Addressing Students' Difficulties and Misconceptions About Electrochemistry
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Introduction
The study of electrochemistry involves understanding, both qualitatively and quantitatively, the transfer of electrons between different chemical species. Students should clearly grasp from the beginning that this transfer is just a specific type of chemical reaction that obeys all the principles that apply to other chemical reactions. Electrochemistry is a complex subject that has considerable importance in many applications, from battery development to neuroscience and brain research. The AP Chemistry Examination can include quantitative questions about electrochemical cells.

To bring order to understanding a complex process, chemists have established conventions -- otherwise known as "rules of the game." Many students have difficulties, not so much in understanding concepts, but in answering applied electrochemistry questions. They do not recognize that, as in any other game, failure to obey the rules can be disastrous. This is no place for being a sloppy chemist.

Student misconceptions and "errors" exhibited in answering questions in electrochemistry are many and varied. Rather than address specific misconceptions, this article offers suggestions and emphasizes issues that I hope will clarify understanding and pedagogy to help instruction.

To observe or measure the transfer of electrons between chemical entities, students must use indicators (colored substances) or probes (electrodes). The amount of transfer, as in all chemical reactions, depends on the quantities of the species present. Unfortunately, real systems are not simple and quickly lead to creating gradients of species concentrations that change as the reaction proceeds. Thus most measured values do not agree with simplistic theoretical predictions, or students must be obtain them at equilibrium or at conditions severely far away from equilibrium -- essentially before any reaction has occurred. Because introductory courses do not always address this issue, students' values in simple laboratory experiments rarely agree with values listed in tables of information.

Students usually learn of homogeneous reactions involving electron transfer under the heading of "redox" reactions. While I will not discuss these types of reactions here, they are really no different in concept, and students should learn that they are closely related. Those processes are normally handled at equilibrium.

Cells
The first challenge for students is to appreciate the notion of building an electrochemical cell. It is unfortunate that biology uses the term cell for something completely different, though students can think of both as examples of nearly isolated "systems."

The common cells encountered in introductory chemistry consist of two solid electrodes, immersed in one or more chemical solutions. A cell is a way of partially separating the two components of an oxidation-reduction reaction system. Cells can be of two types: galvanic (sometimes referred to as "voltaic") or electrolytic. The latter is pretty much the same cell but electrically driven backward by an external source of voltage. So one type of cell (galvanic) can, in fact, "drive" the other (electrolytic). The galvanic cell, with special construction considerations, is the basis of an electrical battery.

Galvanic Cells
In chemical terms, the galvanic cell is usually created far from equilibrium and proceeds toward its equilibrium state as electron transfer occurs. On the other hand, an external energy source drives the electrochemical cell to transfer electrons, with the net effect of moving it further from the equilibrium condition. It is common for beginning students to struggle with defining and distinguishing the two types of cells, so they must practice with these concepts. Much of this article (but not all) deals with galvanic cells, which appear more frequently in AP Examination questions.

Because of the need to take measurements under ideal conditions, students must keep galvanic-cell solutions in...
compartments separated by some form of membrane or ion containing a "salt bridge" that allows electron flow but prevents the solutions from mixing. Only then can the solution concentrations and identities surrounding each electrode remain known and roughly constant.

Conventions establish that when electrons transfer from a solid electrode into a solution that contains ions of the same element as the electrode probe (a usual but not required condition), we call this electrode (and the compartment, if any, in which it is located) the anode. This term relates to the fact that the solid loses electrons, that is, undergoes a process defined as oxidation.

Conversely, when electrons transfer to a solid electrode from ions in solution, we call the electrode the cathode and the associated process the reduction. It is helpful for students to know that these terms and the direction of transfer are language and conventions established by earlier scientists, and all students and future scientists must learn and follow this terminology to accurately communicate their findings. The chemicals will always do the right thing no matter what the terminology is.

It is important for students to learn to automatically diagram and label parts of a cell to delineate a problem even when the question doesn't specifically ask for it. Note that cell diagrams usually specify concentrations of important (that is, reactant or product) species in solution (usually aqueous ions). All the standard texts show galvanic cell diagrams.

Measurements on Galvanic Cells

The key measure of a galvanic cell is usually the cell voltage, taken by connecting a voltmeter between the two electrodes (externally to the cell). In one sense, it isn’t important which “way round” you connect the voltmeter. It is the value of the voltage that matters; the + or - nature of the reading simply confirms the direction of electron transfer in the cell. You can expect the electrode losing electrons (anode) to become more positive and that gaining electrons (cathode) to become more negative. For the measurement to be meaningful, the process must meet two conditions:

- The cell/voltmeter combination must be a complete circuit. This may seem obvious, but many students haven’t dealt with this issue or have seen it only in a “batteries and bulbs” exercise in elementary school. (National surveys have produced alarming statistics on how many adults cannot explain how a flashlight must be a complete circuit to work.)

- Very little current must pass through the cell/voltmeter circuit. This is true for most modern voltmeters, which all operate successfully with high resistance. This implies that the cell must not transfer electrons to get a good answer. Students can understand that at the moment many electrons transfer, something is beginning to change. Initial electron transfer rates are extremely fast, so reaction rates are not a complicating factor here.

So far we have ignored the role of the solution. As in all chemical reactions, the concentrations of reactants and products are important in determining the position relative to equilibrium. In any solid electrodes in galvanic cells, the element or elements have unit concentrations (as long as a solid is present), while solution concentrations are in molarities. As in any other reactions, an important issue for students is to identify the relevant reactant or product species in what may be a complex solution.

A convention standard establishes that all measurements are relative to those obtained when (1) a 1 molar solution of the relevant ionic species is present, (2) any elements are in a normal physical state at 298 K, and (3) the temperature is 298 K. All conditions must be met simultaneously.

[Note that these concentration conventions originate from “Activity Model” principles which are usually dealt with in considerations of chemical equilibrium.]

Once students establish that the cell is under the "standard-state conditions," then (and only then) can they compare the measurements of "cell potentials" or voltages directly with those listed in any reference table for the studied reaction. Again, students may find it helpful to know that this is another “game rule” established so scientists can make realistic comparisons and not a requirement imposed by nature. If you want to play, learn and observe the rules.

The Half-Cell Model

Dealing with complete cells is a lot to think about at once. Chemists recognized this and developed the notion that they could theoretically separate the anode and cathode parts of the cell (impossible in practice, or a complete circuit wouldn’t be present). Using this assumption, they could consider only the reduction or oxidation reaction, one at a time. So the concept of an "electrode potential" value was born. The conventional standard conditions mentioned above express this as a "standard electrode potential." Even then, as in all of thermodynamics, chemists cannot readily establish absolute values. All standard electrode potential values are established relative to a "standard hydrogen electrode" (SHE), which is defined as having a potential of 0.000 volts. Students should consult their textbooks for details on the construction of a standard hydrogen electrode. The AP Chemistry Examination is unlikely to address this subject.
For student reference, the AP Chemistry Exam includes a table of these values called “Standard Reduction Potentials, E° in Water Solution at 25°C (in V).” It is vital for students to understand that the values given are correct only for the half-reaction stated in the table, and only at standard-state conditions. To make the comparisons easier, the table lists all values as if the reaction is a reduction reaction (that is, occurring at a cathode). For this reason, potentials may be either positive or negative. A negative sign means that the reaction proceeds spontaneously from left to right as written toward equilibrium when the reactants and the products are in their standard-state conditions. (The sign direction is also conventional and comes from thermodynamic principles and the convention established for free-energy changes.) A positive sign means the reaction will proceed spontaneously from right to left, again only under standard-state conditions.

Students have considerable difficulty with these concepts. In other areas of chemistry, they have mostly dealt with equilibrium (or close to equilibrium) systems. Standard electrode potentials are values for reaction systems often very far from equilibrium, and the fact that both reactants and products are in their “standard states” is a highly artificial condition, causing confusion for students who have learned about real conditions.

**Calculation of Cell Potentials from Half-Cell Potentials**

1. **Under Standard-State Conditions**
   The AP Exam frequently asks students to calculate a cell potential given the electrode potential table. They should remember the fundamental chemical reaction principle: first determine the reaction you are dealing with and write it out, then split it into oxidation (electron loss) and reduction (electron gain) half-reactions.

   Here a very confusing concept for students pops up -- electrode potentials (because they are standard state related) are already expressed in "mole" units. One way to picture this is that they represent the relative “potential” for 1 mole of electrons to be transferred. They are, thus, intrinsic properties. For this reason, the half-reactions do not need to be stoichiometrically balanced as far as electron transfer is concerned. All students need to do is correctly identify the direction of each half-cell reaction, since both cannot be expressed as reductions. Students must reverse one reaction and express it as an oxidation. This reverses the sign, so the cell potential is simply the algebraic sum of the two half-cell potentials.

   In practice, it is often better to reverse the procedure:
   a. Reverse one of the reactions and thus the sign of its standard voltage.
   b. Add the two voltages together, paying careful attention to the signs. Add the two reactions together.
   c. If the resulting voltage has a positive sign, then you reversed the correct reaction -- the complete reaction will proceed spontaneously from left to right as written.
   d. If the resulting voltage is negative, then you reversed the wrong reaction, and the reaction as written will proceed spontaneously from right to left instead of left to right. Reverse the entire reaction and the sign of the voltage to present the proper result.

   **Note**: This convention creates a different result for the voltage of a cell in terms of whether the reaction is or is not spontaneous as written, as opposed to the sign for the reaction's thermodynamic free energy. This is highly confusing for students, and they will need much practice.

2. **Under Non-Standard-State Conditions**
   Nobel chemist Walther Nernst determined how to calculate cell potentials under any conditions. He did this by working out the connection between cell voltages and thermodynamic parameters for cells, including the equilibrium constant of the cell reaction. The Nernst equation provides the mechanism for making the connection. Since 1996, the AP Examination has given this equation in the “Oxidation-Reduction; Electrochemistry” section of the provided tables. Not surprisingly, in view of the “flip” in sign conventions noted above, the equation derives from the relationship between free-energy change and the cell potential in standard-state conditions where \( DG^\circ = \Delta G \). The negative sign in this connection equation reverses the “spontaneity” conclusion. The Nernst equation applies equally well to half-reactions -- electrode potentials -- as it does to complete cell potentials.

   Obviously the use of the Nernst equation with its many parameters provides many opportunities for student error. Thus they need frequent practice with a focus on absolute attention to the “rules of the game.” Common errors include:

   - Use of the wrong logarithms. For example, the exam may provide equations containing some parameter values and including the change between ln and log in the resultant “constant” value. Students may not recognize this and proceed to use ln values when log is appropriate and vice versa.
   - Failure to truly understand the difference between Q (equilibrium quotient, applicable under any known conditions) and K (equilibrium constant only applying to a system known to be truly at equilibrium).
   - Failure to adequately keep track of signs in either the equation or the voltages used, or in ratios converting to logarithms (values less than 1 should have negative logarithm values).

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*http://apcentral.collegeboard.com/apc/members/courses/teachers_corner/155230.html*
● Failure to appreciate the distinction between \( E \) (any conditions) and \( E^0 \) (only standard-state conditions -- see above).

● Failure to use the correct value for \( n \) (the number of electrons transferred per mole of reactant taking part in the reaction). The understandable confusion here is that in combining standard half-cell potentials to compute the cell potential under standard-state conditions, we don't consider \( n \) (as noted in [1] above); however, we must include it once the conditions are not standard states. Again, you can explain this most easily as one of the "rules of the game." These are no longer intrinsic properties because they depend on the quantities of reactants and products involved.

**Calculation of One Standard Half-Cell Potential by Combining Two or More Other Standard Half-Cell Potentials**

The AP Exam rarely addresses this topic, even though it appears in some standard texts, perhaps because the following issue makes the concept difficult to understand. In this case, students must take into account the number of moles of electrons transferring per mole of the substances involved and return the equation to a "per mole" basis at the end. So students must essentially exit from intrinsic properties as they perform the computation but return an intrinsic property value at the end. Teachers who wish to address this topic should carefully follow the methodology given in a standard text.

**Electrolytic Cells**

These cells, in many ways, are much easier to deal with than galvanic cells. The primary application addressed in the AP Chemistry Exam is to determine the quantity of reaction (how much reactant is turned into how much product) occurring by the passage of a given quantity of electricity. Occasionally the reverse problem may appear (how much electricity is used to create how much product), but the relation is the same.

Lack of attention to detail appears to cause many of the difficulties seen in student responses. Especially common is a confusion (mentioned above) between amps and volts and between amps and coulombs (quantity of electricity = amps \( \times \) time), even though the exam provides the helpful equation \( I = \frac{q}{t} \).

Since this concept deals with nonintrinsic properties, students must take into account the number of electrons transferred per mole (\( n \)) when determining the moles of reaction induced. The equation tables in the AP Exam even provide a hint. The table of constants gives the units of the Faraday as coulombs per mole of electrons. A disappointing number of students fail to pay attention to units when solving numerical problems.

As in all of chemistry, identifying and writing out the key chemical reaction in balanced form is highly desirable, even if it costs precious seconds during the examination.

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