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Professor Oldham's contributions to applied mathematics: a tribute on the occasion of his 80th birthday

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Abstract Based on our 40-year collaboration and friendship, this essay attempts to identify a few of the main themes of Professor Keith B. Oldham's numerous contributions to the field of applied mathematics.

Keywords Fractional calculus · Mathematical models · Numerical methods

Introduction

It is a pleasure to contribute to this special issue of the *Journal of Solid-State Electrochemistry* published in celebration of Professor Keith B. Oldham's 80th birthday. I have known Keith since 1967, not long after both he and I joined the technical staff at the Science Center, North American Rockwell's central research laboratory in Thousand Oaks, California. It was during the period between 1967 and 1970, while we were both at the Science Center, that we began the extensive collaboration that has now spanned more than 40 years and produced wide-ranging research resulting in the publication of two books and a number of joint papers. Other papers in this special issue will surely attest to Keith's accomplishments in electrochemistry and in science beyond. As a mathematician, I thought that it might be interesting to focus my attention on the more mathematical of Prof. Oldham's contributions. Through our collaboration, I have been able to appreciate many of these very directly, but a more complete picture has emerged upon studying a number of his papers. For instance, it has become quite clear to me that his deep knowledge of electrochemistry, together with his intellectual curiosity and lifelong interest in the power of mathematics, has inspired and unified his mathematical contributions. Like the best applied mathematician, his primary concern has been in the effective *use* of mathematics in science and engineering. In this regard, he has been very inventive in seeking novel and powerful techniques with which to enhance understanding of both theory and experiments.

Dedicated to the 80th birthday of Keith B. Oldham.

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Classification of mathematical "themes"

In reviewing his more than 200 papers in diverse subjects, there is clear evidence that some of the dominant themes of Keith's mathematical thinking over the years are:

Mathematical modeling: the formulation and systematic exploitation of economical mathematical expressions that represent widely recurring problems in science and engineering
The fractional calculus: the use of differintegral operators (i.e., fractional-order derivatives and integrals) to provide advantages over more "classical" formulations of problems in electrochemistry and in other fields
Numerical analytical methods: the construction, analysis and implementation of simplified mathematical representations of numerous functions that arise everywhere in science and engineering

It is also easy for me to see how these paradigms thread their way through all of Keith's work and enable useful generalizations and unification of the underlying principles involved in a number of new directions. In carrying out this exercise, I became more acutely aware than before of how much overlap there is between Keith's interests and tastes and my own. This, in turn, has helped me to understand better how his creativity has often fueled and greatly enriched our own collaboration and my own work.

Models for electrochemistry

Mathematical modeling is certainly a central and unifying element of Keith's work. His more mathematical studies seem always to have been inspired by his deep thinking about physical processes. Our work together in the applications of electrochemistry illustrates this very well.

I remember well the time in 1968 when Keith first approached me at the Science Center and outlined his thinking about how half-order derivatives and integrals might improve the analysis of electrochemical experiments. He knew that this should be possible even before either of us fully understood what these operators really were. The ideas about half-order derivatives and integrals and their possible uses that he outlined to me in 1968 struck a responsive chord and we set about immediately to explore the history of this somehow neglected offshoot of "classical" calculus. We also began a systematic exploration of the basic theory and fundamental properties of derivatives and integrals to arbitrary order motivated by our growing belief that these would prove to be invaluable in chemistry (and later, as it turned out, in other fields). Indeed, it is precisely because Prof. Oldham believed strongly that the mathematical relationships to be derived using fractional calculus were powerful, yet economical, and could shed light on diffusive transport processes more generally that the techniques he pioneered are now so widely accepted and utilized.

Already by 1969, Keith and I had begun work on our first book together (*The Fractional Calculus: Theory and Applications of Differential and Integration to Arbitrary Order*, Academic Press, 1974), work that was to occupy our attention quite fully for 5 years. During that interval, we each left the Science Center (Keith in 1970, me in 1971) to take up academic positions but our book collaboration continued vigorously.

Throughout this period we were refining our thinking about ways in which the fractional calculus would prove to be useful in electrochemical experiments and elsewhere. Our early work together appeared in two joint papers ([1, 2]) that outlined the theory and its potential in the context of experiments involving diffusive transport. In parallel with this effort, Keith published a series of papers ([3–11]) introducing the new ideas to the electrochemistry audience and elaborating on their applications in electrochemical diffusion experiments.

The basic ideas involved are easy enough to outline. Many diffusion processes are assumed to obey the partial differential equations (Fick's laws)

$$\frac{\partial}{\partial t}F(x,t) = -\frac{\partial}{\partial x}J(x,t) = k\frac{\partial^2}{\partial x^2}F(x,t) \qquad (1)$$

in which F represents an intensive scalar variable (such as concentration, temperature, vorticity, electric potential, etc.), J its flux, x the spatial variable, t the time, and k a constant characteristic of the diffusing medium and the type of transport (e.g., whether of electroactive transport, heat transport, etc.). This pair of differential equations must then be augmented by appropriate boundary and initial conditions in order to assure that a unique solution $F(x,t)$ can be determined for all values of x and t that are relevant.

Frequently, however, the primary interest is not in a formula for the solution $F(x,t)$ everywhere, but in the relationship between the values of F and J at one of the boundaries; say at $x=0$. In electrochemical experiments, the surface $x=0$ is identified as the electrode surface, where the interconversion of chemicals and electricity occurs as a result of electron transfer at the electrode. It is this interaction that is of paramount interest, and while this interaction is controlled by the diffusion of ions from *everywhere* in the solution to the electrode, it is only the *relationship* between the time-dependent functions $F(0,t)$ and $J(0,t)$ that is sought. The fractional calculus provides just such a relationship *without the need to determine F and J for all values of x and t*. This approach, therefore, describes not one, but an *entire family* of boundary value problems. We'll provide an intuitive argument here for this result for the case when $F(x,t)=0$; the reader is referred to [1, 12] for more rigorous and complete discussions.

If we view Eq. 1 as an algebraic identity, we notice that it can be rearranged and factored formally to produce

$$\begin{aligned}&\left[k\frac{\partial^2}{\partial x^2} - \frac{\partial}{\partial t}\right]F(x,t)\\ &\quad= \left[\sqrt{k}\frac{\partial}{\partial x} - \frac{\partial^{1/2}}{\partial t^{1/2}}\right]\left[\sqrt{k}\frac{\partial}{\partial x} + \frac{\partial^{1/2}}{\partial t^{1/2}}\right]F(x,t)\\ &\quad= 0\end{aligned} \qquad (2)$$

We interpret this factored equation to mean that operating on $F(x,t)$ first by $\left[\sqrt{k}\frac{\partial}{\partial x}+\frac{\partial^{1/2}}{\partial t^{1/2}}\right]$, then by $\left[\sqrt{k}\frac{\partial}{\partial x}-\frac{\partial^{1/2}}{\partial t^{1/2}}\right]$, produces 0. It can, however, be shown ([12], chapter 11) that the first of these two operations alone converts $F(x,t)$ to 0 provided that $F(\infty,t)=F(x,0)=0$. In other words, the semidifferential equation

$$\sqrt{k}\frac{\partial}{\partial x}F(x,t)=-\frac{\partial^{1/2}}{\partial t^{1/2}}F(x,t) \tag{3}$$

holds whenever the diffusion process is initiated with no diffusing substance present in the system and this condition persists sufficiently far from the $x=0$ boundary throughout the experiment. Equation 3 is modified slightly to accommodate the case $F(x,0)\neq 0$.

According to Fick's first law,

$$J(x,t)=-k\frac{\partial}{\partial x}F(x,t), \tag{4}$$

Equation 3 can then be rewritten as

$$J(0,t)=\frac{1}{\sqrt{k}}\frac{\partial^{1/2}}{\partial t^{1/2}}F(0,t) \tag{5}$$

after specializing to $x=0$.

Equation 5 thus expresses a compact relationship between the boundary flux $J(0,t)$ and the semiderivative of the function $F(0,t)$ with respect to time. Because such a relationship is the goal of most electrochemical diffusion experiments, Eq. 5 can be directly exploited in the laboratory in a variety of ways making use of the semicalculus.

For example, if we assume a linear growth in time for the boundary value of F,

$$F(0,t)=At, \tag{6}$$

then, since the semiderivative of t is $2\sqrt{\frac{t}{\pi}}$ [12], we find that

$$J(0,t)=2A\sqrt{\frac{t}{\pi k}}. \tag{7}$$

Alternatively, the surface flux might be sought in terms of measured values of $F(0,t)$. This was the case, for instance, in Meyer's wind tunnel experiments [13] in which the heat flux at the surface of an airfoil was determined by semidifferentiation of the surface temperature.

If, on the other hand, $J(0,t)$ is prescribed rather than $F(0,t)$, then the process of semi-integration is used to extract $F(0,t)$. For example, the case $J(0,t)=\exp(Bt)$ gives rise to

$$F(0,t)=\sqrt{k/B}\exp(Bt)erf(\sqrt{Bt}) \tag{8}$$

found by semi-integrating Eq. 7. In electrochemical experiments [14–17], the surface flux of some electrogenerated substance is proportional to the electrolysis current, and the surface concentration of this substance may then be found by semi-integrating the current.

To appreciate the economies engendered through this approach, it is useful to contrast the procedures invoked in the semicalculus formulation with the more standard methods of solving these problems. The usual route would be to solve the partial differential Eq. 1 *fully*, employing Laplace transform methods or alternate procedures to obtain the solution $F(x,t)$ for all values of x and t in the system. For this to produce a unique solution, it is necessary to stipulate *all* of the boundary and initial conditions. For the case we have treated above, these would be $F(\infty,t)=F(x,0)=0$ (or, more generally, $F(\infty,t)=F(x,0)=C$, a constant) to express that the function F is initially uniform throughout the diffusing medium and that the system is so large that the starting value is not perturbed far from the $x=0$ boundary throughout the experiment. To these initial and asymptotic boundary conditions, one must then either specify the surface values $F(0,t)$ or, more generally, a boundary condition of the form

$$C_1F(0,t)+C_2\frac{\partial}{\partial x}F(x,t)\bigg|_{x=0}=C_3. \tag{9}$$

Specification of such a boundary condition at $x=0$ then will produce a unique function $F(x,t)$ for all values of x and t that can then be evaluated at $x=0$ to provide $F(0,t)$. Use of Fick's first law Eq. 4 then produces $J(0,t)$.

In comparing these two routes to the sought relationship, one should appreciate that the semicalculus approach *appears* to bypass the solution of Eq. 1 entirely, but it does not, as we have already stated. In fact, satisfaction of Fick's second law is implicit in the simpler solution method. However, it is not *necessary* to solve Fick's second law equations repeatedly, as the functions that describe either $F(0,t)$ or $J(0,t)$ are varied from experiment to experiment. Clearly, it is much simpler to apply Eq. 5 to relate these values if the interest is only in that interrelationship as the boundary conditions at $x=0$ are varied.

Recognition of the import of these new ideas was not immediate. That might have been because the mathematical tools used were not very accessible before the appearance of our book on the subject in 1974. Or perhaps it was because the idea that such relatively simple mathematical tools (described by means of the fractional calculus) were valid across a whole range of electrochemical experiments was foreign to most electrochemists at the time that it was introduced.

It is gratifying to report that the book on fractional calculus—which we believe to be the first treatise on the subject—has now been widely read and used to inspire new research applications of the fractional calculus.

As just one explicit example, I was interested in seeing if these same ideas could be applied to atmospheric transport with similar benefits. In fact, this turns out to be the case. In [18], I report that this formulation enables ground-level concentrations of the chemical constituents of air pollution to be expressed in terms of ground-level sources of air pollution (derived mainly from automobile exhaust emissions and industrial effluents) using half-order derivatives and integrals. Here, too, the model incorporates the full three-dimensional complexity of atmospheric transport without resorting to the complete solution of the system of partial differential equations that models that complexity. The fractional calculus has become a very active field in recent years, with its own scholarly journal (*Fractional Calculus and its Applications* (http://www.math.bas.bg/~fcaa/), now in its tenth year of publication; numerous books [19–23]; and thousands of journal articles. Although the original edition of our book on fractional calculus went out of print some years ago, Dover Publications, Inc., reprinted the book in 2006 [24] in response to what it believed was continuing high demand for that volume.

In reviewing Prof. Oldham's publications both prior to our initial work on the fractional calculus and subsequently, it is easy to see the origins of his interests in *numerical analytical methods*. Consider, for instance, his 1968 publication [25]. In this paper, one can clearly see that his motivation to find simple yet reasonably accurate approximations to this function was driven by its frequent appearance in electrochemical diffusion experiments (cf. Eq. 8). In the same year, we find [26], in which his incentives derive from the Koutecky function's applicability to experiments involving the dropping mercury electrode. This publication was followed in rapid order by two of our joint papers ([1] and [2]), exposing the main lines of mathematical thinking that underlie this approach, and then a sequence of papers that set forth the main ideas and uses in electrochemistry of what Keith called "semi-integral electroanalysis" (see [4, 5, 8] and numerous others that followed).

It seems natural for someone with Keith's intellectual curiosity and bent for generalization and unification to see how some of the limitations of our early formulations of semi-integral electroanalysis might be overcome with more effort. To take up just one line of this thinking, we had appreciated that the semicalculus rigorously applies to electrochemical experiments in which transport is by means of semi-infinite planar or spherically symmetric diffusion. For example, in our publication [2], we pointed out that cylindrical geometries could also be accommodated, although the resulting semidifferential equation very accurately models the exchanges at the electrode surface only for short times following the onset of electroactivity. This state of affairs is discussed further in [6], while in [7], Keith shows that analog implementation of semioperators via a ladder network of resistors and capacitors produces output that closely approximates that obtained through digitized numerical algorithms. As the name suggests, analog implementation made use of semi-integrating and semidifferentiating circuits widely available to electrochemical laboratories. In support of efficient implementation in electrochemistry laboratories of these ideas, it was necessary to develop accurate and efficient numerical algorithms that carry out fractional order operations. Keith's article [27] discusses such algorithms using terminology appropriate for an electrochemical audience. Exploitation of these advances, and others, produced a steady stream of publications in which the numerous advantages of semicalculus in electrochemistry were treated and analyzed in ever more general systems. By the mid-1980s, more than a hundred papers authored or coauthored by Keith applied these techniques successfully to a variety of new situations and served to reinforce the power of these methods.

One branch of this sort of thinking seems to culminate in the 1998 and 1999 publications of [28] and [29] jointly authored with Peter J. Mahon. In these papers, the authors enunciate how convolution operators that reduce to the "classical" operators of the semicalculus find use under conditions a good deal more general than those that Keith and I had analyzed 30 years earlier. Even though I am not qualified to capture succinctly the full power of these extensions and generalizations in electrochemistry, it is easy for me to see that Keith is equally comfortable wearing hats as either a scientist or as an applied mathematician. While some scientists are content to limit their deeper involvement to their scientific specialty, Keith is driven to steadily improve upon good ideas and has the talent and tenacity to try to push these to as full generality as is possible. This is the hallmark of a really effective applied mathematician.

Keith's interest in the *representation* and *approximation* of the special families of functions that arise in applied work also grew out of his immersion in electrochemistry over the years. Indeed, from deeper examination of the types of functions arising in electrochemical experiments, a more systematic way of cataloguing such functions, and numerous others, was devised. Because this thrust was taking place simultaneously with the early development of large-scale scientific computing, it was Keith's idea that a compendium of such functions and their general behavior, augmented by simple computer programs capable of calculating their values with substantial accuracy, would usefully supplement the earlier tomes in which function values were laboriously (and often not very accurately) described by vast tables of numbers. The result of this effort was our joint work leading up to the publication, in 1987, of *An Atlas of Functions* [30]. This reference handbook, originally published by Hemisphere Publishing Company and distributed internationally by Springer-Verlag, has been completely revised over the past 5 years and will be reissued in 2008 as both a traditional print volume and as an e-book [31]. This second edition has been thoroughly revised and incorporates much new material developed by Keith that deals with applications of many of the function families included in the *Atlas*. The second edition, however, retains the familiar format and overall design of the first edition. The new book, coauthored by Prof. Oldham, our long-time collaborator Jan Myland, and me, is also being published by Springer.

To illustrate Keith's unique contributions in the new edition that attest to his work in numerical methods, I need only state that he, working closely with our colleague Jan Myland, developed and implemented in the software *Equator* that accompanies the book all of the algorithmic improvements that were needed to bring the ones we had coded for our first edition up to the much more exacting precision requirements set for the second edition. For the 1987 edition, we designed and jointly tested "pseudocode" algorithms to support seven- to eight-digit precision. For the 2008 second edition, the goal was 15-digit precision (the practical limit of most computers) and Keith and Jan managed to achieve that for all but a few of the more than 200 functions treated in the 65 chapters of the book. This design is also implicit in the accuracy and registration achieved for the more than 300 four-color figures that appear in the book. It takes little imagination to appreciate the magnitude of this undertaking. A full book could certainly be devoted just to this work alone!

Taken together, work on these two editions occupied our joint attention for a decade, with 5 years devoted to each. Throughout these periods of renewed intensive interactions, our "home" universities in Canada and southern California prevented our regular face-to-face interaction. Thus, it was necessary that we periodically come together either in Peterborough or in California to talk through substantive matters pertaining to the books. Often, our wives and other members of our families would accompany us on these extended "working vacations" and I have especially fond memories of those times. While our focus on the immediate book-related topics was of paramount concern, discussion of many other topics served to strengthen and deepen our friendship and family connections. It also served to keep each of us apprised of our other professional interests and activities, many of which were at least tangentially connected to the work on our books.

A final comment

I would be remiss not to describe my admiration for Keith's expository skills. I find his lucid, compact way of extracting the very essence of his subject matter to be exemplary. This style has no doubt contributed mightily to his popularity as a conference speaker and research collaborator and, I am certain, to his success as a teacher and mentor. I will conclude by saying that I feel very fortunate to have enjoyed such a long and fruitful collaboration and friendship with Keith, and I salute him on his 80th birthday!

References

1. Oldham KB, Spanier J (1970) The replacement of Fick's laws by a formulation involving semidifferentiation. J Electroanal Chem 26:331–341
2. Oldham KB, Spanier J (1972) A general solution of the diffusion equation for semiinfinite geometries. J Math Anal Appl 39:665–669
3. Oldham KB (1969) A new approach to the solution of electrochemical problems involving diffusion. Anal Chem 41:936
4. Oldham KB (1972) A signal-independent electroanalytical method. Anal Chem 44:196
5. Grenness M, Oldham KB (1972) Semiintegral electroanalysis: theory and verification. Anal Chem 44:1121
6. Oldham KB (1973) Diffusive transport to planar, cylindrical and spherical electrodes. J Electroanal Chem Interfacial Electrochem 41:351–358
7. Oldham KB (1973) Semiintegral electroanalysis: analog implementation. Anal Chem 45:39–47
8. Goto M, Oldham KB (1973) Semiintegral electroanalysis: shapes of neopolarograms. Anal Chem 45:2043–2050
9. Goto M, Oldham KB (1974) Semiintegral electroanalysis: studies on the neopolarographic plateau. Anal Chem 46:1522–1530
10. Oldham KB (1976) Semiintegration of cyclic voltammograms. J Electroanal Chem Interfacial Electrochem 72: 371–378
11. Goto M, Oldham KB (1976) Semiintegral electroanalysis: the shape of irreversible neopolarograms. Anal Chem 48: 1671–1676
12. Oldham KB, Spanier J (1974) The fractional calculus: theory and applications of differentiation and integration to arbitrary order. Academic, New York

13. Meyer RF (1960) Aeronautical report LR-297. National Research Council, Ottawa
14. Grenness M, Oldham KB (1972) Semiintegral electroanalysis: theory and verification. Anal Chem 44:1121
15. Fowler JK, Oldham KB (1975) Voltammetric membrane cell used in the equilibrium mode for dissolved oxygen assay. In: Adams WA, et al (eds) Chemistry and physics of aqueous gas solutions, electrochemical society publications. Princeton, NJ, p 290
16. Goto M, Oldham KB (1973) Semiintegral electroanalysis: shapes of neopolarograms. Anal Chem 45:2043
17. Goto M, Oldham KB (1974) Semiintegral electroanalysis: studies in the polarographic plateau. Anal Chem 46:1522
18. Spanier J (1977) The claremont mathematics clinic. SIAM Rev 19:536–549
19. Kilbas AA, Srivastava HM, Trujillo JJ (2006) Theory and applications of fractional differential equations. Elsevier, Amsterdam
20. Samko S, Kilbas AA, Marichev O (1993) Fractional integrals and derivatives: theory and applications. Gordon and Breach, Yverdon
21. Miller KS, Ross B (eds) (1993) An introduction to the fractional calculus and fractional differential equations. Wiley, New York
22. Podlubny I (1999) Fractional differential equations. An introduction to fractional derivatives, fractional differential equations, some methods of their solution and some of their applications. Mathematics in science and engineering, vol. 198. Academic, San Diego
23. Carpinteri A, Mainardi F (eds) (1998) Fractals and fractional calculus in continuum mechanics. Springer Telos, Heidelberg
24. Oldham KB, Spanier J (2006) The fractional calculus: theory and applications of differentiation and integration to arbitrary order. Dover, Mineola
25. Oldham KB (1968) Approximations for the $x \exp x^2 erfc(x)$ function. Math Comput 22:454
26. Oldham KB, Smith DE (1968) Comparison of two approximate formulations of the Koutecky function. Anal Chem 40:1360
27. Oldham KB (1981) An algorithm for semiintegration, semidifferentiation and other instances of differintegration. J Electroanal Chem 121:341–343
28. Mahon PJ, Oldham KB (1998) Voltammetric modelling via extended semiintegrals. J Electroanal Chem 445:179–195
29. Mahon PJ, Oldham KB (1999) Convolutive modelling of electrochemical processes based on the relationship between the current and the surface concentration. J Electroanal Chem 464:1–13
30. Spanier J, Oldham KB (1987) An atlas of functions. Hemisphere and Springer, Berlin
31. Oldham KB, Myland J, Spanier J (2008) An atlas of functions with equator, the atlas function calculator, 2nd edn. Springer, Berlin