

Conceptual understanding of electricity: Galvanic cells

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In a recent letter to University Chemistry Education,¹ Alan Goodwin comments on one of the conceptual questions (Question 15) involved in our article.² First of all, we would like to thank Alan Goodwin for his valuable comments. He states that he is a little worried by Question 15 and our offered 'correct' answer. In his opinion, Question 15 and our offered 'correct' answer to it suggest that we believe that current between the electrode compartments will not flow along a conducting wire. We are aware of the fact that if a metal wire replaces the salt bridge in a galvanic cell the ammeter connected through the circuit may show a reading, but we also know that this current reading is very low (as also stated by Goodwin) compared to the current measured using a salt bridge. It is necessary to use a very sensitive ammeter to be able to measure such a low current. We could not measure it when we used an ordinary ammeter in the circuit. Therefore, during the construction of the question, we thought that this very low current could be ignored. Question 15 is very similar to the one involved in the article reported by Ogude and Bradley (Question 11).³ The only difference between the two is that the one reported by Ogude and Bradley replaced the salt bridge with graphite while our question replaces it with a piece of platinum wire. Ogude and Bradley's ideas about this issue were probably similar to ours when constructing Question 11, since they offered the same alternative as the 'correct' answer, so we do not believe that it is necessary to correct either Question 15 or our offered 'correct' answer.

In his letter Alan Goodwin cites Ogude and Bradley's article⁴ published in 1996 and states that he found a convincing explanation about how positively charged copper ions are deposited on the copper electrode labelled positive when current is drawn from the cell, but it seems that he was unaware of the article published by Ogude and Bradley³ in 1994 when writing his letter. Had he been aware of this article he would have directed his criticisms towards them since it was published long before our article appeared in this journal.

In his letter,¹ Goodwin suggests a model to explain how the electrical potential differences change across the external circuit and within the cell when electric current flows around the circuit (p.60, his Figures 2 and 3). He states that the outline of his discussion was presented at the 'Variety in Chemistry' Conference in Dublin, September 2003, and proved to be controversial. Perhaps, he will publish this proposed model in a journal to share his ideas with the instructors and electrochemists. We would like to share our common ideas about his model with him in the hope that our comments will help him to improve his model. In his letter it is stated that [his] Figures 2B and 2C indicate *QUALITATIVELY* how the electrical potential differences change across the external circuit and within the cell (p.60), but various potential values are assigned *QUANTITATIVELY* to the internal and external parts of the electrodes. In his Figure 2, cell emf is divided between internal and external parts of the circuit. *Really, this is a very radical approach.* We could not find such an approach in electrochemistry texts. It is not reasonable in terms of basic aspects of cell emf and electrode potentials. The half-cell potential or electrode potential talked about in electrochemistry is the potential difference between the solution and the electrode, and this potential difference cannot be measured, but *the difference between two differences*, or the potential difference between two half-cells, can. In his Figure 2A, the values of +0.34V and -0.76V are assigned to the external parts of the cathode and anode respectively in the absence of current flow; when the cell potential changes from 1.1V to 0.8V as a result of the moderate current flow, these values are given as +0.24V and -0.56 V respectively.

At this point, we need to make an evaluation in terms of the Nernst Equation. When current flow is allowed to pass through the cell, i.e. a low impedance pathway is provided until the cell voltage as read on the voltmeter decreases to a particular value, the concentrations of the electro-

active species in the anode and cathode compartments also change since chemical changes occur at each half-cell (at each interface). There is a strong relation between the electrode and cell potentials, and the concentration of the electro-active species. For example, according to the Nernst Equation, a change from -0.76V to -0.56V in the potential of the anode requires a change from 1M to $4.641589 \times 10^6\text{M}$ in the concentration of Zn^{2+} . Clearly, this is not possible. This evaluation suggests that it is not sensible to assign random values to the electrode potentials after current is allowed to pass through the cell during a time period. As outlined in Figure 1 in this letter, it may be better to adopt a qualitative approach that explains how the potential of each electrode (the potential difference at each metal/solution interface), and the concentrations of electro-active species at each compartment change during the passage of current through the cell until the electrode potentials become equal to each other, i.e. cell potential is zero.

As shown in Figure 1A (in this letter), when each electrode is immersed in a solution containing its ions, the metal electrode and the ions in solution come to an electrochemical equilibrium as a result of the interactions between the metal atoms in the electrode and the ions in solution, and a potential difference develops at each metal/solution interface during the approach to equilibrium. The establishment of this equilibrium takes a very short time, less than a microsecond. During this very short time, either a very small amount of the metal will dissolve or traces of the metal ion in solution will be reduced. Accordingly, a small transfer of charge will occur at metal/solution interface (*electrical double layer*) during the approach to equilibrium. These processes are the origin of all electrode potentials. The net numbers of electrons on the electrode before and after equilibrium $\text{M}(\text{s}) \rightleftharpoons \text{M}^{\text{n}+}(\text{aq}) + \text{n}\text{e}^-$ is established will be slightly different. Thus the electrode acquires a slight electrical charge; the solution acquires the opposite charge. The equilibrium is established for all metals (except for those metals that react with water). However, for some metals the tendency for metal atoms on the surface of the electrode to be oxidized is higher than the tendency for metal ions in solution to be reduced, while for others the tendency for metal ions in solution to be reduced is higher than the tendency for metal atoms on the surface of the electrode to be oxidized. In other words, for some metals the equilibrium has a higher tendency to go to the 'right' (these give extra positive charge into the solution and leave electrons on the electrode) while for others it has a higher tendency to go to the

left (positive ions leave the solution, thus give the surrounding solution an overall negative charge).

Once equilibrium between each electrode and the corresponding metal ions in solution has been established, each electrode is then attached to one of the inputs of a potentiometer to measure the difference between the voltages of the two metal/solution interfaces. The connection of a potentiometer (a special voltmeter with very high resistance) through the electrodes ensures that the potential difference between the two half-cells is measured under the conditions of no current flow; therefore no net electrochemical reactions can occur. The reading on the potentiometer in the external circuit is the *cell potential*, E_{cell} and represents the potential difference between the two half-cells. Since this potential difference is the '*driving force*' for electrons, it is sometimes referred to as *the electromotive force (emf) of the cell*. This term should, however, only be used to denote the potential difference between the electrodes when the cell is not giving current. This potential difference tends to fall when current does flow and only a portion of the total is available for driving current in the external circuit. In other words, when a current flows through the cell, the potential difference between the terminals is less than the emf of the cell. This is why the emf of a cell gives an indication of the *maximum capacity of the cell* to do electrical work. If a very high resistance voltmeter (potentiometer) is used the emf of a cell can be measured. On the other hand, an ordinary voltmeter connected across the poles of a galvanic cell will only approximately measure its emf because an ordinary voltmeter cannot work without a small current flow.

When the electrodes are connected by an ammeter as represented in Figure 1B in this letter (or by a metal wire directly) i.e., when a low impedance pathway is provided, current would flow through the cell. As current passes through the cell, net electrochemical reactions occur at each electrode. The flow of electric current between the metal electrodes occurs as electrons flow from the more negative electrode (anode) to the more positive one (cathode) through the external circuit. On the other hand, the flow of electric current between the solutions must be in the form of *migration* of ions. This cannot occur through a wire but through another solution that bridges the two half-cells; this connection is called a *salt bridge*. During the passage of current through the cell, the potential of the cathode decreases while that of the anode increases; the concentration of electro-active species in each compartment also changes since

Figure 1

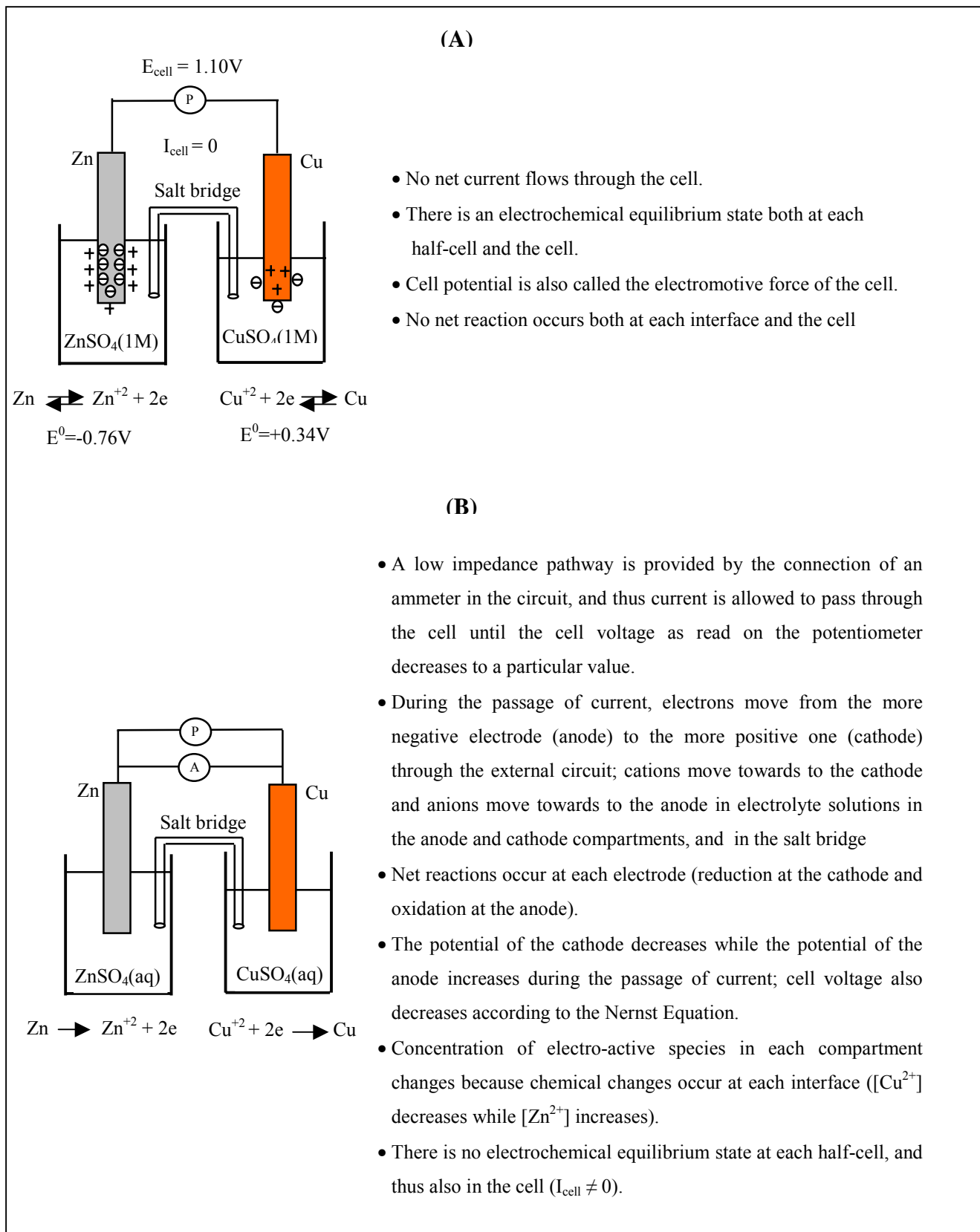
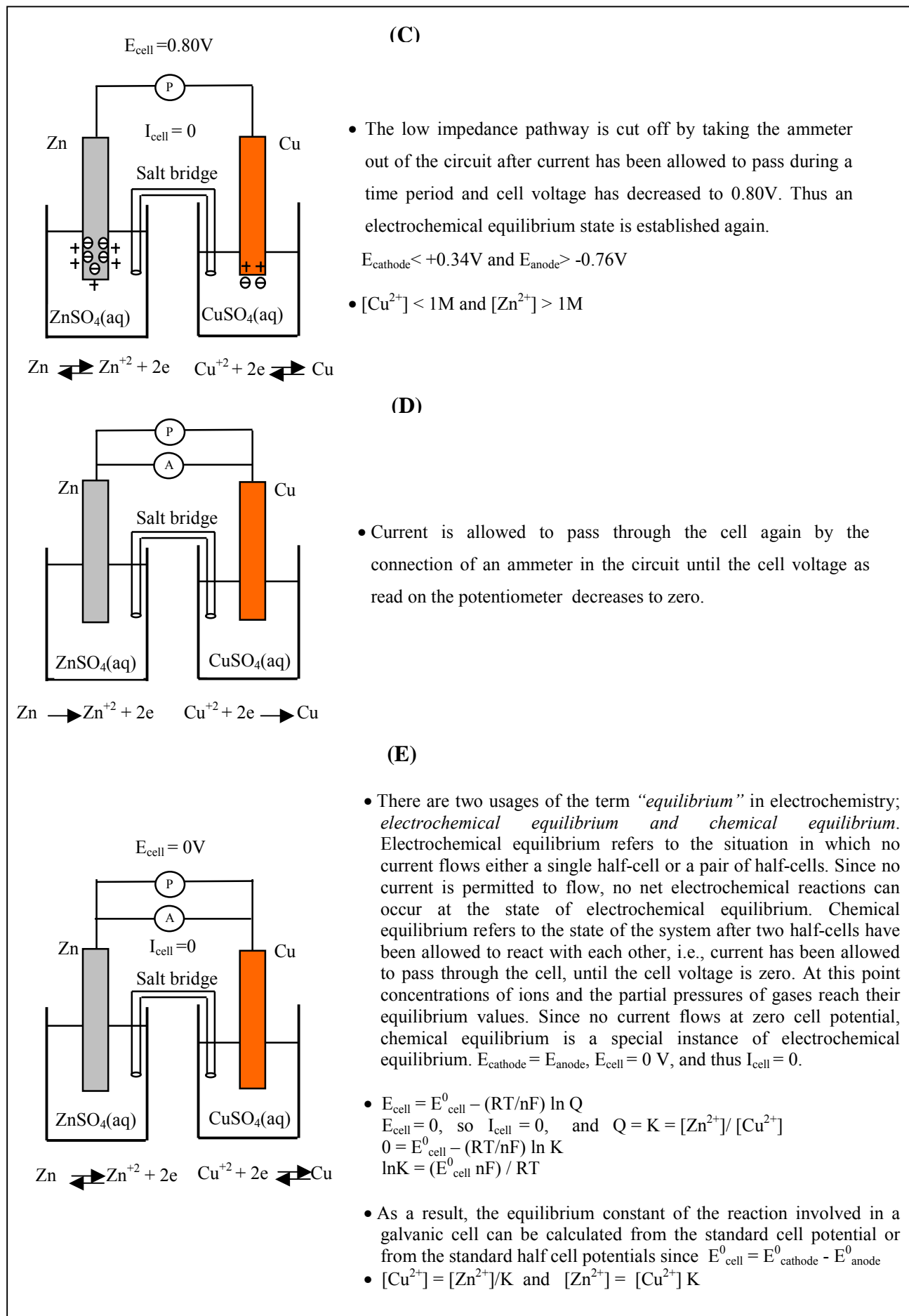


Figure 1. continuing



chemical changes occur at each interface (for the Daniell cell, $[\text{Cu}^{2+}]$ decreases while $[\text{Zn}^{2+}]$ increases). Thus, the potential difference between the electrodes is diminished. If the low impedance pathway is cut off by taking the ammeter out of the circuit after current is allowed to pass during a time period, an electrochemical equilibrium state is established again as shown Figure 1C above.

There are two usages of the term 'equilibrium' in electrochemistry; *electrochemical equilibrium* and *chemical equilibrium*. Electrochemical equilibrium refers to the situation in which no current flows either in a single half-cell or in a pair of half-cells. Since no current is permitted to flow, no net electrochemical reactions can occur at the state of electrochemical equilibrium. Chemical equilibrium refers to the state of the system after two half-cells have been allowed to react with each other, i.e., current has been allowed to pass through the cell, until the cell voltage is zero (Figures 1D and E). At this point concentrations of ions and the partial pressures of gases reach their equilibrium values. This state is called *chemical equilibrium*. Since no current flows at zero cell potential, chemical equilibrium is a special instance of electrochemical equilibrium. When the cell reaches chemical equilibrium, current no longer flows and $E_{\text{cell}} = 0$ V. At the state of electrochemical equilibrium,

$$I_{\text{cell}} = 0$$

$$E_{\text{cell}} = E_{\text{cell}}^0 - (RT/nF) \ln Q$$

while at the state of chemical equilibrium,

$$E_{\text{cell}} = 0, \text{ so } I_{\text{cell}} = 0, \text{ and } Q = K$$

$$0 = E_{\text{cell}}^0 - (RT/nF) \ln K$$

$$\ln K = (E_{\text{cell}}^0 nF) / RT$$

As a result, the equilibrium constant of the reaction involved in a galvanic cell can be calculated from the standard cell potential or from the standard half cell potentials since

$$E_{\text{cell}}^0 = E_{\text{cathode}}^0 - E_{\text{anode}}^0$$

Goodwin states in his letter (p.60) 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. In our opinion, these signs should be assigned to the metal electrode and to the solution containing its ions, not to the different parts of the metal electrode from different perspectives. Moreover, these sign assignments are used not only when current flows but also when it does not flow (at the state of electrochemical equilibrium). Instead of assigning different signs to the different parts of the metal electrodes as in Figure 3 in his letter, it may be better to explain the *separation of charge at each interface (electrode polarity)* by choosing a terminology that for the Daniell cell, in terms of the charges at solution and metal sides of each interface, the potential of the copper metal is higher than that of the copper sulphate solution while the potential of the zinc metal is lower than that of the zinc sulphate solution. This can be modelled assigning charges to both sides of each interface as shown in Figures 1A and 1C in this letter. When the zinc electrode is dipped

into the solution involving its ions, due to the electro-positive character of this element, there is a tendency for zinc atoms to escape into the solution as Zn^{2+} ions, each of them leaving two electrons behind on the strip. On the other hand, there is a tendency for Zn^{2+} ions in the solution to cling on to the metal, each of them attracting two electrons on its surface, but the former tendency is the stronger so that some zinc atoms do escape from the metal surface, which becomes negatively charged by the electrons that are left behind. This results in the electrode having a lower potential than the solution. Similar phenomena occur when the copper electrode is dipped into the solution containing its ions. But copper is less electro-positive than zinc and so its tendency to form ions is not so strong. Hence some copper ions drive on to the metal, each of them transferring two electrons from copper atoms, and give the surrounding solution an overall negative charge. The loss of electrons from the copper electrode causes it to be positively charged and hence raised to a higher potential than the solution. It follows from these phenomena at the half-cells that the zinc electrode will be lower in potential than the copper (V). Thus, the metal electrodes (the metal side of the electrical double layer in each half-cell) in a galvanic cell do have net positive or negative charges; however, these charges are extremely small (only about one electron for every 10^{14} metal atoms) and exceedingly difficult to measure. The magnitude and direction of the charge imbalance between the metal electrode and the electrolyte solution differs from metal to metal and is responsible for the different standard reduction potentials for metals. A galvanic cell is a source of current. Every source of current has two poles. The one with *higher potential* is called the *positive pole*, and the other with *lower potential* is the *negative pole*. Thus, the copper electrode is labelled (+) while the zinc electrode is labelled (-). To obtain a current the poles must be connected by a system of metallic conductors forming the external circuit (by a metal wire directly or via an ammeter).

In Figure 3 in his letter, Goodwin represents the charges on different parts of the electrodes from the two different perspectives according to his ideas. This is not reasonable in our opinion, as explained previously. In addition, in this figure, an arrow that is directed from cathode to anode is used to represent electron flow within the cell (in the electrolyte solutions). The statement appended with the arrow, '*equivalent electron flow within cell*' in this figure may lead students into believing that electrons enter the solution at the cathode, move through the electrolyte and emerge at the anode to complete the circuit during the passage of current through the cell; this is one of the most widely recognized misconceptions among the students. Students' misconceptions and conceptual difficulties were well documented by several researchers as cited in our previous paper.² The researchers also discussed probable sources of student misconceptions. They had the shared idea that a major source of student misconceptions comes from imprecise, insufficient,

and inappropriate textbook or instructor comments. Instructors and authors should use carefully chosen terminology to explain electrochemical processes.

References

1. A. Goodwin, *U.Chem.Ed.*, 2003, **7**, 59.
2. A.R. Özkaya, M. Üce and M. Şahin, *U.Chem.Ed.*, 2003, **7**, 1.
3. N.A. Ogude and J.D. Bradley, *J.Chem. Ed.*, 1994, **71**, 29.
4. N.A. Ogude and J.D. Bradley, *J.Chem. Ed.*, 1996, **73**, 1145.

The Bologna Process and Chemistry Degrees in the UK

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A remarkable change is taking place in higher education across Europe, which has potentially serious implications for university studies in the physical sciences and engineering in the UK. Since the Bologna Declaration in 1999 the pace of change has accelerated, so that many of the 40 signatory countries are now expecting to implement a Bologna-style two-cycle Bachelors and Masters degree structure by 2005. Although not strictly specified, a pattern of 3 years (BA) + 2 years (MA) is becoming widely recognised, with the further assumption that a second cycle qualification will become an essential prerequisite for starting PhD studies. As student mobility has increased in Europe, and a European Credit Transfer Scheme (ECTS) has developed, such a change is long overdue. Comparability between different national HE qualifications was difficult to establish when the time taken to complete a first degree varied between three and seven years; but now there is a real possibility of extending ECTS into a credit accumulation as well as transfer scheme.

Although the Government is a signatory of the original Bologna Declaration, it seems to be largely ignoring its obligations. UK Education Ministers stress that Bologna lays no *compulsion* on any country to reorganise its higher education structure, and even suggest that the pressure is on other European countries to move towards the UK pattern of higher education. This may be true for those academic subjects where a three-year Bachelors degree is the norm, but it raises a particular difficulty for the physical sciences and engineering where the MSci has become the preferred option.

While many European countries struggle to reduce their Bachelor degree to three years, the problems facing English universities are most severe in the second cycle. Current academic opinion is that the four-year integrated MSci (here used as a generic term to include MChem, MPhys, and similar engineering and mathematics qualifications), which science and engineering faculties have worked so hard to establish, is a popular, flexible and entirely satisfactory qualification, equipping graduates to enter doctoral studies or employment as a professional chemist. Funding for the MSci is secure, and universities are unlikely to change unless pressure is applied by the Government through the Funding Councils. This they are unwilling even to consider, believing that with no direct requirement for change stipulated, the MSci can stay as it is, and there is therefore no direct funding implication.

Unfortunately, the Bologna Process will probably not accept the current 4-year MSci as a second cycle qualification, especially as contact hours in UK universities are generally lower than in continental institutions. Neither is there a recognisable exit point and qualification for students, equivalent to the BSc at the end of the first Bologna cycle, nor a clear delineation between first cycle and second cycle study material. If additional credit points have to be added to meet the second cycle requirement (the minimum to open negotiations is thought to be 90 credit points), they could not be incorporated under the present funding regime. All the material in this extended final year would also have to be of recognisably second cycle standard.

The Government refuses to see this as a problem. Again, they see no requirement that a second cycle qualification is necessary for a student to begin PhD studies. They seem not to recognise that when the rest of Europe has adopted a system 'based essentially on two main cycles', such attitudes will no longer be valid.

It is interesting to note that Scotland may be better placed for developing a Bologna pattern from its present degree structures; and that the Republic of Ireland is looking to implement the Bologna proposals. One possible route to acceptance for those English universities who run an MSci including a year's industrial placement could be for them to add a further university-based year to their course. This would also meet the criterion that Bologna-style degrees should seek to improve the employability of European graduates.

Running alongside the Bologna developments is the Chemistry Eurobachelor, an initiative of the European Chemistry Thematic Network, which also has the support of the Federation of European Chemical Societies. The RSC is well represented on both these bodies, and a staff member of the Education Department has recently joined the Chemistry

U.Chem.Ed., 2004, **8**, 29

Eurobachelor Working Group. Ironically, this proposed programme of study, aiming to provide a basis for the first cycle, is substantially based on the UK Chemistry Benchmarking document. The Eurobachelor discussion document, originally submitted to the Tuning Educational Structures in Europe project, but since much revised, addresses aspects of content, learning outcomes, methods of teaching and learning, assessment procedures, and quality assurance. Despite its origins, there is little enthusiasm for this proposal in UK Chemistry Departments, possibly deterred by the inclusion of a second European language and a 'Bachelor thesis' in the specification.

So what might be the implications for UK chemistry if no effort is made to follow the Bologna pattern? At worst, UK graduates without a recognised two-cycle qualification might be considered less well prepared, and so passed over for employment opportunities elsewhere in Europe. MSci graduates might not be accepted for PhD studies in other European countries, and we would not be producing first cycle students qualified to enjoy the social, cultural and educational benefit of pursuing their Masters in a continental university. Correspondingly, we should lose the advantage of students coming to the UK, because there would be no second cycle two-year MSc courses for them to study in our Chemistry Departments. The effect might not be immediate, but as more European countries adopt the Bologna Process, the UK will become increasingly isolated from mainstream European higher education.

Perhaps the most effective way to change current thinking will be for the professional bodies for science and engineering (including the Royal Society), and the employers' organisations, to act in concert to try and influence the government. It is good to see that such activities are under way, and a number of joint meetings have been held, though at the moment the RSC seems to be showing more concern than the

Institute of Physics over the lack of governmental interest.

However, the Government has also indicated that HE institutions should separately consider how they might need to change to remain competitive in the international higher education marketplace. So there is an opportunity for individuals within Departments, who think that the future of UK chemistry graduates will be more assured if higher education becomes more closely aligned with the European developments stemming from Bologna, to influence the opinion of their own universities. If Chemistry Departments are willing to offer support to the RSC in its attempts to influence Government thinking on the importance of the Bologna Process for the UK, there is a chance that we might all share the benefits of chemistry higher education with a European dimension.

For information on these matters, the following websites and documents can be consulted:

The Bologna Declaration and the Bologna Process: 'University Reforms in Europe, the Bologna Process', *RSC Educational Issues*, No. 24, July 2003; 'The Bologna Process and UK Physics Degrees', Institute of Physics, October 2003; The Berlin-Bologna-Webpage (all documents) http://www.bologna-berlin2003.de/en/main_documents/index.htm

The Chemistry Eurobachelor:

'The Eurobachelor is coming', Kathryn Roberts, *Education in Chemistry*, November 2002, p.142; www.cpe.fr/ect/arch/doc/2004/N01/Eurobachelor_2004.pdf

Tuning Educational Structures in Europe

http://www.cpe.fr/ectn/tuning_project.htm

MChem: 'MChem the first decade', RSC 2003

European Chemistry Thematic Network:

<http://www.cpe.fr/ectn/>

Federation of European Chemical Societies:

<http://www.chemsoc.org/networks/enc/fecs.htm>