Letters

Quantity algebra (calculus) – some observations

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I was first introduced to *Quantity Calculus* during the early 1950s in lectures given with absolute clarity, if somewhat dictatorially, by E. A. Guggenheim and Max McGlashan. I have been a devotee of the method ever since and thus welcomed the erudite account given by Joe Lee.[1] Although there is little in his account with which I would disagree, I thought it might be useful to comment on several facets that, when dealt with in a particular way, enhance student performance - they show a greater understanding of what they are doing and make fewer numerical and 'grammatical' mistakes.

The first hurdle is the name *Quantity Calculus*, which is frightening to students and causes many to close their minds to what is a simple and logical approach to handling physical quantities, their measures and their units. In any case it is difficult to see much similarity to what is normally understood as calculus. A less forbidding title is the alternative, *Quantity Algebra*. This name is a truer description of the processes involved and it is sensible to use it when introducing the method. Reference can be made to the more usual name subsequent to students carrying out examples to familiarise themselves with what the method is all about.

Other teaching strategies that I have found to be helpful are
- to encourage students to write down each step in a calculation involving units and when a change is made, to ensure that a note of the relationship used is included e.g. since $Pa = N\ m^{-2}$ and $J = N\ m$ then $Pa = J\ m^{-3}$. It is essential to ensure that students are fully conversant with basic definitions such as pressure, force, energy etc.
- to make extensive use of brackets to eliminate any doubt in calculations involving, for example, the conversion of units. It is better to use too many rather than too few brackets if they lead to a correct solution.
- to keep the measure and the unit together for each physical quantity when their values are substituting into an equation, rather than collect the units separately in a single composite term. This makes it much easier to check the units, a procedure which should always be a prerequisite to carrying out the final calculation.
- to ensure that 'dimensionally homogeneous' additive/subtractive equations are presented in the form illustrated by

$$V/cm^3 = 1.234 + (2.345 \times 10^{-4}\ t/^{o}C)$$

rather than in either of the other two alternative but correct forms given by Lee. Students are more comfortable handling such an equation in this form.
- to use exponents of ten whenever they are necessary in a calculation (a simple volumetric calculation is a possible exception where it is often simpler to use 1000 rather than 10^3). Thus in unit conversion e.g. $m^3 \rightarrow cm^3$ it is preferable to write $m^3 \rightarrow (10^2\ cm)^3$ - and the laws of indices applied - rather than $m^3 \rightarrow (100\ cm)^3$. Similarly, in labelling column / row headings in a table or in labelling the axes of a graph in which a repetitive power of ten multiplier arises, it is preferable to write for example, $T/10^3\ K$ rather than T/kK or $T/1000K$. The use of prefixes here is particularly dangerous. When the multiplier is a negative exponent of ten, less confusion and fewer errors occur if the multiplier and the unit are kept together. Thus although $V/(10^{-3}\ m^3)$ is more cumbersome and less aesthetically pleasing than $10^3\ V/m^3$; it is a much safer bet until a student is conversant and confident with the general approach.

To conclude, I turn to the name 'amount of substance' commonly used for the base physical quantity, symbol n, whose unit is the mole. This is the only three word name among those used for any of the seven base physical quantities and arose, not by choice from the English language but from the translation of the single German word 'Stoffmenge'.[2] It is a clumsy name particularly when used to refer to

a given chemical entity. 'The amount of substance of sodium hydroxide' i.e. n(NaOH), is a verbal marathon that does not flow easily and is difficult for students to use correctly. The Green Book[3] acknowledges the problem in suggesting that the name may often usefully be abbreviated to the single word 'amount'. Unfortunately, in the hands of inexperienced students, this easily becomes synonymous with mass or less frequently volume.[4] The alternative name 'chemical amount', given by Lee without comment, is a more descriptive name that acts as a pointer for beginning students since it can be introduced as the 'chemist's amount'. First suggested by Gorin[5], it was given as an alternative to 'amount of substance' in the second edition of the Green Book[3] (it did not appear in the first edition in 1988), similarly with the suggestion that it may usefully be abbreviated to 'amount'. It is a two-word name, comparable to the base physical quantity, 'electric current' but whereas the common practice of abbreviating the latter to 'current' seldom leads to confusion this is not the case when 'chemical amount' is abbreviated to 'amount'.

I believe strongly that many of the difficulties that arise with calculations involving n would be not arise if it is called 'chemical amount' rather than 'amount of substance': students are very much more at ease with 'the chemical amount of sodium hydroxide' in both the written and spoken word. However I do not believe it is beneficial in the majority of cases, particularly for beginning students, to abbreviate this to 'amount' and recommend for example, that we refer to 'the chemical amount of Cl_2' rather than 'the amount of Cl_2' and 'chemical amount concentration' rather than 'amount concentration'. After all these are still less cumbersome and confusing than 'amount of substance of Cl_2' and 'amount of substance concentration' and lead to fewer mistakes.

References
1. J. Lee, *U.Chem.Ed.*, 2003, **7**, 27.
2. E. A. Guggenheim, *J. Chem. Ed.*, 1961, **38**, 86.
3. I. Mills, T. Cvitaš, K. Homann, N. Kallay and K. Kuchitsu, *Quantities, Units and Symbols in Physical Chemistry*, 2nd ed., Blackwell, Oxford, 1993, p.4.
4. J. I. Hoppé, *Educ. Chem.*, 1990, **27,** 129.
5. G. Gorin, *J. Chem. Ed.*, 1982, **59**, 508.

Conceptual understanding of electricity: galvanic and electrolytic cells.

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I was very interested in reading the recent paper on this topic.[1] While commending the authors on their attempt to unravel the complex understandings of prospective teachers on this matter I would like to take the opportunity to comment on their own explicit understandings and some of their pedagogic implications.

For me this area of study has been of interest for many years, particularly the problematic issue of the conduction of electricity *within* a Galvanic cell.[2] I was still unable to explain to myself – in terms of electrical charges – how it is that in, say a Daniell cell (Figure 1), positively charged copper ions are deposited on the copper electrode *labelled positive* when current is drawn from the cell. (As is discussed below the the a major part of the problem is linked with the labelling of the electrodes. Indeed, a moment's thought demonstrates a fundamental

Figure 1
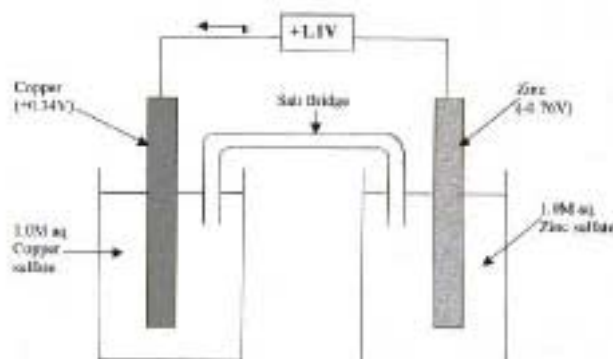
issue – although I did not notice this in forty years – that if the current flows in a complete circuit and the cell electrodes are labelled '+' and '–' then it is *logically not possible* for the conventional current to flow from '+' to '–' in both the external circuit and within the cell.) I was unable to find a convincing explanation in texts and essentially I was left with the idea, consistent with the Ogude and Bradley's[3] statement:

> *"It must be emphasised that the motion of ions in the two half cells is not caused by the charge at either electrode."*

Essentially the idea is that electrons entering the copper electrode from the zinc via the external circuit disturb the pre-existing equilibrium at the interface between the copper and the copper ions in the solution (the equilibrium gives rise to the electrode potential). Since the positive charge is reduced, more copper ions are now deposited at the surface in the attempt to restore the equilibrium. However I was not able to articulate the idea in a way that provided an explanation in terms of 'opposite charges attracting'. I have a deeply held belief (is that scientific?) that that unless there is an *electrical potential difference* it is not reasonable to expect a current to flow! Certainly the research of Ogude and Bradley[3] and others shows that the one relationship that dominates learners' understandings of science is that positive charges attract negative charges and that like charges repel. This relationship invariably *determines* the direction of electron/ion/charge carrier flow in any part of any electrical circuit.

A particular insight can be gained when considering a Galvanic (Daniell) cell on open circuit. With an appropriate salt bridge linking the electrolyte solutions in the electrode compartments the electrodes (Fig 2A) must be at the same potential from the perspective of the electrolyte solution. Thus, within the copper electrode compartment, the excess anions (the solution must carry a net negative charge, although I am now persuaded that this is effectively contained within an 'electrical double-layer' of ions that effectively prevents an electric potential gradient from being 'felt' by ions more than a few ionic diameters away from the electrode surface; See Note 1 at the end of the letter) will shield the electrode such that *from the perspective **within** the solution* the electrode appears uncharged.

Figures 2B and 2C indicate *qualitatively* and as a 'thought experiment' how the electrical potential differences change across the external circuit and within the cell when electricity flows around the circuit. 2B shows a small current when the internal resistance of the cell is equivalent to the resistance of the external circuit (small because the internal resistance of a Daniell cell is quite high.) 2C would be the situation if the cell were completely shorted out (external circuit has zero resistance). The numbers given are not exact (except in 2A for a standard cell) since the cell does not operate under conditions of thermodynamic reversibility. Also it is not being suggested that these could sensibly model the situation in cells actually used to produce electricity since the internal resistance of a cell as shown in Figure 1 would be huge. However, the important factor is that *from the perspective of the solution, when current flows* the sign on the copper electrode is **negative** whereas *from the perspective of the external circuit* the copper electrode is still **positive.** (It now begins to seem obvious that charges on the electrode must be +/- and -/+ from the two different perspectives otherwise it would not be logically possible for a flow of negative charge to complete the circuit (Figure 3). Again it is *not* being suggested that this is how electrodes should be labelled, only that the perspective of the 'user' must be carefully considered before any sign is ascribed. It may well be better if no sign is automatically ascribed to an electrode and any explanations first justify the sign given by reference to the reaction that is taking place *and* make clear the perspective.

The recommendations given in the paper[3] (for teaching require a very careful appraisal before being implemented since, it seems to me, the idea that we should try to persuade students that 'the net charge' on the electrode is 'exceedingly small' and 'simple electrostatic arguments do not correctly explain the direction of ion and electron flow and may be pedagogically and scientifically unsound. Suggesting that the *small amount of charge* on the electrode inhibits confident prediction of the direction of current flow seems equivalent to suggesting that a *small amount of heat in an object* inhibits prediction of the direction of heat transfer. Surely it is the potential difference (or the temperature difference) that is the determining factor and the EMF of a Daniell cell applied to an external circuit is considerable (1.1V) and well known. (The actual *amount* of charge on an electrode is irrelevant and depends only on the
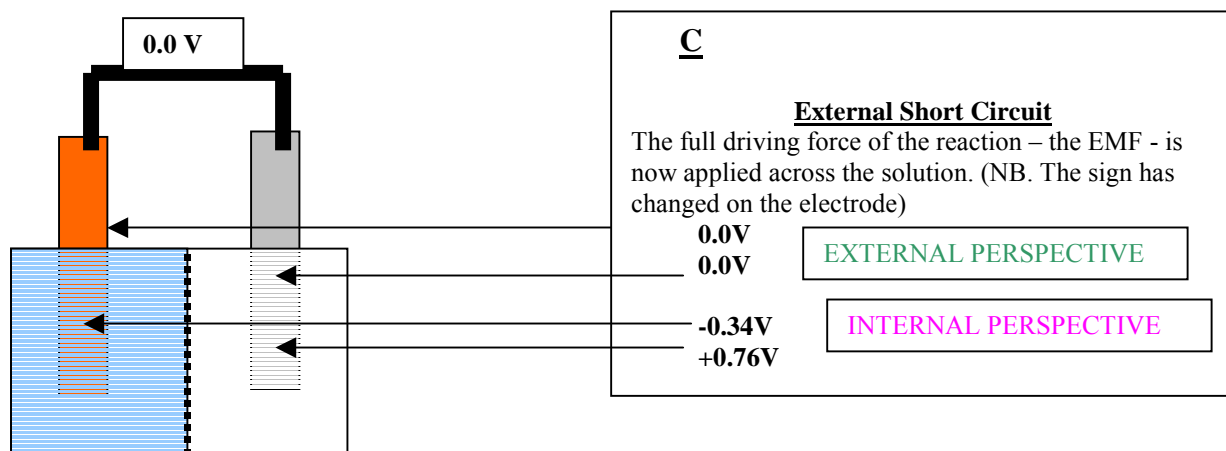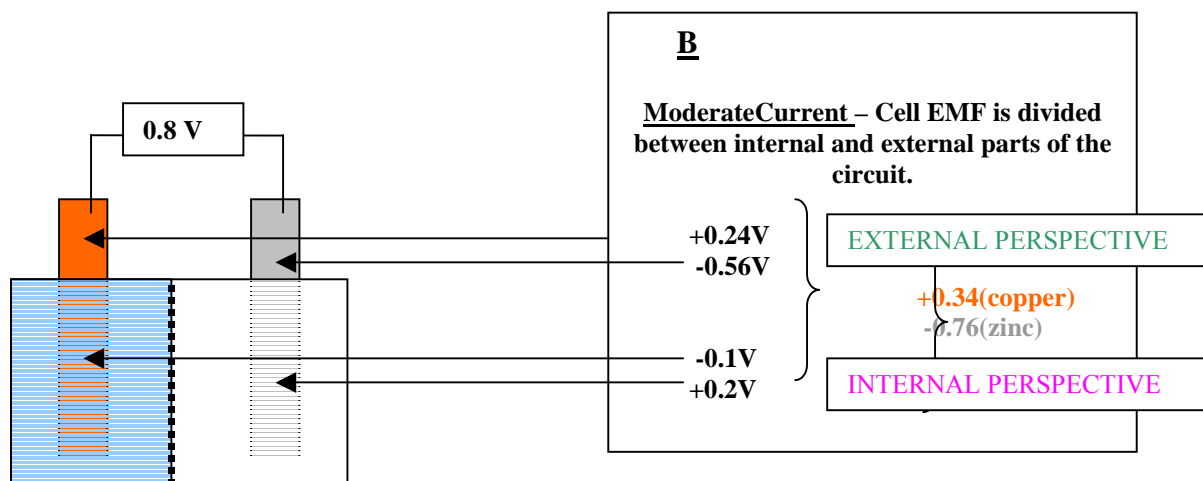
Figure 2

A

No Current flowing – Cell EMF is applied at external terminals.

1.1V

+0.34V
-0.76V

EXTERNAL PERSPECTIVE

0.0V
0.0V

INTERNAL PERSPECTIVE

No internal current, thus no potential difference **across** the solution gap.

B

ModerateCurrent – Cell EMF is divided between internal and external parts of the circuit.

0.8 V

+0.24V
-0.56V

EXTERNAL PERSPECTIVE

+0.34(copper)
-0.76(zinc)

-0.1V
+0.2V

INTERNAL PERSPECTIVE

C

External Short Circuit
The full driving force of the reaction – the EMF - is now applied across the solution. (NB. The sign has changed on the electrode)

0.0 V

0.0V
0.0V

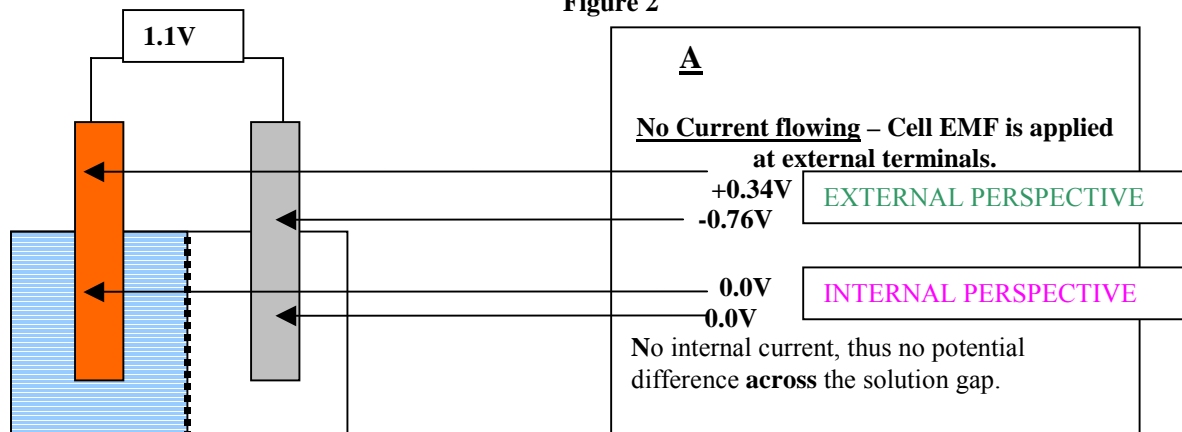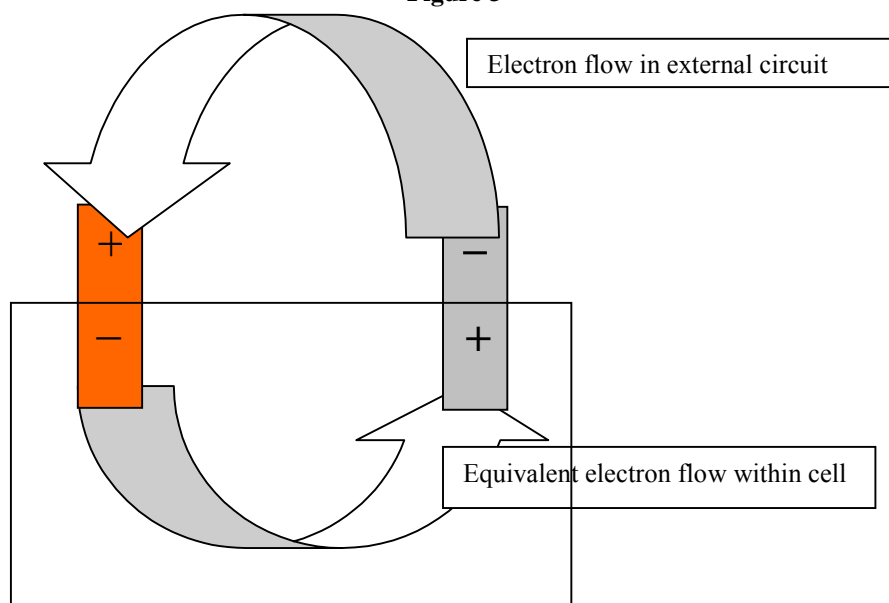EXTERNAL PERSPECTIVE

-0.34V
+0.76V

INTERNAL PERSPECTIVE

Figure 3

chemistry of the materials present and the physical dimensions of the rod that determine its behaviour as a capacitor.)

I agree absolutely with the authors (p.9) that students should be expected to show (qualitative) understanding of the chemical processes involved. However it is also necessary for them to keep a critical eye on their teachers and textbooks to convince themselves that what they are learning is consistent and sensible. Teachers are human, interpretations change, words *do not have unambiguous meanings* – we all hold a variety of alternative conceptions that is neither constant nor entirely consistent .[2] Teachers need to convince their students (and themselves) honestly of the validity of the ideas being considered. I guess that some of my earlier statements still sound/are outrageous. Indeed, I have been warned against entering this debate since I am a relative novice as an electrochemist; however, it is the simple questions that often prove difficult to answer. It may be significant that there seems to be a lack of an accessible qualitative account of the process of electricity flow within galvanic cells in textbooks at any level – at least none that I can find.

One further issue with the suggested pedagogy is the use of computer simulations. This can undoubtedly be effective but the simulation is constrained neither by the facts nor by the laws of science that we are attempting to teach. Simulations will simulate the beliefs of

their authors and must be treated with due criticism.

(I am a little worried by Question 15 in Özkaya's paper.[1] This – and their offered 'correct' answer suggest that the authors believe that current between the electrode compartments will not flow along a conducting wire. This may not be true since dipping the wires in the electrolyte solutions (instead of using a salt bridge) could simply provide another pair of electrodes and thus produces a circuit with two Galvanic cells in series. I would not care to predict the overall EMF, but I am not convinced that it would be ZERO and therefore that no current would flow. I got a current of well over 100μA when I tried it using a silver wire. There was no platinum to hand.)

(Note 1. The outline of the above discussion was presented at the 'Variety in Chemistry' Conference in Dublin, September 2003 and proved to be controversial. Specialists in electrochemistry were very concerned that I was implying that ion movement within the cell when current flowed around the circuit was driven by a potential gradient between the electrodes. Apparently the electrical double-layers (multiple-layers) of ions that surround the electrodes ensure that no potential gradient is present in the solution beyond these layers. The bulk movement of material within the cell is driven by diffusion along concentration gradients (or gross physical disturbance such as convection currents or stirring.) For me this still leaves a problem as to how the charge

'flows' between the electrodes. Presumably as soon as a charge imbalance within the (from the equilibrium value required to maintain the 'electrode potential' – as measured externally between the electrodes) occurs because copper ions are deposited on the copper or zinc ions pass into solution, there is a rapid 'adjustment' in the positions of all charge carriers between the electrodes in order to retain electrical neutrality within the bulk of the solution? I have not really 'explained' this satisfactorily to myself, but it seems to me that this charge adjustment is not simply 'diffusion'.)

References:

1. A.R. Özkaya, M. Űce and M. Şahin. *U. Chem. Ed.*, 2003, **7**, 1
2. A. Goodwin, *Chemistry Education: Research and Practice in Europe*, 2002, **3,** 345.
3. N.A. Ogude and J.D. Bradley*, J. Chem. Ed.*, 1996, **73,**. 1145