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Common sources of confusion;

Electrode Sign Conventions

The subject of electrode sign conventions has received attention from many eminent chemists including Nernst, Gibbs, Lewis, and Latimer.[1] Some of the more recent remarks which have been made on the subject are included in references (*1–7*).

This subject has been worked very hard but some areas of misunderstanding still persist. It is hoped that a consideration from yet another viewpoint of two of the main sources of misunderstanding will be helpful.

One of the biggest single sources of confusion about the sign of electrode potentials stems from a failure to appreciate the simple but very important distinction between an actual physical electrode and the conceptual notion of a half-reaction. J. J. Lingane (*8*) first pointed out the importance of this distinction. In Lingane's words:

> . . . The confusion arises from failure to recognize that "emf, of a half-reaction" and "potential of an actual electrode" are distinctly different concepts. The sign of the emf of the half-reaction at an electrode may either be the same or opposite to the sign of the potential of the actual electrode with respect to some other electrode.
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> . . . Although the sign of the emf or potential of a half-reaction depends on the direction in which the reaction is written the sign of the potential of the actual physical electrode at which the half-reaction occurs with respect to the sign of the potential of the other electrode is, of course, fixed or invariant. . . . The potential of an actual electrode (observed physical quantity) is distinct from the thermodynamic concept of the potential or emf of a half-reaction (defined quantity).

This statement goes straight to the heart of much of the confusion about electrode potentials. It also does much to clarify the real difference between the so-called European and American sign conventions.

An author who adheres to the European convention will write expressions such as:

$$\left.\begin{array}{l} \mathrm{Zn} = \mathrm{Zn}^{++} + 2e^- \\ \mathrm{Zn}^{++} + 2e^- = \mathrm{Zn} \\ \mathrm{Zn/Zn}^{++} \\ \mathrm{Zn}^{++}\mathrm{/Zn} \end{array}\right\} \quad E^\circ = -0.76 \text{ volt}$$

That is, the standard potential of the zinc-zinc ion electrode is taken as -0.76 volt regardless of the way in which the couple is represented. This convention has to do with the potential of an *actual physical electrode* coupled with a standard hydrogen electrode in a cell. Since the potential of a standard zinc electrode is always -0.76 volt with respect to the standard hydrogen electrode regardless of the orientation of the cell on the laboratory bench, advocates of the European sign convention insist on always associating the number -0.76 with the zinc-zinc ion couple. The sign of an electrode potential is never varied in the European Convention.

What is commonly understood as the American sign convention (begun by Lewis and Randall and followed by Latimer) *does not* have to do with an actual physical electrode but rather with a half-cell reaction conceived on paper. American sign convention adherents write:

$$\mathrm{Zn} = \mathrm{Zn}^{++} + 2e^- \quad E^\circ = +0.76 \text{ volt}$$

or equivalently,

$$2e^- + \mathrm{Zn}^{++} = \mathrm{Zn} \qquad E^\circ = -0.76 \text{ volt}$$

These two expressions mean that the spontaneous tendency is for zinc metal to be oxidized to zinc ion and two electrons, the standard free energy change being given by $\Delta F^\circ = -E^\circ n\mathfrak{F}$. With the American Convention the sign of the standard potential of a half-cell reaction is bivariant according to the direction in which the half-cell reaction is written on the paper.

Lewis and Randall and Latimer and their disciples have arbitrarily chosen to list their values of standard half-reaction emf's for half-reactions written as oxidations. Accordingly one most often sees expressions such as

$$\mathrm{Zn} = \mathrm{Zn}^{++} + 2e^- \qquad E^\circ = +0.76 \text{ volt}$$

The fact that the signs of these values for the standard emf's are just opposite to the signs of the standard electrode potentials according to the European Convention has led many authors to state that the European and American Conventions differ only in being opposite ways of measuring the same physical phenomenon. Kortüm and Bockris (*9*) and Delahay (*10*), for instance, explain that in the European Convention a potential difference is measured from electrode to solution while in the American Convention it is measured from solution to electrode. Strictly speaking this is not the case. The European Convention expresses explicitly the sign of a potential difference between actual physical electrodes but the American Convention does not. The standard half-reaction emf's given by Latimer (which are always cited as the chief example of the American Convention in action) give information on the tendency (or lack of it) for the given half-reaction to proceed as written ; they are *not* simply European electrode potentials measured in the reverse direction (*11*).

Another major source of the confusion about signs of electrode potentials has been that in trying to maintain the fundamental distinction between the sign of a physical electrode and the sign of a standard half-reaction emf one is constantly using the words "positive" and "negative" in two very different senses.

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[1] A very complete bibliography is given in reference 2.

The difference between a *positive* and a *negative* free energy change (both of the same absolute magnitude) is thermodynamic, and not at all the same as the electrostatic difference between a *positive* and a *negative* potential difference between two electrodes (both potential differences being of the same absolute magnitude). The former positive-negative relation distinguishes between a tendency for a chemical system to change, or not to change, in a specified direction; the second positive-negative relation distinguishes between one kind of charge and its opposite.

The reason that the European electrode potential for, say, zinc, is -0.76 volt (i.e., 0.76 volt negative) is because *negatively* charged electrons are liberated at the zinc electrode. The completely separate reason that the American standard half-reaction emf for $Zn = Zn^{++} + 2e^-$ is $E° = +0.76$ volt is because the thermodynamic tendency is for this reaction to proceed from left to right as written, i.e., for electrons to be liberated in the zinc electrode (thus making it negative with respect to the S.H.E.).

White and Black; Positive and Negative

It is only a (possibly unfortunate) coincidence that the same two words, "positive" and "negative," are used to describe both the two opposite senses of the free energy changes which accompany chemical changes and the two opposite kinds of electrical charge. The fact that the same word, "negative," is used to describe the sign of the charge on the electron and the sign of the free energy change which occurs when a system proceeds spontaneously towards equilibrium should not lead one to regard these two separate entities themselves as related. Even though the charge on the electron has been described as negative there is no reason to expect correspondence between a negatively charged electrode and a negative half-reaction emf. There is no relation whatsoever. The negativeness of an electron's charge (which is responsible for the negativeness of a physical electrode's potential) is simply not the same as the negativeness of a half-reaction emf—the two are incomparable.

If, in the interest of clarity, one were to insist on complete singularity of meaning for the words to be used in specifying pairs of opposites, then once the words "positive" and "negative" (or "plus" and "minus") were adopted to describe, say, free energy changes, it would be necessary to choose other words to describe other pairs of opposites which were not opposite in the same sense that a positive and a negative free energy change are opposite. For instance, one could distinguish between the charge on the electron and that on the proton by speaking of the electron's charge as *black* 1.603×10^{-19} coulombs and the proton's charge as *white* 1.603×10^{-19} coulombs, where the colors are used to indicate the oppositeness of the charges.

If Benjamin Franklin had decided to call the two opposite kinds of electric charge black and white instead of negative and positive he would very probably have saved electrochemists from much of their confusion over signs.

If the electron's charge were black the European Convention would not be that the standard electrode potential of zinc is -0.76 volt but *black* 0.76 volt. However, even if the electron's charge were black Lewis and Randall and Latimer would still write:

$$Zn = Zn^{++} + 2e^-; \quad E° = +0.76 \text{ volt}$$

and

$$Zn^{++} + 2e^- = Zn; \quad E° = -0.76 \text{ volt}$$

And now the temptation is gone to try to compare the sign of a physical electrode (given in the European Convention) and the sign of a half-reaction emf (given in the American Convention). One doesn't compare blackness with negativeness.

In the author's opinion the use of black and white to describe the opposite kinds of charges would contribute to a decrease in confusion. Because of the prejudices of tradition, however, the general adoption of such a practice does not seem a realistic possibility. One is therefore forced to live with free energy changes which are positive and negative as well as with positive and negative charges. The only way to avoid the latent confusion which results from using words with several meanings is to keep clearly in mind the physical realities which the words describe.

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