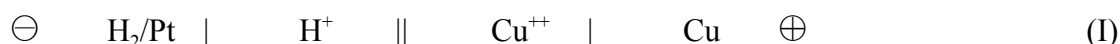


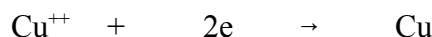
A note on conventions in equilibrium electrochemistry

- 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



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

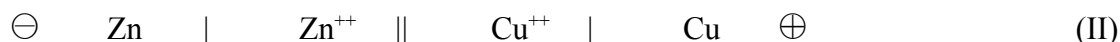


following rule 2. This reaction is a reduction process, so that if the measurement is made under 'standard' conditions (unit activity, $T = 298\text{K}$), the voltage measured is a standard reduction potential, as envisaged by rule 3.

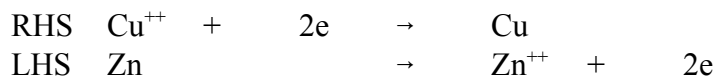
The question is now what to do about the **total** voltage and the **overall** cell reaction of the two cells taken together. There are two ways of going about matters that come ultimately to exactly the same thing. One of them I personally feel to be more straightforward, obvious and foolproof. Unfortunately, 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



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



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.

