc}(z)$  are defined, recurrence relation 46 can be used to show that

$$i^n \operatorname{erfc}(0) = \begin{cases} \frac{\left(\frac{1}{2}n - \frac{1}{2}\right)!}{n! \sqrt{\pi}} & \text{if } n \text{ is odd} \\ \frac{1}{2^n \left(\frac{1}{2}n\right)!} & \text{if } n \text{ is even} \end{cases} \quad [48]$$

for any integer  $n \geq 0$ . Thus the initial values of integrated complementary error functions decrease steadily as the number of integrations rises. At all  $n$ , the function  $i^n \operatorname{erfc}(z)$  decays to zero rapidly with increasing  $z$ . When the argument is negative,  $i^n \operatorname{erfc}(-z)$  increases fast as  $z$  gets further from 0. Figure 5 shows the

characteristic behavior of this family of special functions graphically.

One can use a formula commonly attributed to Cauchy to understand both the error-function differential equation and the recurrence relation. (NB: I could not locate a solid primary reference for this formula; Oldham and Spanier cite the earliest use of it I could find, by Riemann.<sup>13</sup>) Cauchy's formula for repeated integration says that for any analytic function  $h(z)$ , if the  $n$ th integral of  $h(z)$  from base  $a$  to variable  $z$  is defined as the function  $h^{(-n)}(z)$ ,

$$h^{(-n)}(z) = \int_a^z \int_a^{w_1} \dots \int_a^{w_{n-2}} \int_a^{w_{n-1}} h(w_n) dw_n dw_{n-1} \dots dw_1, \quad [49]$$

then the multiple integration can be expressed in the form of a single integral,

$$h^{(-n)}(z) = \frac{1}{(n-1)!} \int_a^z (z-w)^{n-1} h(w) dw. \quad [50]$$

Since  $e^{-z^2}$  is an analytic function, so is  $i^n \operatorname{erfc}(z)$ . Choosing the base to be  $\infty$  in Cauchy's formula and swapping the limits of integration leads to the expression

$$i^n \operatorname{erfc}(z) = \frac{2}{n! \sqrt{\pi}} \int_z^\infty (w-z)^n e^{-w^2} dw, \quad [51]$$

valid for  $n \geq 0$ . Application of the Leibniz rule for differentiation of integrals directly produces the recurrence formula from this result. The Appendix also shows how to derive a formula from this integral that expresses  $i^n \operatorname{erfc}(z)$  explicitly in terms of  $e^{-z^2}/\sqrt{\pi}$ ,  $\operatorname{erfc}(z)$ , and rational polynomials of  $z$ , an alternative to the recurrence relation that can help when implementing numerical algorithms.

The single-integral form of  $i^n \operatorname{erfc}(z)$  from Eq. 51 also can be used to show that both  $i^n \operatorname{erfc}(z)$  and  $i^n \operatorname{erfc}(-z)$  satisfy ordinary differential Eq. 43. Since these two functions are linearly independent and both analytic everywhere in the complex plane, Eq. 44 provides a general solution of the error-function differential equation. These observations answer Ralph's 2015 question from the preamble, not just for  $n = 1$  but for every integer  $n \geq 0$ .

Last it is worth noting that Abramowitz and Stegun present the Laplace transform pair

$$\mathcal{L}^{-1} \left\{ \frac{e^{-a\sqrt{s}}}{s^{1+\frac{1}{2}n}} \right\} = (2\sqrt{\tau})^n i^n \operatorname{erfc} \left( \frac{a}{2\sqrt{\tau}} \right), \quad [52]$$

valid for  $a \geq 0$  and  $n = 0, 1, 2, \dots$ <sup>5</sup> Knowledge of this form is helpful when performing asymptotic expansions of functions in the Laplace domain.

### Thin-film Cottrell Equation

Integrated complementary error functions and the error-function differential equation are useful for analyzing many electrochemical transport problems (some examples from my group's research appear in Refs. 14, 15, and 16). I hope that the following new problem, which brings the methods discussed here together, will anticipate a future question from Ralph.

Consider a thin film of a binary electrolytic solution sandwiched between two electrodes that undergo the same reversible electrochemical half-reaction with dissolved ions. More tangibly, we could picture a lithium-ion battery separator impregnated with an electrolyte like  $\text{LiPF}_6$  in propylene carbonate, sandwiched between lithium-metal electrodes in a Swagelok cell. At time 0, a high voltage is applied, which immediately drives the salt concentration at the inner electrode to 0. We seek a smooth function that models the current response to this step change in voltage. Because of the finite thickness of the film, we expect this result to differ from the standard Cottrell equation, which assumes a semi-infinite geometry.<sup>17</sup>

Here, the physical picture and underlying assumptions match the ones we established earlier when modelling the response of a plane electrolyte slab to a constant current. We again imagine that the electrolyte domain has thickness  $L$ . The salt distribution  $c(t, x)$  across the thin film is governed by transient diffusion Eq. 17, and the system starts with uniform concentration  $c_\infty$ , an initial condition identical to Eq. 19. Because the salt concentration is driven to zero at the inner electrode,

$$\text{BCi: } c(t, 0) = 0 \quad [53]$$

at time  $t$  after the voltage is applied. Since the electrode half-reactions are identical, the rate at which reduction occurs on one face of the film matches the oxidation rate on the other, and the reactants of one half-reaction are the products of the other. Therefore, the total amount of salt dissolved in the film is conserved as current is passed. This provides a second boundary condition, that

$$\text{BCii: } c_\infty L = \int_0^L c(t, x) dx, \quad [54]$$

independent of time  $t$ . Writing BCii in this way avoids the need to make a symmetry argument, or to write a boundary condition involving the current, which is the unknown for which we intend to solve.

Once a function  $c(t, x)$  has been found that satisfies Eqs. 17, 19, 53, and 54, an expression that gives the instantaneous current can be found with

$$i(t) = - \frac{nFz_+ \nu_+ D}{z_+ s_+ + nt_+} \frac{\partial c}{\partial x} \bigg|_{x=0}, \quad [55]$$

derived by isolating  $i$  from BCi in Eq. 18. (That condition governs mass flux at the inner boundary whether or not the current density is constant.) The result for  $i(t)$  determined by the gradient of  $c(t, x)$  at the inner boundary will constitute our modified Cottrell equation.

This problem can be simplified dramatically by non-dimensionalization. Let dimensionless time  $\tau$  and position  $\xi$  be defined as in Eq. 20, and let

$$\theta_2 = \frac{c - c_\infty}{c_\infty} \quad [56]$$

represent the local electrolyte concentration in the thin film relative to the equilibrium bulk concentration, in units of the bulk concentration. (This equals 0 at the bulk concentration and equals  $-1$  when the local electrolyte concentration vanishes.) The essential information in the modified Cottrell equation we seek can be expressed in the form of a dimensionless current  $I$ , defined as

$$I(\tau) = - \frac{i(z_+ s_+ + nt_+) L}{nFz_+ \nu_+ D c_\infty} = \frac{\partial \theta}{\partial \xi} \bigg|_{\tau, 0}, \quad [57]$$

which includes a negative sign to make it naturally positive.

Inside the thin film after the voltage change, the dimensionless equation system

$$\text{GE: } \frac{\partial \theta_2}{\partial \tau} = \frac{\partial^2 \theta_2}{\partial \xi^2} \quad [58]$$

$$\text{BCi: } \theta_2(\tau, 0) = -1 \quad \text{BCii: } \int_0^1 \theta_2(\tau, \xi) d\xi = 0 \quad [59]$$

$$\text{IC: } \theta_2(0, \xi) = 0 \quad [60]$$

governs  $\theta_2(\tau, \xi)$ . In the Laplace domain this becomes

$$\text{GE: } \frac{d^2 \bar{\theta}_2}{d\xi^2} - s \bar{\theta}_2 = 0 \quad [61]$$

$$\text{BCi: } \bar{\theta}_2(0) = -\frac{1}{s} \quad \text{BCii: } \int_0^1 \bar{\theta}_2(\xi) d\xi = 0, \quad [62]$$

solved by the transformed concentration distribution

$$\bar{\theta}_2(\xi) = \frac{e^{-(1-\xi)\sqrt{s}} - e^{-\xi\sqrt{s}}}{s(1 - e^{-\sqrt{s}})}, \quad [63]$$

as described in the Appendix. This Laplace transform can be dealt with in a couple of ways.

A natural plan of attack might be to get a Fourier-series solution. To do this we can exploit Mittag-Leffler expansion. A little rearrangement shows that Eq. 63 can be expressed equivalently as

$$\bar{\theta}_2(\xi) = \frac{\sinh(\xi\sqrt{s})}{s \tanh\left(\frac{1}{2}\sqrt{s}\right)} - \frac{\cosh(\xi\sqrt{s})}{s}, \quad [64]$$

which is meromorphic with a simple pole at  $s = 0$  and other simple poles at

$$s_k = -4\pi^2 k^2 \quad [65]$$

for all positive natural numbers  $k$ . The steady-state concentration distribution is

$$\lim_{s \rightarrow 0} s \bar{\theta}_2(\xi) = \lim_{s \rightarrow 0} \frac{\sinh(\xi\sqrt{s})}{\tanh\left(\frac{1}{2}\sqrt{s}\right)} - \cosh(\xi\sqrt{s}) = 2\xi - 1, \quad [66]$$

allowing the singularity at the origin to be removed by defining a function  $F(s)$  such that

$$F(s) = \bar{\theta}_2(\xi) - \frac{2\xi - 1}{s}; \quad [67]$$

this is analytic at  $s = 0$  and therefore amenable to Mittag-Leffler expansion. The residue of  $F(s)$  at pole  $s_k$  is

$$\text{Res}\{F(s_k)\} = \lim_{s \rightarrow s_k} \frac{(s - s_k) \sinh(\xi\sqrt{s})}{s \tanh\left(\frac{1}{2}\sqrt{s}\right)}, \quad [68]$$

in which a second term that vanishes in the limit was discarded. Introducing a variable  $\omega$  such that  $\frac{1}{2}\sqrt{s} = \frac{1}{2}\sqrt{s_k} + \omega$  makes this a limit at the origin. Observing that

$$\frac{s - s_k}{s} = \frac{4\omega(\sqrt{s_k} + \omega)}{s_k + 4\omega\sqrt{s_k} + 4\omega^2} = \frac{4\omega}{\sqrt{s_k}} + O(\omega^2), \quad [69]$$

the residue of  $F(s)$  at  $s_k$  is therefore

$$\begin{aligned} \text{Res}\{F(s_k)\} &= \lim_{\omega \rightarrow 0} \frac{4\omega \sinh\left[2\xi\left(\frac{1}{2}\sqrt{s_k} + \omega\right)\right]}{\sqrt{s_k} \tanh\left(\frac{1}{2}\sqrt{s_k} + \omega\right)} \\ &= \lim_{\omega \rightarrow 0} \frac{4\omega \sinh(\xi\sqrt{s_k})}{\sqrt{s_k} \tanh(\omega)} = \frac{4 \sinh(\xi\sqrt{s_k})}{\sqrt{s_k}}. \end{aligned} \quad [70]$$

Inserting these residues and the corresponding  $s_k$  values from Eq. 65 into the general Mittag-Leffler series, Eq. 32, and noting that the limit formula from Eq. 33 requires that the  $s$ -independent terms in the Mittag-Leffler expansion cancel out, we are left with

$$\bar{\theta}_2(\xi) = \frac{2\xi - 1}{s} + \sum_{k=1}^{\infty} \frac{2 \sin(2\pi k \xi)}{\pi k} \frac{1}{s + 4\pi^2 k^2}. \quad [71]$$

Inverting this term by term produces

$$\theta_2(\tau, \xi) = 2\xi - 1 + \frac{2}{\pi} \sum_{k=1}^{\infty} \frac{e^{-4\pi^2 k^2 \tau} \sin(2\pi k \xi)}{k}, \quad [72]$$

the Fourier-series solution of the problem.

To get the current density (flux) that results from the step change in voltage, we need the derivative of the electrolyte concentration at the boundary. Analysis of the Fourier series yields

$$\left. \frac{\partial \theta_2}{\partial \xi} \right|_{\tau, \xi} = 2 \left( 1 + 2 \sum_{k=1}^{\infty} e^{-4\pi^2 k^2 \tau} \right), \quad [73]$$

in which the number of terms needed to achieve a given accuracy decreases as time increases. This form of the flux clearly shows the limiting behavior in the steady state (as  $\tau \rightarrow \infty$ ), where the slope reaches a value of 2, which we recognize as the dimensionless limiting flux through a slab.

Ideally we should like to have a series that requires fewer terms at short times, which will also help relate our analysis to the standard Cottrell equation. This can be achieved by deriving an error-function series. Return to Eq. 63 and perform a large- $s$  expansion using the Maclaurin series

$$\frac{1}{1 - e^{-\sqrt{s}}} = \sum_{k=0}^{\infty} e^{-k\sqrt{s}} \quad [74]$$

to see that

$$\bar{\theta}_2(\xi) = \sum_{k=0}^{\infty} \left[ \frac{e^{-[(1-\xi)+k]\sqrt{s}}}{s} - \frac{e^{-(\xi+k)\sqrt{s}}}{s} \right]. \quad [75]$$

Recognizing the form that appears in the transform pair from Eq. 52 with  $n = 0$ , termwise inversion shows that

$$\theta_2(\tau, \xi) = - \sum_{k=0}^{\infty} \left[ i^0 \text{erfc}\left(\frac{\xi + k}{2\sqrt{\tau}}\right) - i^0 \text{erfc}\left(\frac{1 - \xi + k}{2\sqrt{\tau}}\right) \right], \quad [76]$$

which we note arrived much faster than the Fourier series. The derivative of this function at the boundary can also be evaluated directly. After a little rearrangement we get the compact expression

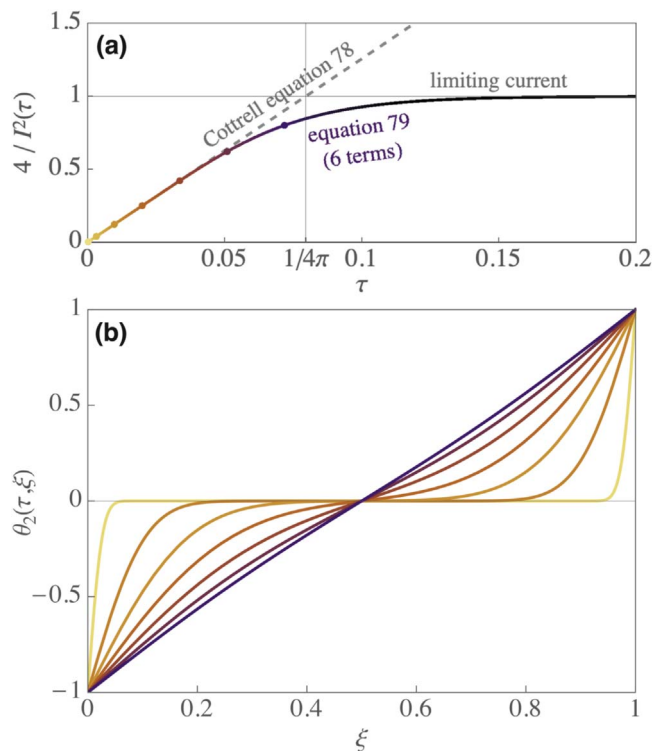
$$\left. \frac{\partial \theta_2}{\partial \xi} \right|_{\tau, 0} = \frac{1}{\sqrt{\pi\tau}} \left( 1 + 2 \sum_{k=1}^{\infty} e^{-\frac{k^2}{4\tau}} \right), \quad [77]$$

which requires fewer terms of the summation at short times. Note that in the asymptotic regime where  $\tau \ll 1/4$  (that is,  $2\sqrt{\tau} \ll 1$ ), this result reduces to

$$I(\tau) \approx \frac{1}{\sqrt{\pi\tau}}, \quad [78]$$

which becomes the familiar Cottrell equation<sup>17</sup> when returned to dimensional variables (see the Appendix).

Surprisingly, the two series expressing the modified Cottrell equation from Eqs. 73 and 77 match exactly when  $\tau = 1/(4\pi)$  (or  $4\pi\tau = 1$ ). At later times expansion 73 requires fewer terms for a given level of precision, while at earlier times, Eq. 77 needs fewer. At  $4\pi\tau = 1$ , the sums to five terms are only  $3 \times 10^{-49}$  below the exact values obtained with an infinite number of terms; the sums to six terms are  $6 \times 10^{-67}$  less than exact. Agreement between the expansions can be probed further by examining time derivatives of



**Figure 6.** A modified Cottrell equation for thin films. (a) Equation 79 (solid colored line) and the standard Cottrell equation (dashed gray line), presented as  $4/I^2(\tau)$ . The limiting current satisfies  $4/I^2 = 1$ . (b) Dimensionless profiles from Eq. 76, at  $\tau$  values corresponding to the circular markers on the modified Cottrell curve from (a).

$I(\tau)$  at  $4\pi\tau = 1$ : the first through fourth derivatives yielded by the Fourier and error-function series agree to more than 40 significant digits when they are truncated at five terms, and 60 digits when truncated at six.

Thus excellent accuracy at all times, with parsimonious numbers of terms in the series, is provided by the function

$$I(\tau) = \begin{cases} \frac{1}{\sqrt{\pi\tau}} \left( 1 + 2 \sum_{k=1}^{\infty} e^{-\frac{k^2}{4\tau}} \right) & \text{if } 4\pi\tau < 1 \\ 2 \left( 1 + 2 \sum_{k=1}^{\infty} e^{-4\pi^2 k^2 \tau} \right) & \text{if } 4\pi\tau \geq 1 \end{cases}, \quad [79]$$

which switches between the two expansions at  $4\pi\tau = 1$ . Figure 6 plots current as  $4/I^2(\tau)$ , which is bounded between 0 initially and 1 at the limiting current, as well as indicative concentration profiles from Eq. 76.

### Conclusions

Although computers are efficient and easy to use, pen-and-paper methods can still aid the understanding of electrochemical transport problems. Most students of transport phenomena know how to solve transient diffusion problems by separation of variables, which yields profiles described by Fourier series. Fourier series do a good job of explaining how systems relax toward steady-state or long-time asymptotic behavior, but they converge poorly at times shortly after sharp changes in boundary conditions. In the short-time regime, values of profiles calculated at given points may also suffer from systematic error due to the Gibbs phenomenon. Error-function series resolve these issues: their individual terms change smoothly and monotonically with respect to position, and they converge rapidly at

short times. Laplace transformation of simple diffusion problems provides a route to derive both types of series.

Given a Laplace transformed profile that solves a diffusion problem, its Fourier series in the time domain can be calculated by exploiting Mittag-Leffler expansion about the poles in Laplace space. Alternatively, an error-function series can be identified by expanding the same Laplace transformed profile around infinitely large values of the Laplace variable. I presented three example problems to demonstrate these techniques: the meltdown problem, constant-current polarization of an electrolytic slab, and Cottrell polarization of an electrolytic thin film.

In closing I would like to thank Ralph for all of his communications over the years. I look forward to further discussion, and anticipate that it will lead to many more interesting problems supported by novel analysis.

### Acknowledgments

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### “Appendix: Selected Details”

*Derivation of Eq. 4 by separation of variables.*—A differential system’s boundary conditions must be homogeneous to separate variables. Typically one homogenizes a problem by expressing the transient relaxation of its initial condition relative to a long-time asymptotic solution that satisfies the inhomogeneous boundary conditions. Most problems reach steady states, for which one can neglect the accumulation term (e.g.,  $\partial\theta_0/\partial\tau$ ) in GE, discard IC, and solve the remaining system to satisfy the BCs. Unusually, the meltdown problem has no steady state: the heat input at one boundary makes the average temperature  $\langle\theta_0\rangle$ , defined as

$$\langle\theta_0\rangle(\tau) = \int_0^1 \theta_0(\tau, \xi) d\xi, \quad [A-1]$$

continue to rise, even after information from the initial temperature distribution has dissipated. To quantify this average temperature rise, integrate both sides of Eq. 1 from  $\xi = 0$  to  $\xi = 1$  to find

$$\frac{d\langle\theta_0\rangle}{d\tau} = \frac{\partial\theta_0}{\partial\xi} \Big|_{\tau,1} - \frac{\partial\theta_0}{\partial\xi} \Big|_{\tau,0} = 1, \quad [A-2]$$

in which BCi and BCii from Eq. 2 have been used to prove the second equality, and integrate both sides with respect to  $\tau$ , using IC from Eq. 3 to show that

$$\langle\theta_0\rangle(\tau) = \tau. \quad [A-3]$$

The long-time temperature distribution,  $\lim_{\tau \gg 1} \theta_0(\tau, \xi)$ , can be thought of as a spatial correction  $\theta_0^\infty(\xi)$  to this rising average,

$$\lim_{\tau \gg 1} \theta_0(\tau, \xi) = \langle\theta_0\rangle(\tau) + \theta_0^\infty(\xi). \quad [A-4]$$

Insertion of this decomposition into GE, BCi, and BCii leaves the ordinary problem

$$\begin{aligned} \text{GE}^\infty: 1 &= \frac{d^2\theta_0^\infty}{d\xi^2}, \\ \text{BCi}^\infty: \frac{d\theta_0^\infty}{d\xi} \Big|_0 &= -1, \quad \text{BCii}^\infty: \frac{d\theta_0^\infty}{d\xi} \Big|_1 = 0, \end{aligned} \quad [A-5]$$

which can be solved directly. Integrating  $\text{GE}^\infty$  twice produces  $\theta_0^\infty(\xi) = \frac{1}{2}\xi^2 + a\xi + b$ , where  $a$  and  $b$  are undetermined constants. Since  $\text{BCi}^\infty$  and  $\text{BCii}^\infty$  are both Neumann conditions, they show redundantly that  $a = -1$ . Consistency of Eqs. A-1, A-3, and A-4 demands that  $\int_0^1 \theta_0^\infty(\xi) d\xi = 0$ , however, so  $b = \frac{1}{3}$ . Finally,

then, to get a problem amenable to separation of variables, we decompose  $\theta_0(\tau, \xi)$  as

$$\begin{aligned}\theta_0(\tau, \xi) &= \langle \theta_0 \rangle(\tau) + \theta_0^\infty(\xi) + \theta_0^t(\tau, \xi) \\ &= \tau + \frac{1}{2}\xi^2 - \xi + \frac{1}{3} + \theta_0^t(\tau, \xi),\end{aligned}\quad [\text{A}\cdot 6]$$

and insert it into equation system 1–3.

The transient relaxation  $\theta_0^t(\tau, \xi)$  introduced in decomposition A·6 is consequently governed by

$$\text{GE}^t: \quad \frac{\partial \theta_0^t}{\partial \tau} = \frac{\partial^2 \theta_0^t}{\partial \xi^2}, \quad [\text{A}\cdot 7]$$

which is subject to the homogeneous boundary conditions and initial condition

$$\begin{aligned}\text{BC}^t\text{i}: \quad \left. \frac{\partial \theta_0^t}{\partial \xi} \right|_{\tau, 0} &= 0, \quad \text{BC}^t\text{ii}: \quad \left. \frac{\partial \theta_0^t}{\partial \xi} \right|_{\tau, 1} = 0, \\ \text{IC}^t: \quad \theta_0^t(0, \xi) &= -\theta_0^\infty(\xi).\end{aligned}\quad [\text{A}\cdot 8]$$

At this stage we can separate variables by supposing that  $\theta_0^t(\tau, \xi) = T(\tau)X(\xi)$  for some  $T$  and  $X$ . GE<sup>t</sup> allows that

$$\frac{1}{X} \frac{d^2 X}{d\xi^2} = \frac{1}{T} \frac{dT}{d\tau} = -\lambda^2, \quad [\text{A}\cdot 9]$$

where  $-\lambda^2$  is an arbitrary constant. We choose a non-positive constant  $-\lambda^2$  here because it makes the second-order ordinary differential system produced by Eq. A·9 a Sturm–Liouville problem:

$$\frac{d^2 X}{d\xi^2} + \lambda^2 X = 0, \quad \text{with} \quad \left. \frac{dX}{d\xi} \right|_0 = 0 \quad \text{and} \quad \left. \frac{dX}{d\xi} \right|_1 = 0. \quad [\text{A}\cdot 10]$$

Every Sturm–Liouville problem generates a countably infinite, well ordered spectrum of non-negative characteristic values, to which correspond basis functions that can be added up in appropriate proportions to match any desired target function. Basis functions corresponding to different characteristic values are orthogonal with respect to the inner product associated with the problem that generated them. In the case of system A·10, the inner product of functions  $f(\xi)$  and  $g(\xi)$  is the integral from  $\xi = 0$  to 1 of  $fg$ . The expansion of any target function in terms of Sturm–Liouville basis functions matches it as best as possible, in the sense that the mean square difference between the target and its series expansion across the domain of the problem converges to zero as more terms are added. Note that expansions will be subject to the Gibbs phenomenon, and will not converge pointwise, when the target function has jump discontinuities, or if the target function does not comply with the boundary conditions of the Sturm–Liouville problem that produced the basis functions.

Integration of the first-order equation in time from Eq. A·9 shows that  $T(\tau) \propto \exp(-\lambda^2 \tau)$ . The governing equation from system A·10 is solved generally by

$$X(\xi) = A \cos(\lambda \xi) + B \sin(\lambda \xi); \quad [\text{A}\cdot 11]$$

the boundary conditions require that  $B = 0$  and  $\lambda = k\pi$  for  $k = 0, 1, 2, \dots$ , but leave  $A$  free. Thus the series

$$\theta_0^t(\tau, \xi) = \sum_{k=0}^{\infty} A_k e^{-k^2 \pi^2 \tau} \cos(k\pi \xi) \quad [\text{A}\cdot 12]$$

generally satisfies GE<sup>t</sup>, BC<sup>t</sup>i, and BC<sup>t</sup>ii.

The last constraint on the transient system, IC<sup>t</sup>, requires that

$$\sum_{k=0}^{\infty} A_k \cos(k\pi \xi) = -\theta_0^\infty(\xi), \quad [\text{A}\cdot 13]$$

which can be solved for  $A_k$  by exploiting the orthogonality property of the basis functions generated by Sturm–Liouville problem A·10. Multiply both sides of Eq. A·13 by  $\cos(m\pi \xi)$ , where  $m$  is some whole number, and integrate both sides from  $\xi = 0$  to 1. Discard the terms where  $k \neq m$ , which must be orthogonal under the integration. Isolating  $A_k$  and noting that  $A_0 = 0$ , we are left with

$$A_k = -\frac{2}{k^2 \pi^2} \quad [\text{A}\cdot 14]$$

for  $k = 1, 2, 3, \dots$ . After inserting  $A_0 = 0$  and this result for  $A_{k>0}$  into Eq. A·12, substitution into Eq. A·6 produces Eq. 4.

*Derivation of Eq. 10 by trial function.*—Since the Laplace variable  $s$  can be treated as a parameter, Eq. 8 is a differential equation with constant coefficients. Insertion of a trial function  $e^{r\xi}$  reduces it to a quadratic equation, with roots  $r = \pm\sqrt{s}$ . Thus the general solution of the equation is

$$\bar{\theta}_0(\xi) = \alpha e^{\xi\sqrt{s}} + \beta e^{-\xi\sqrt{s}}, \quad [\text{A}\cdot 15]$$

where  $\alpha$  and  $\beta$  are constants determined by the boundary conditions. Insertion of the general solution into boundary conditions 9 produces two equations from which the constants can be resolved. This gives

$$\alpha = \frac{e^{-\sqrt{s}}}{s^{3/2}(e^{\sqrt{s}} - e^{-\sqrt{s}})} \quad \text{and} \quad \beta = \frac{e^{\sqrt{s}}}{s^{3/2}(e^{\sqrt{s}} - e^{-\sqrt{s}})}, \quad [\text{A}\cdot 16]$$

and therefore

$$\bar{\theta}_0(\xi) = \frac{e^{(1-\xi)\sqrt{s}} + e^{-(1-\xi)\sqrt{s}}}{s^{3/2}(e^{\sqrt{s}} - e^{-\sqrt{s}})} \quad [\text{A}\cdot 17]$$

solves the system of Eqs. 8 and 9. Using the identity  $e^{\pm x} = \cosh(x) \pm \sinh(x)$  to replace the exponentials that appear here with hyperbolic functions yields Eq. 10.

*Derivation of Eq. 28 with hyperbolic identities.*—Insert Eq. 10 into Eq. 26 to get

$$\bar{\theta}_1(\xi) = \frac{\cosh[(1-\xi)\sqrt{s}] - \cosh(\xi\sqrt{s})}{s^{3/2} \sinh(\sqrt{s})}. \quad [\text{A}\cdot 18]$$

Next, note that  $1 - \xi = \frac{1}{2} + \left(\frac{1}{2} - \xi\right)$  and  $\xi = \frac{1}{2} - \left(\frac{1}{2} - \xi\right)$ , so this is equivalent to

$$\bar{\theta}_1(\xi) = \frac{\cosh\left[\frac{1}{2}\sqrt{s} + \left(\frac{1}{2} - \xi\right)\sqrt{s}\right] - \cosh\left[\frac{1}{2}\sqrt{s} - \left(\frac{1}{2} - \xi\right)\sqrt{s}\right]}{s^{3/2} \sinh(\sqrt{s})}. \quad [\text{A}\cdot 19]$$

The identity  $\cosh(x+y) - \cosh(x-y) = 2 \sinh(x) \sinh(y)$  implies that

$$\bar{\theta}_1(\xi) = \frac{2 \sinh\left(\frac{1}{2}\sqrt{s}\right) \sinh\left[\left(\frac{1}{2} - \xi\right)\sqrt{s}\right]}{s^{3/2} \sinh(\sqrt{s})}, \quad [\text{A}\cdot 20]$$

after which the identity  $\sinh(x) = 2 \sinh\left(\frac{1}{2}x\right) \cosh\left(\frac{1}{2}x\right)$  allows  $\sinh(\sqrt{s})/\sinh\left(\frac{1}{2}\sqrt{s}\right)$  to be replaced with  $2 \cosh\left(\frac{1}{2}x\right)$ , resulting in Eq. 28.

*Limit analysis to get Eq. 38.*—Before starting to analyze Eq. 37, recall that Eq. 34 says

$$\frac{1}{2}\sqrt{s_k} = \frac{1}{2}\pi(2k-1)j \quad [\text{A}\cdot 21]$$

by definition, where  $j$  indicates the imaginary unit. This choice was originally made because the hyperbolic cosine in the denominator of Eq. 28 goes to zero when it takes this as its argument. Indeed, bearing in mind that  $\cosh(jx) = \cos(x)$ , we see that

$$\begin{aligned} \cosh\left(\frac{1}{2}\sqrt{s_k}\right) &= \cosh\left[j\cdot\frac{1}{2}\pi(2k-1)\right] \\ &= \cos\left[\frac{1}{2}\pi(2k-1)\right] = 0, \end{aligned} \quad [\text{A}\cdot 22]$$

and, noting that  $\sinh(jx) = j\sin(x)$ , the hyperbolic sine in the numerator of Eq. 28 simplifies too, as

$$\begin{aligned} \sinh\left(\frac{1}{2}\sqrt{s_k}\right) &= \sinh\left[j\cdot\frac{1}{2}\pi(2k-1)\right] \\ &= j\sin\left[\frac{1}{2}\pi(2k-1)\right] = -j(-1)^k. \end{aligned} \quad [\text{A}\cdot 23]$$

To facilitate taking limits like Eq. 37, it helps to introduce a complex variable  $\omega$  whose origin sits at the location of the  $k$ th pole. Later use of hyperbolic identities is aided by letting  $\omega$  stand relative to the zeroes of hyperbolic cosine, rather than  $s_k$  itself, letting  $\frac{1}{2}\sqrt{s} = \frac{1}{2}\sqrt{s_k} + \omega$  (rather than, say,  $s = s_k + \omega'$ , which confounds the analysis because it branches when square rooted). In Eq. 37, we substitute

$$\sqrt{s} = \sqrt{s_k} + 2\omega \quad [\text{A}\cdot 24]$$

into the hyperbolic cosine in the numerator,

$$s = (\sqrt{s_k} + 2\omega)^2 = s_k + 4\omega\sqrt{s_k} + 4\omega^2 \quad [\text{A}\cdot 25]$$

within the  $s - s_k$  term, and

$$s^{3/2} = s\sqrt{s} = s_k\sqrt{s_k} + 6s_k\omega + 12\sqrt{s_k}\omega^2 + 8\omega^3 \quad [\text{A}\cdot 26]$$

in the denominator. Equation 37 for the residue becomes

$$\text{Res}\{g(s_k)\} = \lim_{\omega \rightarrow 0} \frac{4\omega(\sqrt{s_k} + \omega)\sinh\left(\frac{1}{2}\sqrt{s_k} + \omega\right)\cosh(\xi\sqrt{s_k} + 2\xi\omega)}{(s_k\sqrt{s_k} + 6s_k\omega + 12\sqrt{s_k}\omega^2 + 8\omega^3)\cosh\left(\frac{1}{2}\sqrt{s_k} + \omega\right)}, \quad [\text{A}\cdot 27]$$

which we set out to simplify with hyperbolic identities. Because  $\sinh(x+y) = \sinh(x)\cosh(y) + \cosh(x)\sinh(y)$  and  $\cosh(x+y) = \cosh(x)\cosh(y) + \sinh(x)\sinh(y)$ ,

$$\sinh\left(\frac{1}{2}\sqrt{s_k} + \omega\right) = -j(-1)^k \cosh(\omega), \quad [\text{A}\cdot 28]$$

$$\cosh\left(\frac{1}{2}\sqrt{s_k} + \omega\right) = -j(-1)^k \sinh(\omega), \quad [\text{A}\cdot 29]$$

$$\begin{aligned} \cosh(\xi\sqrt{s_k} + 2\xi\omega) &= \cosh(\xi\sqrt{s_k})\cosh(2\xi\omega) \\ &\quad + \sinh(\xi\sqrt{s_k})\sinh(2\xi\omega), \end{aligned} \quad [\text{A}\cdot 30]$$

where the first two expressions have been simplified with Eqs. A22 and A23.

Also, we are implementing a limit process where  $s_k$  has nonzero modulus and  $\omega$  is arbitrarily small. Thus individual terms in Eq. A27 can be simplified by neglecting contributions of order  $\omega^2$  and higher:

$$s_k\sqrt{s_k} + 6s_k\omega + 12\sqrt{s_k}\omega^2 + 8\omega^3 \approx s_k\sqrt{s_k} + 6s_k\omega, \quad [\text{A}\cdot 31]$$

$$\sinh\left(\frac{1}{2}\sqrt{s_k} + \omega\right) \approx -j(-1)^k, \quad [\text{A}\cdot 32]$$

$$\cosh\left(\frac{1}{2}\sqrt{s_k} + \omega\right) \approx -j(-1)^k\omega, \quad [\text{A}\cdot 33]$$

and

$$\cosh(\xi\sqrt{s_k} + 2\xi\omega) \approx \cosh(\xi\sqrt{s_k}) + 2\xi\omega \sinh(\xi\sqrt{s_k}). \quad [\text{A}\cdot 34]$$

Ultimately the residue of the pole at  $s_k$  can be found by taking the equivalent limit

$$\begin{aligned} \text{Res}\{g(s_k)\} &= \lim_{\omega \rightarrow 0} \frac{4(\sqrt{s_k} + \omega)\cosh(\xi\sqrt{s_k})}{s_k\sqrt{s_k} + 6s_k\omega} \\ &\quad + \lim_{\omega \rightarrow 0} \frac{8\xi\omega(\sqrt{s_k} + \omega)\sinh(\xi\sqrt{s_k})}{s_k\sqrt{s_k} + 6s_k\omega}, \end{aligned} \quad [\text{A}\cdot 35]$$

which leads directly to Eq. 38.

*Integration of Eq. 51.*—Applying the binomial theorem to expand  $(w-z)^n$  turns the integrand of Eq. 51 into a sum of terms with the form  $z^k e^{-z^2}$ , which can be integrated one by one. This integral is best treated in cases. If  $k$  is an odd number, i.e.,  $k = 2n + 1$  for some non-negative integer  $n$ , then a  $u$ -substitution shows that

$$\int_z^\infty z^{2n+1} e^{-z^2} dx = \frac{e^{-z^2}}{2} \sum_{k=0}^\infty \frac{n!}{k!} z^{2k}, \quad [\text{A}\cdot 36]$$

where we understand that  $0! = 1$ . If  $k$  is even, such that  $k = 2n$ , repeated integration by parts gives

$$\begin{aligned} \int_z^\infty z^{2n} e^{-z^2} dz &= \frac{(2n)! \sqrt{\pi}}{2 \cdot 4^n n!} \text{erfc}(z) \\ &\quad + \frac{e^{-z^2}}{2} \sum_{k=1}^n \frac{(2n)! k! z^{2k-1}}{4^{n-k} (2k)! n!}. \end{aligned} \quad [\text{A}\cdot 37]$$

These results allow each term of the binomial expansion to be integrated separately. Introducing a symbol  $g_{km}$ , defined as

$$g_{km} = \begin{cases} \frac{\left(\frac{m-1}{2}\right)!}{\left(\frac{m-1}{2} - k\right)!} & \text{if } m \text{ is odd} \\ \frac{m! \left(\frac{m}{2} - k\right)!}{4^k (m-2k)! \left(\frac{m}{2}\right)!} & \text{if } m \text{ is even,} \end{cases} \quad [\text{A}\cdot 38]$$

simplifies the notation further. Ultimately the integral from Eq. 51 can be written in closed form as

$$\begin{aligned} i^n \text{erfc}(z) &= \text{erfc}(z) \sum_{m=0}^{\lfloor \frac{n}{2} \rfloor} \frac{(-1)^n z^{n-2m}}{4^m m! (n-2m)!} \\ &\quad + \frac{e^{-z^2}}{\sqrt{\pi}} \sum_{m=0}^n \sum_{k=0}^{\lfloor \frac{m-1}{2} \rfloor} \frac{(-1)^{n-m} z^{n-2k-1} g_{km}}{m! (n-m)!}, \end{aligned} \quad [\text{A}\cdot 39]$$

in which  $\lfloor x \rfloor$  represents the greatest integer less than or equal to  $x$ .

*Derivation of Eq. 63 by trial function.*—The trial-function method needed to solve Eqs. 61 and 62 was used when deriving Eq. 10 earlier in this appendix. It does help to make an observation that eases the application of boundary conditions in this type of problem, however. Although  $e^{\xi\sqrt{s}}$  and  $e^{-\xi\sqrt{s}}$  arise naturally when inserting trial function  $e^{rx}$  into Eq. 61, either function can be rescaled by a constant and still satisfy the original equation. Rather than using  $e^{\xi\sqrt{s}}$  as a complementary solution, the boundary conditions are simpler to apply if  $e^{-\sqrt{s}} \cdot e^{\xi\sqrt{s}} = e^{-(1-\xi)\sqrt{s}}$  is used instead.

Write the general solution of Eq. 61 as

$$\bar{\theta}_2(\xi) = pe^{-\xi/\sqrt{s}} + qe^{-(1-\xi)/\sqrt{s}}, \quad [\text{A-40}]$$

where  $p$  and  $q$  are constants. BCii from Eq. 62 gives

$$0 = \frac{(1 - e^{-\sqrt{s}})(p + q)}{\sqrt{s}}, \quad [\text{A-41}]$$

immediately showing that  $q = -p$ . BCi then produces

$$-\frac{1}{s} = p(1 - e^{-\sqrt{s}}) \quad [\text{A-42}]$$

directly. Inserting the  $p$  and  $q$  values so determined into Eq. A-40 yields Eq. 63.

*Derivation of Cottrell's equation from Eq. 78.*—To describe the current induced by a step change to zero surface concentration at the edge of a semi-infinite electrolytic solution, Cottrell wrote

$$i_{\text{Cottrell}}(t) = -\frac{nF\nu_k c_\infty}{s_k} \sqrt{\frac{D}{\pi t}} \quad [\text{A-43}]$$

where  $\nu_k c_\infty$  is the bulk concentration of reactive ion  $k$ , and  $s_k$ , its stoichiometry in the interfacial half-reaction that consumes it. Insertion of the dimensional variables that underpin  $\tau$  and  $I$  (definitions 20 and 57) into Eq. 78 gives the similar but not identical result

$$i(t) \approx -\frac{\nu_+ \nu_-}{s_+ \nu_- t_- + s_- \nu_+ t_+} \cdot nF c_\infty \sqrt{\frac{D}{\pi t}}. \quad [\text{A-44}]$$

Here we have introduced the anion transference number,  $t_- = 1 - t_+$ , to clarify the physical interpretation of the prefactor.

The discrepancy between Eqs. A-43 and A-44 stems from Cottrell's assumption that reacting species are diluted in a well-supported electrolytic solution. In that situation, inert ions from the supporting electrolyte are expected to carry the vast majority of the ionic current, so the transference number of the reacting species is effectively zero. Using the present language: Cottrell took  $t_k$  for ion  $k$  to be zero whenever  $s_k$  is nonzero.

When a reactive ion comes from an unsupported solution of a simple salt, Cottrell's assumption requires that its transference

number be zero, which forces the transference number of the salt's nonreacting counterion to be unity. This constraint on parameters is somewhat aphysical. Nevertheless, it makes the prefactor in Eq. A-44 become  $\nu_+/s_+$  when cations react and  $\nu_-/s_-$  when anions react, so that our modified formula matches Cottrell's. In practice, Eq. A-44, including the prefactor to account for migration, should provide a better model of the voltage-step response of an unsupported binary electrolytic solution.

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