A note on conventions in equilibrium electrochemistry

- 1 The Right-Hand Side (RHS) of the cell as written is always taken as **positive*** (and the LHS as negative).
- 2 A reaction that abstracts electrons from the electrode makes it positive (and one that liberates electrons to the electrode makes it negative).
- 3 Tables of electrode potentials are **always** of reduction potentials these days.

These three conventions make perfect sense taken together. Single standard electrode potentials are always referenced to the standard hydrogen electrode (SEH). For example, a cell with Cu^{++} on the RHS and an SEH on the left thus looks like

 Θ H₂/Pt | H⁺ || Cu⁺⁺ | Cu \oplus (I)

The half-cell reaction that will make the RHS positive in accordance with rule 1 is the reaction

 Cu^{++} + 2e \rightarrow Cu

following rule 2. This reaction is a reduction process, so that if the measurement is made under 'standard' conditions (unit activity, T = 298K), the voltage measured is a standard reduction potential, as envisaged by rule 3.

The question is now what to do about the **total** voltage and the **overall** cell reaction of the two cells taken together. There are two ways of going about matters that come ultimately to exactly the same thing. One of them I personally feel to be more straightforward, obvious and foolproof. Unfortunately, this method is not the one that has often been presented in Oxford courses, and I think that it may be worthwhile setting out the two alternatives, and then explaining what I think is better about the first. You can choose for yourselves!

Method 1

If the RHS of the cell is a reduction process (it always should be written as that to make the electrode positive*), then the LHS is of necessity an oxidation. It is true even in the case of the hydrogen electrode of the cell (I) just presented, but let us consider a slightly more complex cell in which the LHS is a Zn/Zn^{++} electrode

 Θ Zn | Zn⁺⁺ || Cu⁺⁺ | Cu \oplus (II)

The two cell reactions according to this first method are written exactly as they occur to make the RHS electrode positive and the LH electrode negative

RHS	Cu^{++}	+	2e	\rightarrow	Cu	
LHS	Zn			\rightarrow	Zn ⁺⁺ +	2e

We now regard this full cell as made up of two half-cells in series

*Note carefully! The RHS is *assumed* to be positive: that is, the electrode gives ions to the electrolyte (reduction). However, the electrode potential may turn out in reality to be a positive or negative value as revealed from the tables of potentials. Similarly, the LHS is *assumed* to be negative (oxidation), but the electrode potential for that half cell may be a positive or negative value. Always just 'assume' that the RHS is *called* positive, and the LHS *called* negative, then insert the actual positive or negative values for the electrode potentials as given for the reduction or oxidation process.

Since the total EMF, E_{Total} of two cells in series is the algebraic sum of the EMFs of the two individual cells,

$$E_{\text{Total}} = E_{\text{Left}} + E_{\text{Right}}$$

The overall cell reaction is also the algebraic sum of the two half reactions, obtained by adding the two LHS reactions and the two RHS reactions

 Cu^{++} + Zn \rightarrow Cu + Zn^{++}

with two electrons having been transferred in the process.

If you need to consider thermodynamic quantities such as ΔG , ΔH and ΔS , then they, too, can also be added in the same way for the half cells as written in exactly the way they are normally, for example in Hess's Law calculations.

The one action that the user has to take is to remember if using an EMF in a table of reduction potentials (or in an examination paper!) to change the sign of it for use in the left-hand cell, because an oxidation rather than a reduction process is occurring there.

Method 2

This (Oxford) method focuses more on the reduction potentials in the tables than on the reality of the chemistry! Both half cells are written as **reduction** reactions, and both electrode potentials as **reduction** potentials (which I will represent here by $\mathcal{E}_{\text{Left}}$ and $\mathcal{E}_{\text{Right}}$). You can look both these values up directly in the table, but since the LH reaction is really an oxidation, we have to write out

$$\mathcal{E}_{\text{Total}} = \mathcal{E}_{\text{Right}} - \mathcal{E}_{\text{Left}}$$

and the cell reactions are now

RHS	Cu^{++}	+	2e	\rightarrow	Cu
LHS	Zn^{++}	+	2e	\rightarrow	Zn

so that the overall cell reaction has to be written as RHS - LHS

Comparison

Of course, if you do everything correctly, $\mathcal{E}_{Total} = E_{Total}$, and the final overall cell reaction is the same in both cases. However, with method 1 **you do not have to remember** which side to subtract from the other, so it is more foolproof. It is easier to **add** reactions (and even voltages) than to subtract them. Finally, the method seems – to me at least – to be more intuitive in terms of adding voltages of cells in series, in terms of adding thermodynamic quantities (to which the voltages are intimately related), and in adding up chemical reactions in an overall balanced equation. It is actually quite difficult and confusing to perform the subtractions for quantities such as ΔG in a redox reaction with complicated numbers of electrons being transferred.

It might be worth stating the similarity and difference another way. The relation between the \mathcal{E} and *E* quantities is

 $\mathcal{E}_{\text{Right}} = E_{\text{Right}}; \qquad \mathcal{E}_{\text{Left}} = -E_{\text{Left}}; \qquad \mathcal{E}_{\text{Total}} = E_{\text{Total}}$

so that the only difference is in the quantities for LHS.