# Unsung hero of the electrochemical cell: the wave front traveling near c

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**Abstract**:

We present the electrochemical cell in a schematic that emphasizes distance traveled by an electromagnetic wave doing laps around the cell's notional perimeter at near light speed. What could be the impetus for focusing on such an "exotic" aspect of the cell? A desire to close the gap between 20 minutes and 78 million years, where the former is the observed duration of a representative procedure (for the electrolysis of, say, 0.15g Cu), and the latter is the same procedure's calculated duration based on the (generic) electrochemical cell presentation found in our textbooks. Per long-standing convention, where the student might reasonably expect a pedagogical MODEL she is presented instead with a picture whose labels speak of a self-evident REALITY, wherein "electrons flow" from anode to cathode via a battery/lead system that serves as the "conduit" while ions migrate in solution "to complete the circuit." If we take to heart that familiar picture, assigning rates 0.0002 m/s for electron drift and 0.000004 m/s for ion migration, the time required to react 0.15g of copper appears to be many millions of years; whereas, if we re-do the picture as a proper electric circuit, the calculated duration falls easily within the ballpark of the observed 20 minutes. The term 'electron flow' seems to speak of something tangible and edifying, but it should be accompanied by a warning label: Hard-Science Factoid. As it turns out, charges wafted by an ephemeral electromagnetic wave near c are what we need instead to make the numbers work.

*Keywords*: electron flow, electrochemistry, conventional current, photon, drift velocity, charge transport, science education

**Introduction**

In Part One, I present a scheme for (re-)introducing electricity (not to be confused with *electrons* creeping at a snail's pace), as the driving force of electrochemistry. For a preview, please refer to Figure 1. In Part Two, I try to impose some structure on the no-man's-land where electrochemistry and physics overlap. There too the presentation relies heavily on graphics; see Figures 2-4.

Next, I document the use of the term 'electron flow' (and symbol '$e^{-}\rightarrow$') in a variety of texts. The examples that I've culled from general chemistry texts comprise Part Three; the examples from specialized electrochemistry texts comprise the fourth and final part of the article. (This longish documentation step is important for substantiating my claim that 'electron flow' is the ubiquitous term/concept around which a conventional representation is built, and for showing, in part, why 'electron flow' is, nonetheless, a factoid.)

In Concluding Remarks, I sketch out the underlying philosophy that motivated me to devote time to "the 'electro' in electrochemistry," a topic that might seem obvious and/or frivolous at first glance.

**Part One: Photons surfing the wave front: The unsung heroes of electrochemistry**

My first order of business will be to persuade you that the schematic in Figure 1 *is* in fact a reasonable representation of an electrochemical cell. Its appearance, relative to the usual textbook representation, is admittedly exotic. To achieve some perspective, think of the doughnut/coffee mug equivalence that the science journalist uses as an introduction to topological thinking. (See inset in northwest quadrant, courtesy of arizona.edu.) My departure from the standard representation of an electrochemical cell involves some stretching and shrinking, yes, but on balance the distortions I introduce are comparable to (or somewhat milder than) those required for a doughnut to become a mug. Next question: But *why* did I apply these transformations? My immediate goal was to present a picture where the gap between the electrodes, and the lengths of the three leads, are all roughly to scale, so that one might quantify the electrical circuit's perimeter and associated attributes.

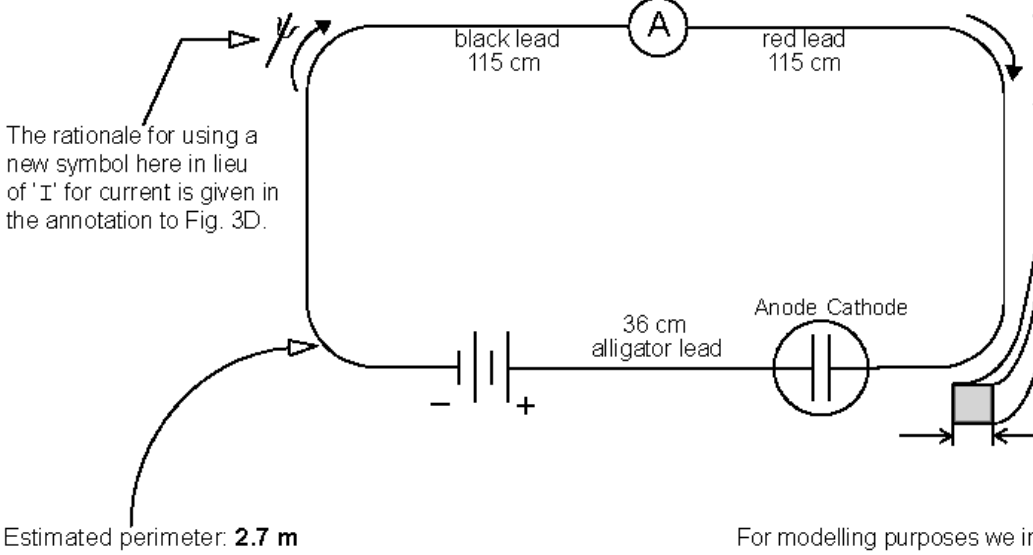
The diagram below is my proposed ***generic*** scheme for representing a wide variety of electrochemical cells. For the purpose of rounding out the picture and bringing it to life, I also borrow (arbitrarily) these ***specific*** data from a published procedure, one whose goal happens to be the determination of Avogadro's number by electrolysis, using two copper electrodes submerged in $CuSO_4$: I = 0.400 A, t = 1200 s, Δm = 0.1575 g. Source: Seiglie [1], who presents the well-known Estimated $N_A$ Formula in this form:

$$N_A = \frac{Q \bullet M}{e \bullet Z \bullet \Delta m}$$

where $Q = I \bullet t$
M is Gram Atomic Mass of the metal
e is the elementary charge, $1.602 \times 10^{-19}$ C/e⁻
Z is the charge state
Δm is the mass of metal gained/lost via electrolysis.

With the help of a multimeter in Ammeter mode we observe that approximately $3 \times 10^{21}$ charges are transported during each 1200-second run of a certain $N_A$ estimation experiment.

How many laps? *If* the wires were 1-dimensional, then $1.33 \times 10^{11}$ laps per 1200 s. Actual laps: from $2.3 \times 10^{18}$ to $2.5 \times 10^{24}$ laps in 1200 s. See text for details.




The rationale for using a new symbol here in lieu of 'I' for current is given in the annotation to Fig. 3D.

Estimated perimeter: **2.7 m**
The subtotal for leads is 115 + 115 + 36 = 266 cm. Add an arbitrary 3 cm for Anode/Cathode separation within the cell; add another 2 cm to allow for distances between multimeter terminals and battery terminals, bringing the total to 271 cm. Round 2.71 m to 2.7 m.

For modelling purposes we imagine that the wire of the three leads is square. The American Wire Gauge values for AWG 17 and AWG 18 are 1.04 $mm^2$ and 0.82 $mm^2$, respectively. Here we split the difference and depict an even 1 $mm^2$.

How fast does electricity travel in copper? At 2/3 *c*. For our purpose, though, let's keep it simple and say: At *c*. (The difference has negligible impact on an order-of-magnitude calculation.) Borrowing some data from [1], we take the quotient of 480 C ÷ $1.602 \times 10^{-19}$ C/e⁻, and round it to $3 \times 10^{21}$ charges. (Why 'charges'? The symbol 'e⁻' is overloaded, as discussed in Part Two of this article. Here it refers to charge, e, because — stated in terms of the Estimated $N_A$ Formula above — it is the quotient Q/e that we are taking.) So, **$3 \times 10^{21}$** is the approximate number of charges transported during the 1200 s run of the procedure, a quantity that is readily accommodated by the lap capacity (or bandwidth) of the circuit, which must fall between $2.3 \times 10^{18}$ and $2.5 \times 10^{24}$ laps (per 1200 s). The point of all this: Our scheme reconciles a 1200s procedure with the observed gain/loss of 0.1575g Cu whereas the conventional representation implies a process that would take millions of years to finish. See text for further details.

Figure 1: Why does the electrolysis of 0.15g Cu require only1200 seconds, not 72 million years? The short answer, distilled from the graphic: Because charge transport occurs near c.

(Not that I would encourage the pursuit of such detailed parallels, but *if* one wished to form a direct analogy, one could say the conventional representation of an electrochemical cell, with its focus on a round beaker, corresponds to the doughnut in the Figure 1 inset, while my scheme corresponds to the coffee mug, whose looped handle, last vestige of the doughnut, corresponds to our circular diode symbol, last vestige of the beaker.)

To prevent the circuit diagram in Figure 1 from being too abstract and generic, I marry it to specific data from the electrolysis procedure in an article by Seiglie [1], a synopsis of which can be seen in the northeast quadrant. Near the bottom of Figure 1, I derive the number $3 \times 10^{21}$ indirectly from Seiglie's article, and identify it as the number of charges transported during a 1200-second run of his procedure. Given the crucial role played by that number in my overall formulation, I compute it here a second way, as a check on myself, so to speak: Divide Seiglie's $\Delta m$, which is 0.1575 g, by 63.5, the Gram Atomic Mass of copper, and multiply that quotient by $N_A$, then double the result to convert from bivalent ions to individual charges. This distinctly different path leads us around to the same number, $3 \times 10^{21}$ charges.

Now, in those 1200 seconds, how far can we go? Assuming $3 \times 10^8$ m/s for an order-of-magnitude calculation (rather than 2/3 c in copper) the distance is $3.6 \times 10^{11}$ m. Divide that figure by an estimated perimeter of 2.7 m (assuming for the moment a 1-dimensional circuit, meaning wire of negligible thickness) to obtain the corresponding number of laps feasible in 1200 seconds: $1.33 \times 10^{11}$ laps. Next, factor in the copper wire's thickness. Copper's density is $8.5 \times 10^{19}$ atoms/mm$^3$, so its cross-sectional density is approximately $1.9 \times 10^{13}$ atoms/mm$^2$ (obtained by taking the cube root of $8.5 \times 10^{19}$, which is 4330085, and squaring it; cf. [18, 34]). Referring to the 1 mm$^2$ wire depicted in the diagram, the number of channels available for "parallel processing" of charge transport must fall between 4330085, if we count only the "skin" of the wire, and $1.9 \times 10^{13}$ channels, if we treat the wire as a solid. Accordingly, the number of charges transportable must fall between $2.3 \times 10^{18}$ and $2.5 \times 10^{24}$. (Calculation details: To account for all four sides of the square wire, 4 * 4330085 = 17320340. Multipying the latter times $1.33 \times 10^{11}$ laps per channel gives us $2.3 \times 10^{18}$. Multiplying $1.9 \times 10^{13}$ channels above by $1.33 \times 10^{11}$ gives us $2.5 \times 10^{24}$ laps after cancellation of channels.) This much lap capacity (or bandwidth) easily accommodates the actual quantity of charge transport observed in this instance, which is **$3.0 \times 10^{21}$ charges**.

When all is said and done, the above annotation to Figure 1 involves only plain logic and simple arithmetic (albeit with some large figures). Why, then, should one be impressed by or excited about the resultant numbers? Because there is a striking disparity between the Figure 1 results and their textbook counterparts. Not that one can go directly from one to the other in a single step, but if we were to take certain conventional electrochemical rates to their logical conclusion, we would be looking at 78 million years for Seiglie's electrolysis procedure to run, instead of 1200 seconds. (Based on experiences that you and I have had with countless similar procedures, one judges the 1200-second duration given in Seiglie's article as entirely plausible. As for my half-facetious "78 million years," please refer to Part Three for calculation details.)

**Part Two: Glossary**

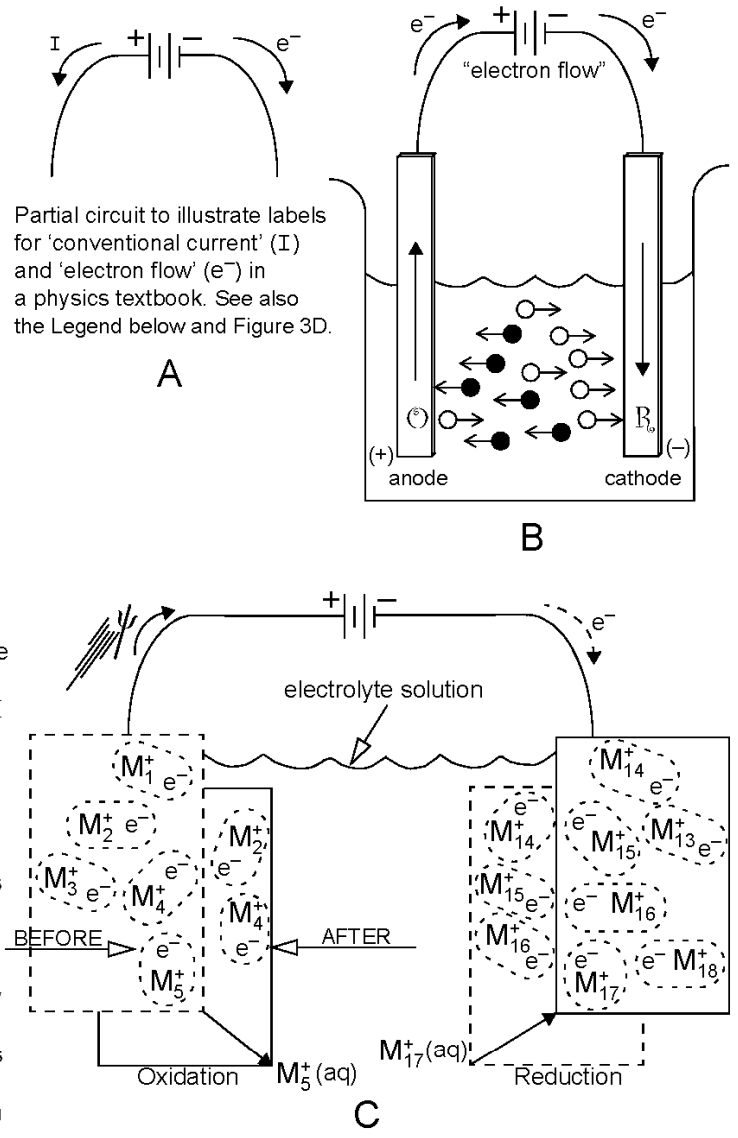
With Figure 1, I have already presented the gist of the article; accordingly, one may skip from here to Concluding Remarks. But for the reader who might be interested in knowing what drove me to that unusual view of the terrain, this section contains a set of definitions, the details of which recount the story, indirectly. The process entailed both critical reassessment of and much zigzagging between certain physics and electrochemistry definitions. When first working out the definitions, these are the questions that were occupying me: Why do textbooks show 'electron flow' in connection with electrochemistry, and nothing ever about electric current (i.e., electricity) itself? What *is* 'electron flow'? How can we best depict (actual) electricity in the electrolysis context? The questions are deceptively simple in appearance, and my search for their answers took me longer than I care to admit. Along the way, those questions sometimes became entangled with the definitions themselves; saying it another way, some of these will not be pure definitions, rather definitions with a slight "agenda" baked into them, and no apology.

ELECTRON DRIFT and DRIFT VELOCITY: In metal, there is a sea of delocalized electrons, each of which traces out its own Brownian Motion-like zigzags. In the presence of an electric field, this "drunkard's walk" has superimposed upon it a secondary movement called *electron drift*. A measurement of the latter phenomenon, which proceeds at a glacial rate, is called its *drift velocity* [1, 3]. Note the counterpoint of phenomena that are rapid (but unvectored) with phenomena that are exceedingly slow (though vectored), *neither* of which has yet the slightest resemblance to *electricity*, which is where we are headed ultimately in this glossary.

**Panel A** shows how current is represented in a physics textbook (after [33] with the geometry flipped to facilitate comparison with Panels B and C).

**Panel B** contains a generic portrayal of what I call the Orthodoxy, whereby electrons flow up *through* the anode to take a semicircular route through the battery wires, then down *into* the metal of the cathode; cf. [7].
Remark: It is true that some electrons take that *path*, but only at a glacial rate on the order of $2.22 \times 10^{-4}$ m/s [16]; so their contribution to the overall electrolysis can be trivial at best. True, oxidation occurs at '⊖' in this picture, but the ancillary idea that negative ions "complete the circuit" and give up surplus electrons that travel north inside the metal of the conduit-like electrode is, again, myth-laden at every step. (Ions can only dog-paddle their way through a solution by electrophoresis, at ca. $4.1 \times 10^{-6}$ m/s [20].)

**Panel C** I intend as an illustration of Gileadi [4], whom I quote in the text. My symbols differ but the overall message is meant to be the same as that conveyed by his scheme wherein $M^{z+} + ze^- \rightarrow M$ is revised to $M^{z+}{}_{soln} + ze^-{}_M \rightarrow M^{2+}{}_M + ze^-{}_M$ [sic] then to this: $M^{z+}{}_{soln} \rightarrow M^{2+}{}_M$, where his subscript 'M' means "in the metal." This panel is
(a) a correction of sorts to Panel B, showing how far the latter is from contemporary models, and
(b) a preface to Figure 3, where I borrow Gileadi's $M^+$ formulation. **N.B.** A certain electron becomes associated with $M_4$ instead of $M_5$, another with $M_{17}$ instead of $M_{16}$. Such realignments are not to be read as "electron capture" events. Rather, they are bookkeeping notes that allow me to show a *charge imbalance* which in turn is what engenders *charge transport*. Each oval marks an arbitrary "bookkeeping pair" to suggest charge neutrality in a more realistic way than the fairy-tale $M$ (or $M^0$).




LEGEND

I — The 'conventional current' label of physics texts which says in effect: "If we were tracking the protons inside the copper, and if they were mobile, their positive charges would flow this way." Used in Panel A only.

O→ Positive ion (ad hoc generic symbol for $Cu^{2+}$, $H^+$, etc.)

←● Neg. ion (generic symbol for $SO_4^{2-}$, $CH_3CO_2^-$, etc.)

Direction of 'electron flow'. This arrow is employed in both Panels A and B but with a substantially different meaning for physics versus electrochemistry; see discussion in text.

The glacial progress of $e^-$ as mere charge *carrier* in Panel C. This corresponds to $V_d$ in Figure 3.

Speed lines to differentiate processes that transpire near light speed from those that are glacial.

Charge transport with a speed near *c*. Note: This is *actual* negative charge in motion, not the *putative* positive charge symbolized by I.

Details of a given electrode are portrayed BEFORE (broken line) and AFTER (solid line) a redox event.

$M^+_5$ The subscript is an arbitrary ID tag for tracking individual metal ions; '+' stands for any valence.

Figure 2: The Physics Legacy; the Orthodoxy; and Redox à la Gileadi

CURRENT: *charge transport per unit of time*. This may be represented algebraically as $I = \Delta Q/\Delta t$ or physically in terms of amperes, which is to say as coulombs per second: A = C/s. For more about 'I' please skip ahead to Figure 4. There are several oddities of linguistic usage to beware: While the word 'current' alone means charge transport per unit of time, the words 'electric current' together are usually employed as a synonym for 'electricity' — meaning charge transport *en masse*, let's say, not per unit of time; see definition below. As for 'conventional current,' see separate entry, next.

CONVENTIONAL CURRENT: The 'conventional current' label of physics says in effect: "If ours was an antimatter galaxy, positrons would drift, and the positive charges would fly, through (anti-copper) wires in the direction of this arrow." (The arrow itself goes arbitrarily clockwise or counterclockwise; cf. Figure 2A.)

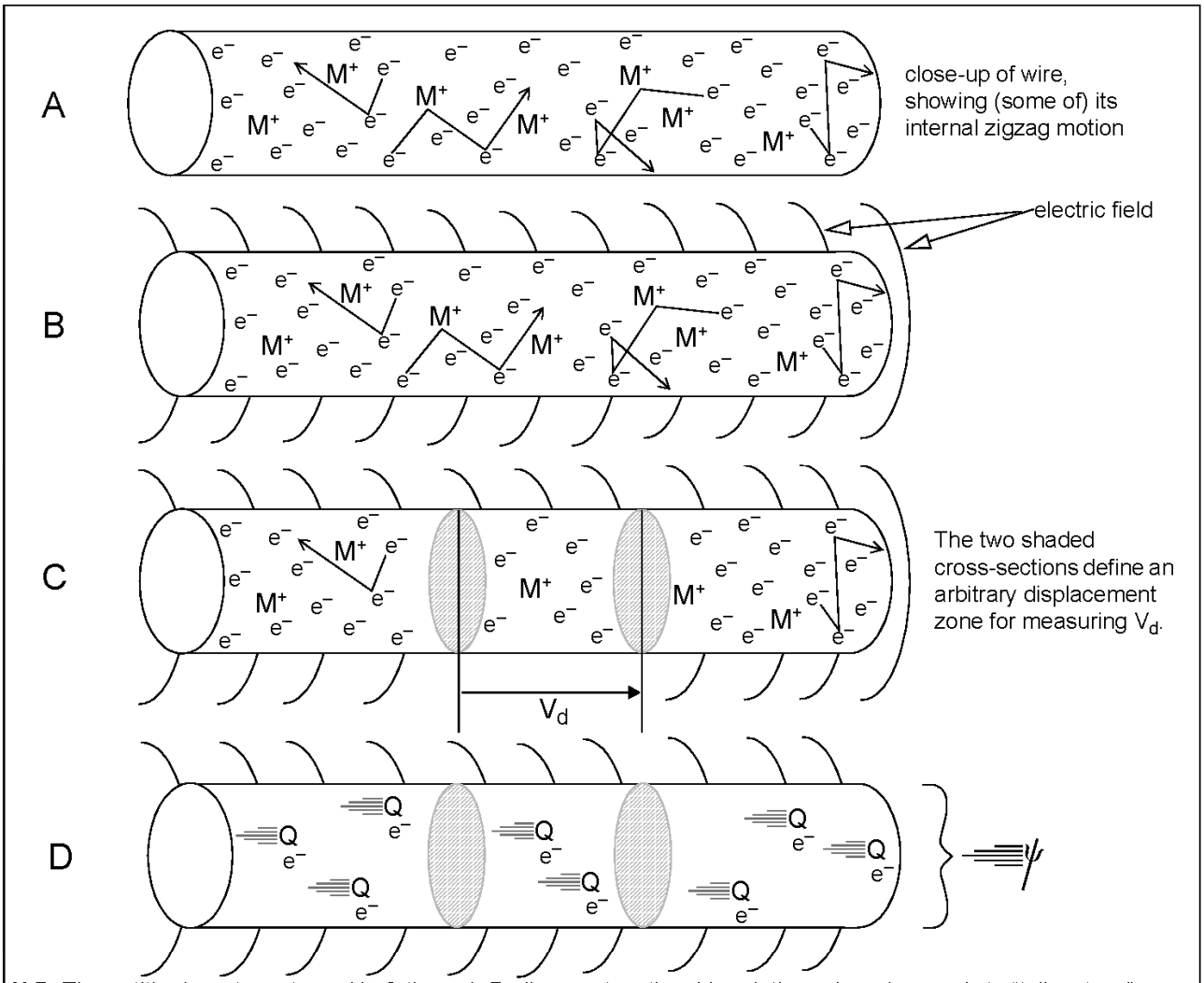
THE TERM 'ELECTRON FLOW' IN PHYSICS: In freshman physics, the term 'electron flow' plays the following **minor role**: It is kept on hand to provide a counterpart to CONVENTIONAL CURRENT (I↽) so that actual electric activity likewise has a name, and a matching retrograde symbol, that's all. Meanwhile, conventional current and electron flow are regarded as "exactly equivalent" [33]. This formalism has unintended adverse consequences: Just when a discussion should move forward to distinguish 'electron flow' from 'electron drift,' and to observe the speed contrast that is mentioned in our definition of ELECTRON DRIFT above, it takes a left turn into the argument for treating clockwise and counterclockwise as topologically equivalent, thus directing the students' attention to a mathematical formalism — when it should be focused instead on learning about electricity.

THE TERM 'ELECTRON FLOW' IN ELECTROCHEMISTRY: Meanwhile, the same term plays a **major role** in electrochemistry (with 'conventional current' typically absent from the picture until it is mentioned for completeness' sake in certain of the fourth-year specialized electrochemistry texts). But what does 'electron flow' *mean* in electrochemistry, absent its counterpart as *raison d'être*? Feeling no need to define the term, the author of an electrochemistry chapter invariably presents it as the name of a self-evident phenomenon, as if to say, "Obviously, electrons flow through wires; we all know *that* already." (But an objective observer, far from accepting 'electron flow' as axiomatic, might well wonder if it is not a factoid. It is.)

ION FLOW: In the standard representation, while electrons are said to flow through the several metallic components of an electrochemical cell, ions migrating in the aqueous region are said to "complete the circuit." This may sound plausible at first glance, but the only way a circuit can actually be completed is by electricity. I.e., an electric field, too, must be present in the solution, advancing at near light speed in the same direction as the dog-paddling ions.

THE ORTHODOXY: To the tradition built on 'electron flow' and 'ion flow,' I assign the name 'the Orthodoxy,' for easy reference. (The Orthodoxy is characterized by an idea of the electrochemical cell that involves a notional conduit, the two ends of which are submersed in a tub or beaker wherein "the circuit is completed"; see Figure 2B. Note that there exists no such *model* in the literature, only a *notion*, underscored by innumerable pictures. Here I use 'notion' in a special sense. The phrase 'racial tension' today occupies a conceptual plane of its own. Physical anthropologists and biologists may heatedly debate whether there is such a thing as race, but in the meantime, the term 'racial tension' lives on in perpetuity, in a mental space that is immune to the workaday modeling, hypotheses and (presumptive) facts of scientific inquiry. Like 'brain-fever' in 19th century literature or 'racial tension' today, 'electron flow' is (only) a notion. Not that any of these seems to result from an intentional end run around the scientific process, but such terms appear on the scene — somehow — as faits accomplis.)

ELECTRICITY aka ELECTRIC CURRENT: the *transfer of charge* near *c*; the propagation of electromagnetic waves in metal, e.g., in copper wire. Note that neither of my defining phrases contains the word 'electron.' In the literature, meanwhile, we are inundated by the notion, expressed explicitly in some physics contexts and implicitly throughout electrochemistry, that Electricity Equals Electrons-in-Motion. That definition is blatantly false. When electrons move by dint of their 'drift velocity,' that is merely a condition that *correlates* with electric current. If we aspire to represent the role of electrons in electricity, there can be no shortcuts: we must tell the *whole* story, as portrayed in Figure 3.




**N.B.** The entities/events portrayed in **A** through **D** all occur *together*. I break them down here only to "tell a story." Conversely, 'charge imbalance' as discussed in connection with Figure 2C is a separate event, *after* the fact.

In **A**, we depict a wire with no electric field present. It is characterized by a "sea" of delocalized electrons, crudely depicted here by repeated instances of $e^-$. (Regarding $M^+$, please refer to discussion in text of [4], and to Figure 2C.) Each electron exhibits a meandering "drunkard's walk" (only partially represented in the diagram). These zigzags are performed on the order of $10^6$ m/s [3]. I.e., at high speed, but this is nothing remotely resembling electricity yet.

At **B**, we show the same wire now placed in or subjected to an electric field, e.g., by attachment to a battery.

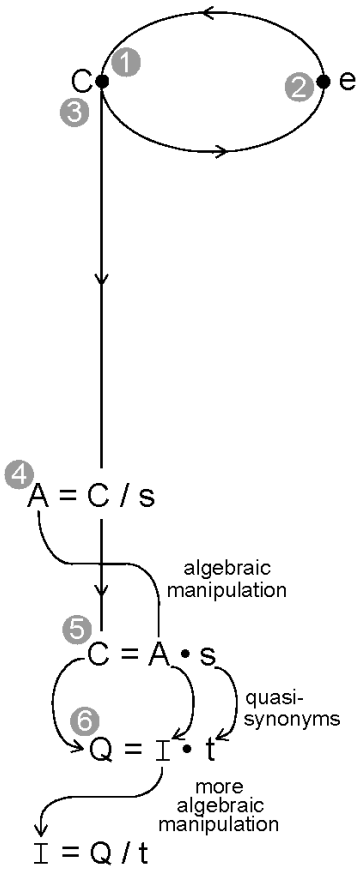
At **C**, under the influence of an electric field the electrons evince a vectored motion (superimposed upon their zigzag motion); this is called their *drift velocity* ($V_d$); it is on the order of $10^{-4}$ m/s [3], i.e., a snail's pace, so by no stretch of the imagination is this electricity yet.

At **D**, we come finally to electricity itself: When the electrons are in their drift velocity mode, they engender the transport of charge (Q) at near light speed (symbolized here by cartoon speed lines), say at 2/3 *c* in copper or $2 \times 10^8$ m/s. Collectively, these *charge transport* phenomena are called *electricity* aka *electric current*, for which I use the symbol $\psi$. (Why not 'I'? The over-cleverness of the 'conventional current' tradition (see text) leaves one literally with no way to teach *actual* electricity unless one is willing to move beyond 'I' and use a brand-new symbol.)

Figure 3: Electricity defined as a phenomenon with four distinct (though simultaneous) layers

(Regarding $M^+$ in Figure 3 please refer to Figure 2C which is my illustration of the following redox formulation by Gileadi: Metal deposition "is often represented [as $M^+ + e^- \rightarrow M$] [but] metals do not consist of neutral atoms. They consist of positively charged metal ions 'immersed' in a sea of delocalized electrons. [The] electrons are in the metal, both in the initial and in the final states. The only species that is moved from one phase to the other is the metal cation." [4] If we used conventional notation, Gileadi's version of redox would come down to these two statements: Oxidation is $M^+(s) \rightarrow M^+(aq)$. Reduction is $M^+(aq) \rightarrow M^+(s)$. Expressed thus, the idea will seem strange. With the schematic in Figure 2C, I endeavor to illustrate Gileadi's thinking. At the same time, 2C provides a layer of infrastructure that I reuse for my own purpose in Figure 3.)

Further notes on the physics legacy: In Figure 4, I use a flow chart to represent the tangled genealogy of certain coulomb-related terms. In the commentary panel, I indicate which parts make sense, which parts are subtle, and which parts are just barnacle-like appendages to the underlying logic. Similar to the case of conventional current, the family of pseudo-definitions surrounding 'C = A • s' numbs the mind with puzzles that leave over just enough *psychological* energy to worry about Getting the Right Answer. I stress 'psychological' because the puzzles are never intellectually challenging, only messy — a test of the student's tolerance for cipher-manipulation, not her intelligence.




1 In the electrochemistry milieu, it is natural that the multistep, newton-based definition of the coulomb should fade into the background (while competing definitions hold center stage), but that definition is where ***we must begin*** because it alone provides a solid foundation for everything to follow, which becomes increasingly abstract and arbitrary as we step our way down through the flow chart. So, by way of review, here it is: $F = k\frac{Q_1 Q_2}{r^2}$ where $k = 9 \times 10^9$ N • m$^2$/C$^2$

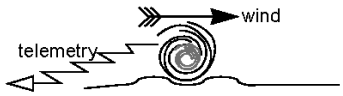
2 Next, the elementary charge, e, is found to be $1.602 \times 10^{-19}$ C / e$^-$, and since

3 1 C ÷ $1.602 \times 10^{-19}$ C / e$^-$ = $6.24 \times 10^{18}$ e$^-$, the coulomb can now be defined alternatively as the charge on $6.24 \times 10^{18}$ electrons. But take care with this use of e$^-$: In 'C / e$^-$' the '/e$^-$' denotes 'per electron.' The next instance of e$^-$, if read casually or out of context, might seem also to mean 'electron(s)' but really, in (re)defining C, it must refer to *charges*; in short, 'e$^-$' has morphed into a synonym for 'e.' (This seeming nicety is crucial in discussing Figure 1.)
Note that all-told 'e$^-$' is a *triply overloaded symbol*, after we add its dubious rôle in electrochemistry to its two slippery physics definitions above.

4 As prelude to the ampere, A, I propose two axioms:
[i] *There can be mass without density but not density without mass.*
[ii] *There can be charge without current but not current without charge.*
Hence, density = mass ÷ volume, not "mass = density • volume" except to solve a specific problem on an exam paper. Accordingly, we *should* be able to read A = C/s as the straightforward representation of a 'derived unit.' But...
...ignoring all the above considerations, the *Conférence Générale des Poids et Measures* redefined A as a 'base unit' (at the 11th CGPM in 1960).

5 What, the coulomb *again*? But of course. Because C is now eligible to take on a *third* definition, as a (pseudo) 'derived unit,' by algebraic manipulation of **A = C/s** above. In fact, per the SI, **C = A • s** is the sole definition of the coulomb, although unofficially, all three definitions continue apace, and are referenced as required by context. For example, the definitions shown in our steps 3 and 5 coexist in [3], while our steps 1 and 5 coexist in [1], where the notion of an 'operational definition' is introduced in an attempt to rationalize the dysfunction.

6 At step 6, the coulomb is taken through a fourth transformation, by having the quasi-synonym, Q, assigned to it. Ampère used 'I' to stand for *intensité du courant* (strength of the current) but nowadays 'I' is equated more often with plain 'current.' These two distinct definitions make it an overloaded symbol. Also, as "I = Q/t" it is only a reprise of "A = C/s"; i.e., it is made to be the mirror of a derived unit that is not legitimate. For a discussion of 'I' as 'conventional current' see text.




Excerpt from the Desert Botanical Committee Proceedings:

Traditionally, **speed = m/s**, where m and s are base units. But advances in technology have caused us to rethink that relation. For a tumbleweed in motion over bumpy terrain, the distance traveled in s seconds is well nigh impossible to measure. However, an instrument implanted in the tumbleweed can transmit the frequency and timbre of the wind that whistles through and propels it, allowing us to determine, by proxy, the tumbleweed's instantaneous speed with great precision and accuracy. Accordingly, the following 'operational definitions' are under consideration by the Subcommittee on Desert Botanical Metrics Standardization: [i] speed shall henceforth be classified as a base unit since it is readily obtained by telemetry; [ii] the meter, being less amenable to measurement, shall be reclassified as a derived unit, thus: **m = speed • s**.

Remark: Repeated exposure wears us down until we stop noticing how bizarre certain things are. This tumbleweed analogy mirrors the logic of **A = C/s** and **C = A • s** above. It is intended to cut through our jadedness and help us see/recall the surreal nature of such committee-bred 'logic.'

Figure 4: The many faces of C (the coulomb) and the pedigree of I (current)

For relief from the unpleasantness of Figure 4, let's spend a moment looking at a positive counterexample: Leonard Susskind's reinvention of temperature as a derived quantity, which implicitly turns the kelvin from an SI base unit into a derived unit. In a 2013 lecture, Susskind said: "Temperature is the rate of change of energy with respect to entropy" [5]. And on the whiteboard he wrote $dE = T \bullet dS$, thus turning on its head the entropy formula that you and I learned by rote ($\Delta S = q/T$), mindful to express our answers in units J/K. Similarly, five years earlier in *The Black Hole War* Susskind had written: *Temperature is the increase in the energy of a system when you add one bit of entropy* [6]. This was a great stride forward in resolving the riddle of black hole information loss, he felt. Regardless of one's stance on that thorny (and still *un*resolved) issue, one has to admire his boldness with the units: Without waiting half a century to see if a faceless committee might eventually agree with him, Susskind has summarily replaced 'base unit' K by a 'defined unit' of the same name, and perhaps even transformed the 'defined unit' S into a 'base unit,' trading in nearly two centuries of $\Delta S = q/T$ for his own $T = q/\Delta S$ epiphany. Here we have the flip side of the unthinking algebraic manipulation that is thrown into relief by Figure 4. The point of this interlude about Susskind is that if one proposes the revision of a base/derived relation *in good faith*, it can be a legitimate exercise, even a highly valuable one (granted most of us lack the clout to go public with such a maneuver as Susskind's).

Sources: In the various definitions above, much of the wording is my own, but I draw also on several physics texts [1-3] to provide some of the technical underpinning, along with [4], already cited. For the definitions at steps 1, 3 and 5 in Figure 4, I rely on [3] and [33].

**Part Three: Where and how 'electron flow' appears in the instructional literature**

The instructional literature I divide into two categories: (a) the electrochemistry chapters in general chemistry textbooks and physical chemistry textbooks; (b) specialized electrochemistry texts that straddle the fourth-year and graduate school levels. In these pages (Part Three) I document the widespread use of the term 'electron flow' and label '$e^{-}\rightarrow$' in literature category (a). In Part Four, I do a survey of (b), the specialized electrochemistry texts, to see if/how they move beyond the notion of 'electron flow' as presented to freshmen.

"I am challenging the conventional model of the electrochemical cell," is what one would like to say here. But we are precluded by the circumstance from doing so. We find ourselves dealing with a fixed, canonical NOTION of something; this is substantially different from having an abstract

MODEL set before us. Thus, having no MODEL to critique, we are inclined at first to try rationalizing the NOTION by asking: Could it be that the textbook author *writes* 'electron flow' (and/or '$e^{-}\rightarrow$') but *thinks* 'electric current,' by virtue of a simplifying assumption or math-style formalism? No, there is no support for that idea either. Eventually we are driven to conclude that *literal electrons* are the object of discussion (and this is troubling, because 'electron flow' is a factoid, occupying a conceptual limbo, in-between electromagnetic waves that soar and [actual] electrons that creep).

The following excerpts are taken from a random sampling of chemistry and physical chemistry texts. Here we find that the notion of 'electrons flowing' was endorsed by Linus Pauling [7], no less, and has been canonized in books that span more than half a century. Not shown: Each quoted passage is reinforced by a graphic (immediately or a few pages hence) that features the label '$e^{-}\rightarrow$' and/or 'electron flow.' All italics and bolding are added. Cumulatively, the various italicized terms demonstrate the prevalence of the Orthodoxy over the period 1947-2011 (at the very least). The terms that I've bolded are ones that seem to hint at a broader view — but usually these disappoint us by failing to definitively challenge the Orthodoxy.

> A. When the circuit is closed *electrons flow* as through a tube [...] The battery acts as an *electron pump* [...] An electron is *pumped into* the cathode [...] The **charge** [...] is conducted across the liquid *by the motion of the ions*. [7]
>
> B. A battery causes **charge** to move through a wire [...] **Current** is defined as the **charge** passing a point per unit of time [...] *electrons flow* [...] *through the wire*. [8]
>
> C. When the reaction between $MnO_4^{-}$ and $Fe^{2+}$ occurs in solution, the electrons are transferred directly when the reactants collide. Thus no useful work is obtained [...] thus requiring the *electron transfer* to occur *through a wire*. The **current** produced in the wire by the *electron flow* can then be directed [...] to produce useful work [...] obtain the total *coulombs of* **charge passed** *into* the $Cu^{2+}$ solution [...] 0.187 mole of *electrons flowed* into the $Cu^{2+}$ solution. [9]
>
> D. [*E*]*lectrons flow* from one metal electrode to another *through an external circuit*, while *ions flow* [through the solution]. [10]

E. In an electrochemical cell [reactions can occur] only if *electrons flow* through an *outside* conductor [...] *Electrons move* from the negative electrode (anode) to the positive electrode (cathode) *through the external wire*. The electrical circuit is *completed* in the solution *by the movement of ions*. [11]

F. [The anode] *supplies electrons to the external circuit*. [12]

G. [The] term 'electrode' [...] is also used to mean the piece of metal that *conducts electrons in and out* of the solution. [13]

H. The two half-cells [of a Daniell cell] are connected in two ways: by wire (or *electron conduit*) which allows [the] *flow of electrons* and by [...] The electrons released in the zinc block *flow through the wire* toward the copper block. [14]

I. Electrons are transferred [...] to the oxidizing agent after *passing through an external circuit* [...] The *electrons* [...] *travel through* the external circuit to the Cu(s) electrode, where they are consumed in the reduction of $Cu^{2+}$. [15]

Comments: In passage A, the first instance of 'as' (in "as through a tube") might lead one to assume that the author is building a model, but the passage overall is declarative: "An electron [...] is pumped [...] The charge [...] is conducted by the motion of the ions." And yet no valid statement of fact emerges, so we must consign the passage to the realm of *notions*. (My use of the term 'notion' is explained in the definition of ORTHODOXY above.) In B, the authors speak first of a battery causing "charge to move through a wire," etc. So far so good. But later they lapse into the Orthodoxy whereby *electrons flow through the wire*. This creates a mixed message, teetering on the fence between science and fiction. In passage C, mixed in with the obligatory 'electron flow' patter we find two realistic-looking terms, 'current' and 'charge passed.' To us, this might suggest that the author's *own* interests extend beyond the Orthodoxy to things more substantive, but that fleeting shift in the level of discourse is not much help to the naïve *student* using his textbook. (For perspective on the many instances of 'electron flow' in the electrochemistry literature as documented here and in Part Four below, consider the following 'Pitfall Prevention' from a freshman physics text [3]: "A battery does not provide electrons to the circuit. It establishes the electric field that exerts a force on electrons already in the wires.")

Here I've assembled some specifics on electron drift and ion mobility, as context for the problem in the next paragraph: The drift velocity of an electron in copper is 1 meter per 75 minutes or

$2.22 \times 10^{-4}$ m/s [16; see also 17, 18]. Ions migrate at rates on the order of $6.8 \times 10^{-4}$ cm/sec, 0.246 mm/min, or 2 cm/hr [19, 20, 21]. Expressed in m/s equivalents, that gives us: $6.8 \times 10^{-6}$, $4.1 \times 10^{-6}$, $5.5 \times 10^{-6}$. Let's note in passing that *current* makes indirect appearances in the literature as the numerator of the current density definition: J = I/A. But when expressed in terms of one-dimensional velocity, these rates too are found to belong, as usual, to the realm of electron drift, not electricity near *c*. Here are three such examples: "At a current density of $10^4$ mA/cm$^2$, the rate of iron dissolution is about 0.15 mm/min" [22], m/s equivalent: $2.5 \times 10^{-6}$ . "[For] iron at $j = 90$ Acm$^{-2}$, the rate of dissolution is 2 mm/min and for $j = 540$ Acm$^{-2}$ it is 12 mm/min" [21], m/s equivalents: $3.3 \times 10^{-5}$, $2.0 \times 10^{-4}$ . Paraphrase: Pass 3 mA through cell with cross-sectional area of 3.25 cm$^2$ for 45 min; the boundary moves 2.13 cm. Rate: 2.13 cm/45 min $\cong 7.8 \times 10^{-6}$ m/s [23].

To gain a better understanding of what these numbers mean in practical terms, let's now do a variation on a cell-charging problem. In paraphrase, the problem itself runs as follows: "If 10 A were passed through a lead storage cell for 1.5 hours, how much $PbSO_4$ would decompose? Answer: 170 g" [24]. Now, suppose we apply a representative drift velocity and migration rate to that procedure. It would take 352 million years for the 170 g to react, instead of 1.5 hours (as plausibly stated in the problem itself).

Assumptions/calculation: Let the electrode separation be 3 cm, as shown in Figure 1, where the circuit depicted is generic and may therefore be borrowed as an ad hoc adjunct to the $PbSO_4$ problem. The 3 cm separation accounts for 1% of the circuit's perimeter. For the 99% metallic regime, 99% of 1.5h is 1.485h; for the 1% electrolyte regime, 1% of 1.5h is 0.015h. Divide $3.0 \times 10^8$ m/s by $2.22 \times 10^{-4}$ m/s (a representative electron drift velocity) and multiply the dimensionless result by 1.485h to obtain $2.00 \times 10^{12}$ hours, or 228 million years. Divide $3.0 \times 10^8$ m/s by $4.1 \times 10^{-6}$ m/s (a representative ion migration rate) and multiply by 0.015h to obtain $1.09 \times 10^{12}$ hours, or 124 million years. Sum of years: 352 million years. (If applied to the procedure featured in Figure 1 itself, these same considerations require that the duration be revised from 1200 seconds to 78 million years.)

How can such a contradictions arise in elementary teaching materials? Short answer: The term 'electron flow' is the culprit; it should never have been coined so cavalierly on the physics side nor adopted so naïvely by electrochemistry. The makings of a longer answer are suggested in Tsaparlis: *In high school and college instruction, the quantitative/manipulative aspects of electrochemistry are*

*emphasized, while qualitative understanding is neglected. When asked about their misconceptions, students attribute them chiefly to those traditional methods of teaching, which fail to reflect the complex and interwoven concepts of our field.* [25, paraphrase]

**Part Four: More Citations, now from specialized electrochemistry texts**

In Part Three I documented the widespread use of the term 'electron flow' and label '$e^{-}\rightarrow$' in literature category (a). Here I conduct a survey of category (b), the specialized electrochemistry texts, to see if/how they move beyond the notion of 'electron flow' as presented to freshmen.

Except for "there *is* net transport" in passage J and "*or* ions" in M below, all italics in the quotations to follow are mine. As before, the italics flag manifestations of the Orthodoxy. Again, some terms hint at (or reflect clearly: passage N) a view that transcends the Orthodoxy, and I differentiate these terms by bolding.

> J. The Quantitative Link between *Electron Flow* in the Electrodes and *Ion Flow* in the Electrolyte: **Faraday's Law** [...] electron **current $I_e$** in the metallic part of the circuit must be equal to the ion **current $I_i$** [...] The bulk situation [for ions that are not in proximity to either electrode] is like the **random walk of electrons**; it can never yield *electron transport*. The interface situation is like the **drift**, *or flow*, of electrons; there *is* net transport and a **current** [...] There will be a *flow of electrons* in the metallic part of the circuit and an ionic flow in the electrolytic solution. [From context, it appears that Bockris & Reddy are speaking only of the *interface* vicinity, not the whole "metallic part."] Follow the path of the **drifting** *charge* [...] If the external power source can keep *pumping electrons through the system* [...] [26]
>
> K. [A] current source "pumps the electric fluid" [The] mobility of electrons [...] is responsible for electrical **conductivity** [E]lectricity as a "fluid" [...] naive model [...] ionic conductors [...] possess **conductivity** by virtue of the motion of anions and/or cations [E]lectronic conductivity [...] allows the *passage of electrons* [The] **electricity** is carried by the motion of hydrogen ions $H^{+}$ from right to left and by the motion of bisulfate ions $HSO_4^{-}$ from left to right [...] Note that *electrons flow* through the load from right to left but, because electrons are negatively charged, we speak of **electricity**, or **electric current**, flowing from left to right through the load. [The current] flows clockwise as our cell is diagrammed. [27]

L. ...*supplying electrons* to the copper electrode with an external power supply [...] *electron flow* from a solution species *into the electrode* [...] Since ***i*** represents the number of electrons reacting with $Cd^{2+}$ per second, or the number of **coulombs** of electric charge flowing per second, the question 'What is *i*?' is essentially the same as 'What is the rate of the reaction, $Cd^{2+} + 2e \rightarrow Cd$?' [28]

M. Electric currents in electrolyte solutions *are* the directed motions of the ions under the influence of an applied electric field [i.e., ion migration] To sustain steady current flow, one needs a steady sink for the *particles arriving* and a steady source for *those departing* [...] At an anode, *electrons go away* from the junction into the metal [...] at a cathode, *electrons supplied by the circuit* must react [...] the interface [...] is crossed by species of one type: electrons [at the anode in the present example] *or* ions [at the cathode]. [29]

N. If the ions in an electrolyte solution are subjected to an **electric field** [the resultant force will] induce motion in or against the direction of the field [...] This *ion motion leads to the* **transport of charge** and hence to the flow of **electrical** [sic] **current** through the electrolyte solution [...] When current flows [...] ions migrate [The] fundamental difference between **charge transport** [...] **by** ion migration and [...] **by** electron migration. [30]

Comments: In passage J, if we only glance at the symbols $I_e$, and $I_i$ it might seem that we have found an example of a specialized electrochemistry text compensating, at last, for the silence on (real) electric current at the freshman level. But look again. The meanings assigned to those symbols by the authors are 'Electron Flow' and 'Ion Flow', respectively; so this is the Orthodoxy dressed up to look technical. In II:848-854, the authors scramble terminology in ways that are embarrassing even in the context of the Orthodoxy. For example, they tell us the electron donations from ferric to ceric ions, adrift in the bulk solution, exhibit a 'random walk,' so there can be no 'electron transport' in the bulk solution. Not only is that way of alluding to the random walk of electrons wrongheaded and misleading (compare Figure 3), but having identified a mechanism that contributes *no* current to the ionic bulk solution they fail to offer an alternative mechanism that *does* account for completion of the circuit (viz., an electromagnetic wave aka electricity). Also, they have tacitly rechristened *charge transport* as "electron transport," seen nowhere else in the literature. Next, by virtue of the word 'or' they equate *electron drift* (something real and measurable) with *electron flow* (something jargony and unreal). Finally, they juxtapose "flow of electrons" with

"drifting charge." This simultaneously (a) denies the distinction between *electron drift* and *charge transport* and (b) confounds (nonexistent) electron flow with (real) electric current.

Oldham & Myland [27] start their book with a whole chapter on The Conduction of Electricity. It is heartening to see this feature, which is lacking in a number of other specialized electrochemistry texts. In passage K above, Oldham & Myland even employ the word 'model' which provides relief from the literalism of the Orthodoxy. And they say the mobility of electrons is *responsible for* electrical conductivity; similarly, ions are said to *provide* conductivity. All true statements. But the conclusion of Chapter 1 is disappointing. Ostensibly, this is where electric current itself will be defined in detail but in fact the discussion takes a detour (as I see it) into electron drift rates (without using that terminology). Never does the circle close on electricity itself. At the end of the chapter, attention turns instead to conventional current, signaled (implicitly) by the appearance of '$e^{-}\leftarrow$' versus '$I\rightarrow$'. (Unaccountably, the term 'conventional current' itself is never mentioned.)

As for L, in another context the discussion of ***i*** and **coulombs** could make sense, but as presented it is tainted by language of the Orthodoxy that occurs two pages earlier.

Like the opening chapter in Oldham & Myland, the first chapter in Bagotsky (Electric Currents in Ionic Conductors) goes a long way toward remedying the silence on electricity that pervades the freshman-level literature. Yet though Bagotsky's description of the cell in passage M is more precise and technical-*sounding* than what we see typically at the freshman level, it is in essence the same old Orthodoxy, dressed up a bit: At the anode, two $Cl^{-}$ (*aq*) ions supply a pair of electrons that flow counterclockwise through wires, necessitating the plating out of one $Zn^{2+}$ at the cathode; such is Bagotsky's scheme (paraphrased here). Contrast this with [4] where the notion of *any* $M^{+}$ plating out to $M^{0}$ is shown to be false. (Also, with "are" Bagotsky explicitly equates "electric currents" with "the directed [i.e., vectored] motions of ions." This too harks back to the Orthodoxy and concomitant confusion about speed(s). Contrast this with N.)

In N, the authors (Hamann, Hamnett and Vielstich) provide a level of detail appropriate to a specialized text *and* their details are accurate. *Here at last we find an example that departs definitively from the Orthodoxy*, not just momentarily by veiled hints as noted in a few of the earlier examples. (I would have closed this series with a sixth passage labeled 'O' from Gileadi, except that he has been cited already in our definition of ELECTRICITY (Figure 3), and in Figure 2C. In [4],

Gileadi too offers a clear challenge to the Orthodoxy, although not in the comprehensive manner of passage N.)

## Concluding Remarks

Already, everyone knows electrochemistry has *something* to do with electricity. Why, then, have I labored here to clarify and expand on that one small point? I did not do this work in a vacuum; it was motivated by an underlying philosophy of the macroscopic and atomic realms. Up here at the macroscopic level (where so much is illusory on the Vedānta viewpoint), there are precious few options available to us for 'communing' with entities down there at the atomic scale (where the only credible reality prevails, according to my bias). One way to bridge the gulf is through thought experiments based on the von Koch snowflake, an exercise that might be dubbed Twenty Degrees of Separation, by analogy with Six Degrees of Separation in the social sphere [34, 35].

Another way of communing with the atom is simply to *do chemistry*, with increased awareness of its bridge-building aspect, across the macroscopic/microscopic abyss. But for this to work one must have full confidence in the modeling of a given process. Early on, I could not help noticing that 'electron flow' is a factoid. My knee-jerk reaction to that disappointment was to review freshman physics, where surely I would find a wealth of material to fill in the blanks on the electrochemistry side. But as we have seen, it turns out that the electricity tradition in physics pedagogy possesses its own problems. Eventually, I felt there was no course open but to build my own model, by choosing selectively from physics texts then adding in Gileadi's $M^+$ (in Figure 3).

Naïvely stated, one of the primary mottos related to my philosophy would be: Make Atoms Real (for the student). But this would not sit well with the Copenhagen interpretation of quantum theory, wherein atoms are not things, only tendencies [36]. Accordingly, one should revise the motto to read: Make the Atomic *Realm* Real. This does not mean, however, that we have agreed to a full retreat from Make Atoms Real. How so? Nick Herbert points out that a rainbow is object*ive* (in one's brain) even if it is not an obj*ect* (in the sky) [37]. By the same token, a mercurial atom, even if it is just a bundle of tendencies, is still object*ive* from a certain vantage point. (An objection might come from the opposite direction, as follows: "Neither the atom nor even its nucleons are now regarded as elemental; rather, quarks play that role." In that case, my response would be to cite Douglas Hofstadter on chunking in general, and on the chunking of quarks in particular [38]. From

the chemistry viewpoint, never mind the commonsense viewpoint, the atom is the appropriate chunking level.)

A final thought on the term 'electron flow' as presently used in electrochemistry pedagogy: Not only does it break the science compact (because it is a fairy-tale), but it does double harm by simultaneously robbing the student of the opportunity to contemplate something truly wondrous: namely, charge transport near *c*, a phenomenon that, in its way, is just as remarkable as the one Einstein found so mesmerizing as a child of four or five: the movement of a compass needle [32]. Given its ubiquity, one cannot imagine the term 'electron flow' being abandoned, ever. By definition, factoids are forever. But at least future authors might try to recast the term as part of an explicit simplifying *model* (albeit a poor model, grandfathered in) rather than allowing it to persist as the centerpiece of a silently entrenched *myth*.

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