An Analysis of College Chemistry Textbooks As Sources of Misconceptions and Errors in Electrochemistry

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This analysis was inspired by a student comment made during a clinical interview in electrochemistry (*1*). The student was asked to identify the anode and cathode of an electrochemical cell consisting of a Ni/Ni^{2+} half-cell on the left and a Ag/Ag^+ half-cell on the right.

> STUDENT: I was just told that this would be the anode on the left [Ni] and the cathode on the right [Ag].
>
> INTERVIEWER: But what if we gave you a diagram like this? [Reversing the half-cells.]
>
> STUDENT: Well then, it [nickel] would be reducing—the cathode, right. That's just so far how the book has shown it to me and the way on the board it's been shown.

Analysis of textbooks for misleading or erroneous statements is also warranted because of the singular importance of textbooks in the classroom as a source of both content and curriculum (*2*). This role was first documented by a National Science Foundation (NSF)-supported needs assessment conducted in the mid-70s (*3–5*), which reported that teachers view the textbook not only as the sole source of information regarding the subject matter, but also as deciding the content covered in the classroom. The 1985–1986 National Survey of Science and Mathematics Education (*6*) reported that more than 90% of secondary science classes use published textbooks and that a majority of science teachers report covering 75% or more of the textbook content in their classes. Chiang-Soong and Yager (*7*) reported that students expected the textbook to be the source of nearly all classroom information and the framework from which science was experienced, and parents expressed concern if textbooks were not issued and used as the central source of assignments. Although these reports were based on elementary and secondary students, the results are likely to be valid for college students as well.

The theory of constructivism recognizes that students bring to any new learning situation a set of preconceptions based on their previous knowledge and experiences (*8, 9*). Student preconceptions that are inconsistent with or different from the commonly accepted scientific consensus and are unable to adequately explain observable scientific phenomena are defined as *misconceptions* (*8, 10*). Some student misconceptions are capable of adequately explaining the student's experiences and observations, appear quite logical to the student, and are consistent with his or her understanding of the world. In these instances, student misconceptions are very resistant to change (*11*).

Several researchers have documented student misconceptions concerning electrochemistry (*1, 12–17*) and most of them (*1, 13-17*) have implicated textbook or instructor comments as possible sources of student misconceptions. The list of student misconceptions in electrochemistry used in this study was prepared by combining the misconceptions reported by Garnett and Treagust (*15*) and Sanger and Greenbowe (*1*) and appears in Table 1.

Method

Ten college-level chemistry textbooks were analyzed for examples of statements or drawings that could lead to a student misconception in electrochemistry: *General Chemistry*, by Atkins and Beran (*18*); *Chemistry*, by Birk (*19*); *Chemistry: An Experimental Science*, by Bodner and Pardue (*20*); *Chemistry: The Study of Matter and Its Changes*, by Brady and Holum (*21*); *Chemistry: The Central Science*, by Brown, LeMay, and Bursten (*22*); *Chemistry*, by Chang (*23*); *Chemistry & Chemical Reactivity*, by Kotz and Treichel (*24*); *Chemistry: The Molecular Science*, by Olmsted and Williams (*25*); *Chemistry: Principles & Practice*, by Reger, Goode, and Mercer (*26*); and *Chemistry*, by Zumdahl (*27*). These textbooks will subsequently be referred to by the authors' initials. For example, *Chemistry: Principles & Practice* will be referred to as *RGM*.

The oxidation–reduction and electrochemistry chapters of these textbooks were reviewed using the student misconceptions listed in Table 1 for misleading or erroneous statements and for statements that do not foster these misconceptions. For each textbook, these statements were transcribed and classified by the misconception that they did or did not foster. The textbook statements relating to each misconception were summarized and analyzed for common and unique examples of both misleading statements and statements that would not lead to the misconception. The statements quoted in this paper and the interpretations of these statements were reviewed by four college chemistry professors and their comments were incorporated in the analysis and critique of the textbooks.

Results and Discussion

Analysis of the oxidation–reduction and electrochemistry chapters of these textbooks provided misleading statements and illustrations related to misconceptions 3, 7, 8–10, 12–17, 26, and 27. The misconceptions are labeled from 1 to 32

and are not consistent with the labeling used by Garnett and Treagust (*15*) and Sanger and Greenbowe (*1*). Not all of these misconceptions were supported by vague or misleading statements in these textbooks: several (misconceptions 1, 5, 6, 18–20, 22, 23, 25, 30, and 31) were directly refuted by every statement found in the textbooks, while others (misconceptions 2, 4, 11, 21, 24, 28, 29, and 32) were not addressed by a majority of these textbooks. The textbook statements made concerning the misconceptions that remain and the implications of these statements are discussed in detail and serve as the basis for this paper.

"The Anode Is Always on the Left"

The notion that the identity of the anode and cathode depends on the placement of the half-cells was suggested by a student who observed that the textbook and the instructor always drew the anode half-cell on the left and the cathode half-cell on the right. The relative placement of the anode and cathode half-cells as depicted in the illustrations in each textbook was analyzed, ignoring drawings of commercial batteries, commercial electrolysis cells, and the corrosion of iron. Two textbooks (*B, KT*) had an equal number of illustrations in which the anode was drawn as the left and as the right half-cell, four textbooks favored one position over the other (*AB, OW,* and *Z* preferentially drew the anode as the left half-cell, whereas *BH* preferentially drew the anode as the right half-cell), and four textbooks (*BP, BLB, C, RGM*) exclusively drew the anode as the left half-cell.

A second convention that may suggest that the anode is always the electrode on the left is the cell notation (also called the line notation or the cell diagram), which is used by five of the textbooks (*AB, BP, BH, C, Z*). The cell notation, in contrast to the drawings discussed above, requires by IUPAC convention that the anode be placed on the left and the cathode be placed on the right (*28*). Only three (*BP, BH, C*) of these textbooks explicitly state that the arrangement of half-cells in the cell notation is done by IUPAC convention.

The placement of the anode and cathode with respect to the (–) and (+) terminals of a voltmeter leads to the similar misconception that the anode is always the electrode connected to the (–) terminal of the voltmeter. Two textbooks

Table 1. Common Student Misconceptions

Type	No.	Misconception
Galvanic cells	1	In an ordered table of reduction potentials, the species with the most positive $E°$ value is the anode.
	2	Standard reduction potentials list metals by decreasing reactivity.
	3	The identity of the anode and cathode depends on the physical placement of the half-cells.
	4	Anodes, like anions, are always negatively charged; cathodes, like cations, are always positively charged.
	5	The fact that the $E°$ for H_2(1 atm)/H^+(1 M) is zero is somehow based on the chemistry of H^+ and H_2.
	6	There is no need for a standard half-cell.
	7	Half-cell potentials are absolute in nature and can be used to predict the spontaneity of the half-cells.
	8	Electrons enter the solution from the cathode, travel through the solutions and the salt bridge, and emerge at the anode to complete the circuit.
	9	Anions in the salt bridge and the electrolyte transfer electrons from the cathode to the anode.
	10	Cations in the salt bridge and the electrolyte accept electrons and transfer them from the cathode to the anode.
	11	Cations and anions move until their concentrations are uniform.
	12	Electrons can flow through aqueous solutions without assistance from the ions.
	13	Only negatively charged ions constitute a flow of current in the electrolyte and the salt bridge.
	14	The anode is negatively charged and releases electrons; the cathode is positively charged and attracts electrons.
	15	The anode is positively charged because it has lost electrons; the cathode is negatively charged because it has gained electrons.
	16	Cell potentials are derived by adding individual reduction potentials.
	17	Half-cell potentials are not intensive properties.
Electrolytic cells	18	In electrolytic cells, the direction of the applied voltage has no effect on the reaction or the site of the anode and cathode.
	19	No reaction will occur if inert electrodes are used.
	20	In electrolytic cells, oxidation now occurs at the cathode and reduction occurs at the anode.
	21	In electrolytic cells with identical electrodes connected to the battery, the same reactions will occur at both electrodes.
	22	In electrolytic cells, water is unreactive toward oxidation and reduction.
	23	When predicting an electrolytic reaction, the half-cell reactions are reversed before combining them.
	24	The calculated cell potentials in electrolytic cells can be positive.
	25	There is no relationship between the calculated cell potential and the magnitude of the applied voltage.
	26	Inert electrodes can be oxidized or reduced.
	27	When two or more oxidation or reduction half-reactions are possible, there is no way to determine which reaction will occur.
	28	Electrolytic cells can force nonspontaneous reactions that do not involve electron transfer to happen.
Concentration Cells	29	The direction of electron flow in concentration cells is not dependent on the relative concentration of the ions.
	30	The products produced in the indirect reaction of electrochemical cells are different from those produced in the direct reaction of the starting materials.
	31	The cell potential in concentration cells is not dependent on the relative concentration of the ions.
	32	Because there is no net reaction in concentration cells, the reaction quotient cannot be calculated.

NOTE: Misconceptions reported in Garnett and Treagust (*20*) and Sanger and Greenbowe (*1*).

(*KT, RGM*) consistently showed the anode connected to the (–) terminal and the cathode connected to the (+) terminal of the voltmeter. However, while *KT* uses an analog voltmeter (which can only report positive potentials) and includes a discussion about why the anode must be connected to the (–) terminal of the analog voltmeter, *RGM* uses a digital voltmeter in its drawings and includes no comment that this arrangement is necessary only for a positive voltmeter reading. None of

the textbooks discussed how to interpret a negative voltmeter reading—an event that students experience in laboratory experiments, in lecture demonstrations, and in computer animations (*29, 30*). Because most modern voltmeters have floating inputs with red (+) and black (–) terminals, neither input is "grounded" and the use of the terms "active" and "ground" should be avoided (*30*).

While it may seem logical for authors and instructors to consistently place the anode half-cell on the left side and consistently connect it to the (–) terminal of the voltmeter, this may mislead students into believing that these are viable methods to identify the anode and cathode in electrochemical cells. These conventions pose problems when students are asked to analyze electrochemical cell diagrams on exams or to build and diagram cells in the laboratory (*29, 30*).

Calculating Cell Potentials Using the Additive Method

Although all of the textbooks contain explicit statements that absolute half-cell potentials cannot be measured and that all standard reduction potentials are measured with respect to the standard hydrogen electrode (SHE), several of these textbooks contain statements suggesting that standard reduction potentials are absolute—that is, half-reactions with positive reduction potentials are spontaneous and half-reactions with negative reduction potentials are nonspontaneous and spontaneous in the opposite direction (misconception 7). Eight of the ten textbooks (*AB, B, BP, BLB, C, KT, RGM, Z*) calculate cell potentials using the equation $E^\circ_{cell} = E^\circ_{ox} + E^\circ_{red}$, where E°_{red} is the reduction potential of the reduction half-reaction and the E°_{ox} value is determined by taking the reduction potential of the oxidation half-reaction and changing its sign.[1] Although this is technically the same as calculating the cell potential as a potential difference (i.e., $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$, where $E^\circ_{cathode}$ and E°_{anode} are the standard reduction potentials of the reduction and oxidation half-reactions, respectively), calculating the cell potential as a sum may suggest to students that these individual half-cell potentials have significance—when in reality only the potential difference has any significance. Students may also get the impression that each half-cell potential can be measured without a second (reference) half-cell. Indeed, statements presented in two textbooks (*AB, B*) and a quote from a student in Sanger and Greenbowe's interview study (*1*) are very similar and suggest that student misconceptions that individual E°_{ox} and E°_{red} values are independent of each other, meaningful, and measurable may result from imprecise or misleading textbook statements:

> Therefore, of the 1.23 V from the current supply [needed for the electrolysis of water], 0.42 V is needed for the reduction of [water to] H_2 and 0.81 V is needed for the oxidation of [water to] O_2. *AB*, p 683

> [In the electrolysis of aqueous NaI] we see that it requires 0.54 V to oxidize iodide ion and 0.82 V to oxidize water. *B*, p 793

> So, Cu to go from its solid state to its ionized state will need 0.34 volts so nothing's going to happen there. But with the Zn to go from its solid state to its ionic form gives up 0.76 volts so it's going to spontaneously happen. *Student*

B makes another statement implying that individual reduction potentials are significant. After introducing the equation relating ΔG° to E°_{cell} ($\Delta G^\circ = -nFE^\circ_{cell}$), the textbook calculates the free energy of an individual reduction half-

reaction. Using the Cu^{2+}/Cu reduction potential (+0.34 V), a ΔG° value of -66 kJ is calculated (p 783). However, students need to be cautioned that since the initial reduction potential was referenced to the SHE, the ΔG° value calculated is actually the value for the reaction of the Cu^{2+}/Cu half-cell with the SHE (i.e., $Cu^{2+} + H_2 \rightarrow Cu + 2 H^+$).

An additional problem arises from using the additive method ($E^\circ_{cell} = E^\circ_{ox} + E^\circ_{red}$). Although this equation works only for balanced oxidation–reduction reactions (i.e., half-reactions that have the same number of electrons transferred), only two textbooks (*B, RGM*) point out this limitation. As a result, students may be misled into believing that the oxidation and reduction potentials for any half-reactions can be added together. For example, they may believe that $E^\circ_{red}(Fe^{3+}/Fe^{2+})$ can be calculated by adding $E^\circ_{red}(Fe^{3+}/Fe)$ to $-E^\circ_{red}(Fe^{2+}/Fe) = E^\circ_{ox}(Fe/Fe^{2+})$,[1] which is demonstrated below. Converting the E° values into ΔG° values and adding these values using Hess's law yields

$$\Delta G^\circ_{red} = -74.5 \text{ kJ}$$

and

$$E^o_{red}\left(Fe^{3+}/Fe^{2+}\right) = \frac{-\left(-74{,}500 \text{ J}\right)}{\left(1 \text{ mol e}^-\right)\left(96{,}485 \text{ C/mol e}^-\right)} = 0.772 \text{ V}$$

which is very close to the tabulated value of 0.771 V (*28*).

	Adding E° values	Adding ΔG° values
$Fe^{3+}(aq) + 3e^- \rightleftharpoons Fe(s)$	$E^\circ_{red} = -0.036$ V	$\Delta G^\circ_{red} = 10.4$ kJ
$Fe(s) \rightleftharpoons Fe^{2+}(aq) + 3e^-$	$E^\circ_{ox} = 0.440$ V	$\Delta G^\circ_{ox} = -84.9$ kJ
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	$E^\circ_{red} = 0.404$ V	$\Delta G^\circ_{red} = -74.5$ kJ

The terminology used in some of these textbooks also leads students to believe that standard reduction potentials are additive (misconception 16). Four textbooks use terms such as "overall potential" (*B, BP*), "net potential" (*KT*), and "total potential" (*Z*) to describe the potential difference of the cell. Other textbooks (*BLB, C, KT*) inconsistently describe the cell potential as a "potential difference" but then calculate the cell potential by adding oxidation and reduction potentials.

Students demonstrating misconception 17 believe that cell potentials and individual reduction potentials are extensive properties. Misconceptions 16 and 17 are clearly related: Hess's law states that when individual reactions are added together, the values of extensive thermodynamic properties such as ΔH or ΔG can be added together. Although all the textbooks contain explicit statements that half-cell and cell potentials are intensive properties, several contain statements suggesting that half-cell potentials can be added together. Two textbooks (*AB, BLB*) make statements suggesting that Hess's law applies to half-cell potentials:

> In the discussion of Hess's law in Chapter 6, the sign of ΔH was changed when the reaction was reversed; therefore, the cell reaction is treated like the thermochemical equations in Chapter 6, and the cell potential is the analogue of ΔH. *AB*, p 668, Note to Instructor

> As with energy-related quantities, such as ΔH and ΔG, reversing a reaction changes the sign of E°. *BLB*, p 733

These statements clearly overemphasize the similarities between the intensive half-cell and cell potentials and the ex-

tensive ΔH and ΔG values. Other textbooks make comments that, while not explicitly stating that half-cell and cell potentials follow Hess's law, certainly imply this relationship. All eight textbooks using the additive formula for calculating cell potentials (*AB*, *B*, *BP*, *BLB*, *C*, *KT*, *RGM*, *Z*) include a statement suggesting that reversing a chemical equation changes the sign but not the magnitude of the cell potential. One textbook (*B*), however, includes a discussion and mathematical examples demonstrating that, while ΔG values can always be added using Hess's law, $E°$ values are only additive when considering a balanced oxidation-reduction reaction (i.e., when the number of electrons transferred in each half-cell is the same).

The preceding discussion suggests that calculating cell potentials using the additive method can lead to three distinct student misconceptions: (i) half-cell potentials are absolute and measurable; (ii) individual half-cell reduction potential are additive; and (iii) half-cell and cell potentials are extensive properties that obey Hess's Law. Therefore, it is strongly recommended that textbook authors and instructors calculate cell potentials using the potential difference method. Although it may appear that choosing to use the potential difference method over the additive method is simply a matter of instructor preference, the results of Sanger and Greenbowe's interview study (*1*) and this textbook analysis suggest that using the additive method can reinforce student misconceptions (misconceptions 7, 16, and 17). Further research is needed to determine whether the additive method does in fact reinforce these misconceptions. Using the potential difference method also precludes the need to explain why the sign of the half-cell potential is changed when the equation is reversed (consistent with Hess's law) but that the potential is not multiplied by a numerical coefficient when the equation is multiplied by this coefficient (which contradicts Hess's law).

Runo and Peters (*32*) describe a particularly effective method of calculating cell potentials using the potential difference method and line diagrams called "potential ladders". The potential ladder is a vertical line diagram in which half-cells are arranged in order of increasing reduction potentials with the negative values at the bottom. In galvanic cells and for spontaneous chemical reactions, the cathode is always the upper "rung", the anode is always the lower "rung", and electrons flow upward. In contrast, electrolytic cells and nonspontaneous reactions always have the anode as the upper rung and the cathode as the lower rung, and electrons flow downward. The potential ladder is also effective at predicting the electrolysis products of aqueous solutions.

Electron Flow in Aqueous Solutions

The misconception that electrons can flow through an electrolyte solution (misconceptions 8 and 12) is one of the most prevalent student misconceptions in chemistry (*1, 12, 14–17*). Illustrations from the 10 textbooks were analyzed, paying particular attention to oxidation–reduction reactions occurring at the metal–solution interface (simple electrochemical cells, corrosion reactions, etc.). Several textbooks included drawings accurately depicting electron transfer as occurring at the metal surface–solution interface (the more effective examples being *BP*, p 755; *BLB*, pp 757–758; *C*, p 790; *KT*, p 960; *OW*, pp 831, 858, 861, 863; and *Z*, p 848). However, three textbooks (*AB*, pp 109, 656, 674; *OW*, pp 830, 833; *Z*, p 813) included drawings that depict electrons

flowing into and through the electrolyte solutions from the oxidized to the reduced species. Although *OW* and *Z* contain pictures depicting correct and incorrect current flow in solution, *AB* only contains pictures of free electrons in solution.

Two textbooks (*BH*, *Z*) present a thoughtful written description of the charge imbalance occurring in the half-cells when the salt bridge is not present and both explain that cations and anions migrate to neutralize the charge buildup. Unfortunately, statements suggesting that free electrons exist in solution and that their migration accounts for the current flow in electrolyte solutions are prevalent in other textbooks. The following textbook statements and the quote from a student interview (*1*) suggest that students may derive their beliefs that electrons can flow in solution from vague or misleading terminology used by textbook authors.

> Increasing the potential between the electrodes forces electrons into the electrolyte and can bring about a reduction…   *AB*, p 687

> We have to build a model for **electrochemical reactions**—chemical reactions that involve the flow of electrons.
> *BP*, p 726

> An electrode conducts electrons into and out of a solution.
> *KT*, p 959

> One mole of nickel metal (58.69 g) is produced for each two moles of electrons that pass through the solution.
> *RGM*, p 756

> The electrons are what actually are the current. Current's a measure of electron flow. …The salt bridge allows electrons to pass through it without allowing the solutions to mix.   *Student*

Even when these statements are clearly within the context of the chapter, students and instructors may interpret them very differently.

Six textbooks (*AB*, *B*, *BH*, *KT*, *OW*, *RGM*) make comments that could imply that ions in solution can accept or deposit electrons at the electrode surface without undergoing any chemical change (misconceptions 9 and 10). Several of these statements are listed below.

> Electrons cannot just be released; they must be transferred to some other atom or ion.   *B*, p 727

> Ions in the solution can transfer electrons to or from this inert electrical conductor [inert electrode].   *RGM*, p 732

> The transport of electrical charge by ions is called **electrolytic conduction**.   *BH*, p 764

> The salts dissolved in the two vessels are essential for the flow of electrons because pure water does not contain enough charged species to support charge flow. Charge can flow only when the solutions contain ions that are provided by an **electrolyte**.   *OW*, p 831

Authors and instructors need to emphasize that the process of transferring electrons to ions at the electrode–solution interface results in a chemical change. The description of current in the electrolyte as the flow of "electrical charge" or "charge" by ions might suggest to students that ions are carrying electrons through the electrolyte (*13, 15, 16*).

Authors and instructors need to make certain that they clearly describe the current flow in electrolyte solutions and the salt bridge as the flow of cations and anions. Illustrations included in textbooks should visually emphasize that electron

transfer occurs at the metal–solution interface and that electrons do not enter the electrolyte solution. *BH* and *Z* provide an excellent written description of the flow of cations and anions in simple electrochemical cells and several textbooks (*BP*, *BLB*, *C*, *KT*) provide accurate illustrations of this process. Computer animations which depict the movement of ions in the electrolyte solution and the salt bridge have been shown to be effective at alleviating this misconception (*17*).

"Cation Movement in Solution Is Not an Electrical Current"

Three of the textbooks (*AB*, *KT*, *OW*) suggest that current flow in the electrolyte solutions consists solely of the flow of anions—each of these textbooks mentions that cation flow also occurs, but implies that cation flow does not constitute an electrical current. Although *AB* includes an insightful description of both cation and anion flow in electrolyte solutions as current, the illustration on page 657 shows a thick red circle representing the "circuit": the arrows on the circle that pass through the electrodes and the wire represent electron flow and the arrows that pass through the electrolyte solutions and the salt bridge represent anion flow. This drawing may imply to students that cation flow does not constitute a current in the aqueous solutions.

Although *KT* discusses anion and cation flow in the electrolyte solutions, the statements in this textbook clearly emphasize the flow of anions as the electrical current and imply that cation flow is not an electrical current: "The function of the salt bridge is to allow anions to pass freely from the compartment where cations are being lost to the compartment where cations are being generated" (*KT*, p 960). Although some of the illustrations show both cation and anion flow through the salt bridge, two of them (*KT*, pp 959, 972) depict only anion flow through the salt bridge. *OW* discusses the flow of ions through a porous barrier (the equivalent of a salt bridge) only briefly, and although it includes a disclaimer that all ionic species in solution diffuse through the porous barrier, all the drawings of simple galvanic cells show only anion flow across the porous barrier. The implication that only anion flow is an electrical current is even more apparent in the description of the functions of the K^+ and OH^- ions in a mercury battery: "OH^- migrates from the Hg electrode to the Zn electrode, carrying charge; K^+ balances the negative charge on OH^-" (*OW*, p 858).

Electronic Charges of the Electrodes

Metal electrodes do have net positive or negative charges (*31*, pp 623–639); however, these charges are extremely small and exceedingly difficult to measure. Metal electrodes in contact with electrolyte solutions reach an equilibrium, in which either a small amount of metal dissolves (resulting in a net negative charge on the electrode from the released electrons) or a small amount of metal ions in solution attach themselves to the electrode (resulting in a net positive charge on the electrode). 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 (*OW*, *30*). When two different half-cells are connected in a galvanic cell, electrons will flow from the electrode that has the more negative charge (anode) to the electrode with the more positive charge (cathode). As the electrons flow in the wire from the anode to the cathode, the salt bridge allows a net migration of anions into the anode half-cell and cations into the cathode half-cell to neutralize this charge imbalance. Only one of the textbooks discusses the net charges of the electrodes in a galvanic cell, and it mentions that the net charge on the electrodes is exceedingly small—only about one electron for every 10^{14} metal atoms (*OW*, p 839).

The difficulty students have in dealing with the net charges associated with the electrodes, however, is that they overestimate the magnitude of this charge. Students routinely apply simple electrostatic arguments to determine electron and ion flow with respect to the charged electrodes. Six of the textbooks (*AB*, *B*, *BP*, *BH*, *BLB*, *KT*) suggest that the anode of an electrolytic cell is positively charged—either because negatively charged anions are attracted to it (*AB*, *B*, *BP*, *BH*, *BLB*, *KT*) or because negatively charged electrons flow away from it, leaving it positively charged (*B*, *BP*, *BLB*, *KT*). While these observations are consistent with a positively charged anode, students have difficulty understanding why electrons would flow away from a positively charged anode toward a negatively charged cathode. Similarly, four textbooks (*B*, *BH*, *BLB*, *KT*) suggest that the anode of a galvanic cell is negatively charged because the anode generates electrons that flow toward the positively charged cathode. However, students have difficulty understanding why anions flow toward a negatively charged anode and cations flow toward a positively charged cathode. The following quote from *B* suggests that the anode is both positively *and* negatively charged at the same time and may be an additional source of confusion concerning electrode charges.

> Because oxidation occurs at the anode, electrons must flow away from this electrode into the external circuit. As a result, the anode has a negative charge from the viewpoint of the external circuit, but removal of electrons gives it a positive charge from the viewpoint of the solution in the cell. *B*, p 771

Considering that the net charges on the electrodes are extremely small and that simple electrostatic arguments concerning electrode charges do not correctly explain the direction of electron and ion flow, it is not surprising that two textbooks (*C*, *Z*) do not discuss electrode charges at all and that one (*RGM*) emphasizes the signs as electrode polarities (i.e., the positive electrode has a higher potential than the negative electrode) instead of electronic charges.

Analysis of student interviews (*1*) demonstrated that students have difficulty identifying the correct direction of ion and electron flow in electrochemical cells using electrode charges. To minimize students' use of simple electrostatic arguments to determine the direction of ion and electron flow in electrochemical cells, textbook authors should include a detailed description of the net electronic charges on the electrodes (*OW*, *30*). Authors should also emphasize that the net charge on each electrode is exceedingly small and should refrain from using simple electrostatic arguments to explain the direction of electron and ion flow. Some authors or instructors may decide that this description is too complex for some students to understand and instead may choose to emphasize the electrode signs as electrode polarities. In this case, they should carefully choose terminology that does not suggest that these electrodes carry a substantial charge.

Reactions Involving Inert Electrodes

Although all the textbooks state that platinum or graphite electrodes are used in electrochemical cells because they are unreactive toward oxidation and reduction, several ignore or underemphasize this concept when discussing the products of electrolysis reactions. Two (*AB, Z*) never specify the composition of the electrodes used in electrolytic cells and fail to mention that although these electrodes are typically made of inert substances, it is possible for electrodes to react. Five textbooks (*B, BP, BH, C, KT*) state that electrodes used in electrolytic cells are typically inert; however, only two (*B, C*) describe the electrode composition (platinum or graphite) and none discuss *why* these particular electrodes are inert or why other electrodes can react in electrolysis reactions.

Only three textbooks (*BLB, OW, RGM*) discuss the possibility of metal electrodes reacting in electrolysis reactions. *BLB* and *RGM* describe the electrolysis of molten salts and aqueous solutions without specifying the composition of the electrodes, although they both state that these electrodes are assumed to be inert. *BLB* does explain how one would predict whether an electrode was active or inert: "When aqueous solutions are electrolyzed using metal electrodes, an electrode will be oxidized if its oxidation potential is more positive than that for water" (*BLB*, p 750). Only *OW* specifically addresses whether an inert electrode would react when predicting the products of an electrolytic cell: "Platinum is used for passive electrodes because the metal is resistant to oxidation and does not participate in the redox chemistry of the cell" (*OW*, p 865).

Students have difficulty determining when an electrode will be active or inert (misconception 26). Textbook authors need to discuss some of the factors that make electrodes inert. Some electrodes participate in reactions that have large positive reduction potentials (e.g., $Au^{3+} + 3e^- \rightarrow Au$, $E°_{red} = +1.50$ V) that make them less reactive than water (*33*). Others have reduction potentials which suggest that they should react with water (e.g., $C + 4H^+ + 4e^- \rightarrow CH_4$, $E°_{red} = +0.13$ V, and $CO_2 + 4H^+ + 4e^- \rightarrow C + 2H_2O$, $E°_{red} = +0.20$ V; $PtO_2 + 4H^+ + 4e^- \rightarrow Pt + 2H_2O$, $E°_{red} = +1.0$ V) (*33*). However, these electrodes (or the thin layer of PtO_2 initially formed) are kinetically inert. Half-reactions that are kinetically unreactive are usually described in terms of overpotentials that must be applied to make the reaction occur at an appreciable rate. For these electrodes, the overpotential needed to make the electrode reactions feasible is typically larger than the potential needed to oxidize or reduce water.

Predicting Electrolysis Reactions

When predicting the products of an electrolytic cell, students do not have a systematic method for determining all the possible oxidation and reduction half-reactions and once they have these half-reactions, they cannot decide which oxidation and reduction half-reactions actually occur (misconception 27). The previous section revealed that only three textbooks (*BLB, OW, RGM*) point out that the electrodes could react in an electrolytic cell. Similarly, six textbooks (*AB, B, BH, C, OW, Z*) comment that the electrolysis of water requires the addition of an electrolyte, but ignore the possibility that these ions could be oxidized or reduced. Four of these textbooks (*B, BH, C, OW*) discuss the electrolysis of sulfuric acid to produce hydrogen and oxygen gas without considering the possibility that sulfate ions could be oxidized or reduced.

Another textbook comments that the "addition of even a small amount of a soluble salt causes an immediate evolution of bubbles of hydrogen and oxygen" (*Z*, p 841). This comment also ignores the possibility of ion oxidation or reduction and contradicts a subsequent statement that the electrolysis of aqueous NaCl produces hydrogen and chlorine.

Predicting electrolysis products using standard reduction potentials requires textbook authors and instructors to present students with a simplified view of electrolysis reactions. The use of standard reduction potentials assumes that all aqueous species are at 1.0 M concentrations and all gases are at pressures of 1.0 atm, and in many instances, the electrolysis products predicted from the standard reduction potentials do not correspond to the observed products. All the textbooks discuss the concept of an *overpotential* as the reason electrolysis reactions of chloride solutions typically produce chlorine gas instead of the thermodynamically favored oxygen gas, and most of them suggest that the origins of overpotentials are based on kinetic effects. However, most of the textbooks imply that the preferential formation of chlorine gas over oxygen gas is the only instance where standard reduction potentials fail to correctly predict the reaction products, which is simplistic and may be misleading to the students.

One textbook uses this example as proof that predicting electrolysis products is very difficult and instead narrowly focuses on predicting electrolysis products empirically: "Although it can be hard to anticipate beforehand what will happen in the electrolysis of aqueous solutions, we still can use what we learn experimentally about one electrolysis to predict what will happen in others" (*BH*, p 767). Although electrolysis reactions are complex and predictions of electrolysis products using standard reduction potentials are often wrong, standard reduction potentials represent a useful tool for predicting electrolysis products and we believe that textbooks should present this method to students. Ultimately, each instructor must consider these advantages and disadvantages before deciding whether to teach students how to predict electrolysis products.

The potential ladder advocated by Runo and Peters (*32*) is an effective method for predicting the electrolysis products of aqueous solutions. All half-reactions involving the starting materials at standard conditions (1.0 M and 1.0 atm) are plotted vertically on the chart by increasing reduction potential with the starting material underlined (Fig. 1). When the chart is completed, the oxidation and reduction half-reactions are determined by finding the smallest distance between reduction reactions that have starting materials on opposite sides of the equation. Figure 1 shows the potential ladder diagram for 1.0 M H_2SO_4 under standard conditions using inert platinum electrodes. Because the platinum electrodes are inert (large overpotential), the half-reaction for platinum is omitted from the chart. In this electrolysis reaction, the smallest potential difference occurs when water is oxidized to oxygen gas and H^+ ions at the anode and H^+ ions are reduced to hydrogen gas at the cathode: $2H_2O \rightarrow 2H_2 + O_2$ ($E° = -1.23$ V).

If textbooks authors or instructors decide to discuss the prediction of electrolysis products, they should use a systematic approach such as the potential ladder method to make these predictions and should emphasize that there are unpredictable effects (overpotentials, concentration effects, ion complexations, etc.) that make these predictions difficult and sometimes incorrect. On the other hand, if they decide not to discuss the

prediction of electrolysis products, it is still not appropriate to suggest to students that the only way to determine electrolysis products is by empirical observations when simple calculations can be effective.

Conclusions

The result of this study is the following list of general suggestions concerning electrochemistry instruction intended for the instructors of introductory college level chemistry courses and the authors of the textbooks used in these courses.

1. Authors should avoid the use of simplifications such as always drawing the anode as the left-hand half-cell or only describing the flow of anions in electrolyte solutions and the salt bridge.

2. Authors should avoid using vague or misleading statements and terminology (such as "external pathway" or "ionic charge carriers") in favor of simple, direct descriptions of the processes occurring in electrochemical cells.

3. Authors should calculate cell potentials using the difference method ($E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode}$) instead of the additive method ($E^{\circ}_{cell} = E^{\circ}_{ox} + E^{\circ}_{red}$).

4. Authors should avoid using simple electrostatic arguments to predict ion and electron flow in electrochemical cells.

5. Authors should always consider all possible oxidation and reduction half-reactions when predicting the products of electrolysis, including the reactions of the electrodes, water, and aqueous ions.

These implications for textbook authors are certainly not new; most of these suggestions have been reported previously. Several researchers have cautioned authors about the use of simplifications (*16, 34*), vague and misleading statements (*14, 16*), the additive method for calculating cell potentials (*30, 32, 35*), and simple electrostatic arguments to predict the direction of electron and ion flow in electrochemical cells (*15, 16, 34, 35*).

The misconceptions discussed here are supported to different degrees by comments from these textbooks. Misconception 3 (the anode is always the left-hand half-cell) was supported by comments from 9 of the 10 textbooks (all except *B*); misconceptions 7, 16, and 17 (which concern the notion that half-cell potentials are absolute, measurable, and extensive) were supported by 8 of the 10 (all but *BH* and *OW*); misconceptions 8–10 and 12 (which concern the flow of electrons in electrolyte solutions) and 14 and 15 (electrodes have net electronic charges) were supported by 6 textbooks (*AB, B, BP, BH, BLB, KT*); and misconception 13 (only anion flow constitutes a current) was supported by 3 textbooks (*AB, KT, OW*). It is not surprising that misconceptions that have not been widely reported (e.g., 3, 7, 16, and 17) are supported to a greater extent in these textbooks than those that have received a great deal of attention recently (8–10, 12, 14, and 15).

The 10 textbooks reviewed in this study also vary in the extent to which they contain statements and illustrations that could be misinterpreted by students. Two textbooks (*AB, KT*) contain vague, misleading, or incorrect statements that could be construed as corroborating all ten misconceptions discussed here.[2] On the other hand, 3 textbooks (*BH, BLB*, and *OW*) contain statements corroborating only five of the ten misconceptions discussed above. The extent to which these

+2.01 ——— $S_2O_8^{2-} + 2e^- \rightleftharpoons \mathbf{\underline{2SO_4^{2-}}}$

+1.23 ——— $O_2 + 4H^+ + 4e^- \rightleftharpoons \mathbf{\underline{2H_2O}}$

e^- flow

0.00 ——— $\mathbf{\underline{2H^+}} + 2e^- \rightleftharpoons H_2$

platinum is inert (not included)

net reaction: $2H_2O \longrightarrow 2H_2 + O_2$

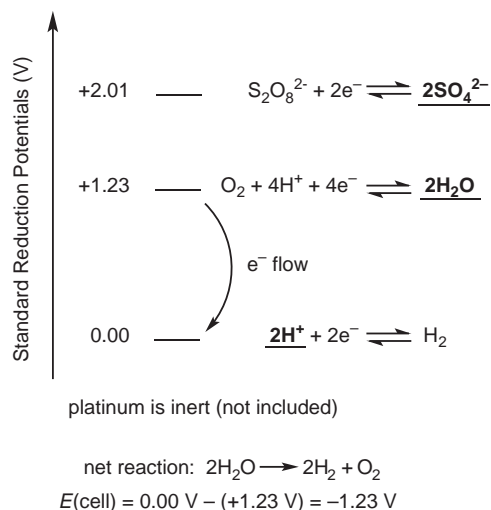$E(cell) = 0.00\ V - (+1.23\ V) = -1.23\ V$

Figure 1. Potential ladder diagram for the electrolysis of 1.0 M sulfuric acid under standard conditions.

textbooks contain vague, misleading, or incorrect statements in the oxidation–reduction and electrochemistry chapters could be used as a basis for textbook selection.

Acknowledgments

Notes

1. When the sign of the standard reduction potential is changed, it is converted into a standard oxidation potential. Although tables of standard oxidation and reduction potentials have been tabulated in the past, the International Union of Pure and Applied Chemistry (IUPAC) concluded that half-cell potentials should be reported for the reduction reactions because the signs of these reduction potentials correctly describe the polarity of the half-cells of interest with respect to the SHE electrode (*31*, pp 1115–1120).

2. Although 13 misconceptions are discussed in this paper, misconceptions 8 and 12, 9 and 10, and 14 and 15 are clearly related to each other and are treated as one misconception in the following discussion.

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