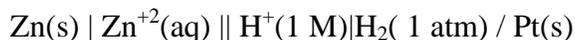


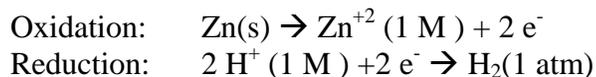
Standard Electrode Potential

The galvanic cell has two electrode potentials; anode potential and cathode potential. When the cell potential is measured with voltmeter, it gives the difference of both potentials but not an individual potential. It is impossible to measure the potential of just one electrode, but it can be circumvented by selecting a particular electrode as a standard electrode and assigning it a zero electrode potential and then measure the relative potential of an electrode in question in reference to that standard electrode potential (this concept is similar to the concept of assigning the atomic masses to elements based on the standard atomic mass of Carbon-12). Here, the hydrogen electrode is chosen as the standard electrode that consists of hydrogen gas bubbled through platinum electrode at 1 atm into 1M hydrochloric acid at 25⁰ C that has assigned zero as a standard electrode potential. Then all the electrode potentials are measured in relation to this standard electrode and are termed as standard potentials and are indicated by the symbol E⁰ (the E stands for electromotive force or the EMF).

Suppose, we want to measure the standard electrode potential for zinc electrode, then we construct the cell according to the following cell diagram



and measure the electrode potential, which is 0.76 V at 25⁰ C. This also happens to be the standard potential for zinc electrode. Let us see how? The above cell diagram is broken up into two half-reactions:



By convention, the **standard emf** of the cell (E_{cell}⁰) is the sum of oxidation and reduction potentials, is given by the following equation.

$$\begin{aligned} E_{\text{cell}}^0 &= E_{\text{ox}}^0 + E_{\text{red}}^0 \\ \text{or} \quad 0.76 \text{ V} &= E_{\text{ox}}^0 + 0 \end{aligned}$$

Thus the standard oxidation potential for Zn is +0.76 V.

The standard electrode potentials are listed as either **standard oxidation potential** or **standard reduction potential**. It does not make any difference because one is just the opposite of the other, that is,

$$E_{\text{ox}}^0 = - E_{\text{red}}^0 \quad \text{or} \quad E_{\text{red}}^0 = - E_{\text{ox}}^0$$

In the above example, E_{red}⁰ for Zn is -0.76 V.

Many textbooks list standard reduction potentials going from positive standard half-electrode potential to negative standard half-electrode potential in the form of a table. Here is the abridge version of that.

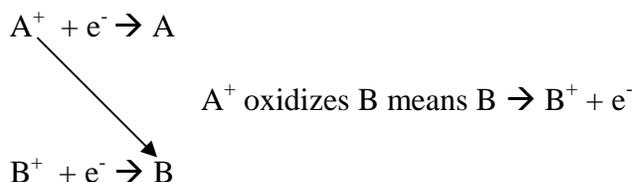
Reduction Half-Reaction	Standard Reduction Potentials at 25 ⁰ C
	E ⁰ (V)
F ₂ (g) + 2 e ⁻ → 2F ⁻ (aq)	+2.87
O ₂ (g) + 2 H ⁺ (aq) + 2 e ⁻ → O ₂ (g) + H ₂ O	+2.07
·	·
·	·
·	·
Sn ⁺⁴ (aq) + 2 e ⁻ → Sn ⁺² (aq)	+0.13
2 H ⁺ (aq) + 2 e ⁻ → H ₂ (g)	0.00
Pb ⁺² (aq) + 2 e ⁻ → Pb(s)	-0.13
·	·
·	·
·	·
K ⁺ (aq) + e ⁻ → K(s)	-2.93
Li ⁺ (aq) + e ⁻ → Li(s)	-3.05

Get yourself familiarized with these standard potentials. The following few things you should know about this table.

- The E⁰ values apply only to half-reduction reaction – reading from left to right.
- The greater positive E⁰ means stronger the oxidizing agent – it gets reduced (strong attraction of electrons). For example, F₂(g) is comparatively better oxidizing agent than any other species fall below it on the left side of the half-reaction, like, O₂(g), Sn⁺(aq), H⁺(aq), Pb⁺²(aq), K⁺(aq), and Li⁺(aq) and hence it (F₂(g) gets reduced because it is a better electron attractor due to its higher electronegativity.
- The half-reactions are reversible – can be made oxidizing half-reactions instead of reducing half-reactions. In that case, the sign on E⁰ is reversed.
- The values of E⁰ do not depend on the stoichiometric coefficients in the half-reaction. For example Li⁺(aq) + e⁻ → Li(s) and 5 Li⁺(aq) + 5 e⁻ → 5Li(s) have the same E⁰ value of -3.05.
- Most importantly, any species on the left of a given half-cell reaction will oxidize the species that appear on the right of any half-cell reaction existing below it.

For example,

$F_2(g)$ will oxidize $O_2(g)$, $Sn^{+2}(aq)$, $H_2(g)$, $Pb(s)$, $K(s)$, and $Li(s)$, means $F_2(g)$ makes these species to lose electrons by accepting electrons from them.



Uses of Standard Electrode Potentials

There are basically two uses of standard electrode potentials:

- To calculate the total cell potential
- To predict the spontaneity of the reaction – the reaction proceeds the way it is written

Let us take some examples to illustrate these uses.

To calculate the total cell potential

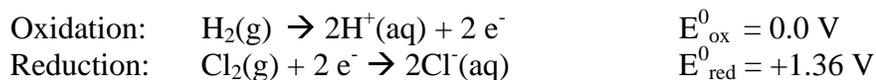
Example

Calculate the total cell potential for the following reactions.

- (a) $H_2(g) + Cl_2(g) \rightarrow 2H^+(aq) + 2Cl^-(aq)$
(b) $Sn^{+2}(aq) + 2Fe^{+3}(aq) \rightarrow Sn^{+4}(aq) + 2Fe^{+2}(aq)$
(c) $Al^{+3}(aq) + 3Cr^{+2}(aq) \rightarrow Al(s) + 3Cr^{+3}(aq)$

Answer

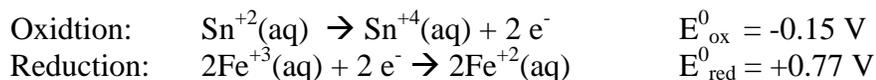
- (a) First write oxidation half-reaction and reduction half-reaction, get the standard potential values from the table, and add them up.



Then

$$E^0_{\text{cell}} = E^0_{\text{ox}} + E^0_{\text{red}} = 0.0 \text{ V} + 1.36 \text{ V} = +1.36 \text{ V}$$

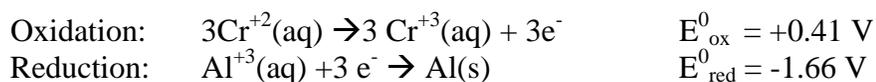
(b) Half- reactions are



Then

$$E_{\text{cell}}^0 = E_{\text{ox}}^0 + E_{\text{red}}^0 = -0.15 \text{ V} + 0.77 \text{ V} = +0.62 \text{ V}$$

(c) Half-reactions are



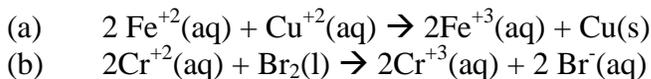
Then

$$E_{\text{cell}}^0 = E_{\text{ox}}^0 + E_{\text{red}}^0 = +0.41 - 1.66 \text{ V} = -1.25 \text{ V}$$

To predict the spontaneity of the reaction

Example

For each of the following reactions, predict the reaction is spontaneous or not.

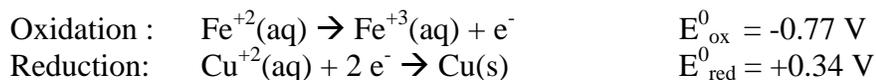


Answer

First calculate the cell potential and predict the spontaneity based on whether it is positive or negative. Use the following rules:

- $E_{\text{cell}}^0 =$ positive (+), reaction is spontaneous or occurs the way it is written
- $E_{\text{cell}}^0 =$ negative (-), reaction is nonspontaneous or does not occur the way it is written

(a) Separate the reaction into oxidation part and reduction part, and get the respective standard potentials from the table.

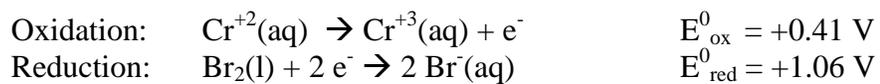


Now you add both potentials:

$$E_{\text{cell}}^0 = E_{\text{ox}}^0 + E_{\text{red}}^0 = -0.77 \text{ V} + 0.34 \text{ V} = -0.43 \text{ V}$$

The negative sign on the potential indicates that it is not spontaneous, means it does not go the way it is written or proceeds in the reverse direction.

(b) Break the equation into oxidation half-reaction and reduction half-reaction:



Add both potentials to get the cell potential:

$$E_{\text{cell}}^0 = E_{\text{ox}}^0 + E_{\text{red}}^0 = +0.41 \text{ V} + 1.06 \text{ V} = +1.47 \text{ V}$$

Therefore, the reaction is spontaneous or proceeds the way it is written.