
The Nernst equation for cells

When an electric cell is out of equilibrium, a current will occur. Electrons move from the side getting oxidized to the side getting reduced, and you can measure a difference in electric potential. This difference in electric potential is the electromotive force (EMF), also called open-circuit voltage. For a cell, this is denoted as E . In some cultures, e.g. in Denmark, U_0 has traditionally been used for denoting the EMF for electric cells, but here we use the international E . EMF can be calculated from the electrode potentials for the two half cells it consists of, and it is, and it has a directional orientation specified by the cell diagram.

EMF is calculated using the formula

$$E = E_{\text{right}} - E_{\text{left}}$$

To prevent mixing up which EMF is for the cell and for the two half cells, you can use notations like:

$$E_{\text{cell}} = E_{\text{right half cell}} - E_{\text{left half cell}}$$

The notation for the half cells are usually self explanatory, as you write the redox pair, e.g. $E(\text{Zn}/\text{Zn}^{2+})$

At 1.0 M solutions and 25 °C you have standard conditions for electromotive force/open-circuit voltage, which is written like this:

$$E^\circ = E^\circ_{\text{right}} - E^\circ_{\text{left}}$$

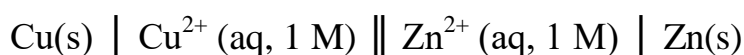
This is the **Nernst equation**, also known as **Nernst's law** for the cell. E° for a redox pair is usually something you look up.

As the calculation of E is dependent on the orientation of the cell diagram, the positive or negative sign for the calculated E will be a marker for the direction of the reaction. You cannot have negative electric potentials per se, but you can

measure or calculate them, due to the orientation. If E is positive, the reaction producing a current is the same as the one specified by the cell diagram. On the other hand, if E is negative, the reaction producing a current is going the opposite direction of what is specified by the cell diagram.

EMF calculations at standard conditions

If we look at the cell diagram for the Daniell cell under standard conditions, it can be written as either



giving the EMF (E° values found by looking them up):

$$E^\circ = E^\circ(\text{Zn}/\text{Zn}^{2+}) - E^\circ(\text{Cu}/\text{Cu}^{2+}) = -0.762 \text{ V} - 0.340 \text{ V} = -1.102 \text{ V}$$

or



giving the EMF:

$$E^\circ = E^\circ(\text{Cu}/\text{Cu}^{2+}) - E^\circ(\text{Zn}/\text{Zn}^{2+}) = 0.340 \text{ V} - (-0.762 \text{ V}) = 1.102 \text{ V}$$

From this we can see that the cell is a 1.1 volt battery, and that it is the reduction of copper(II) ions by zinc, that produces a current.

EMF calculations when outside the standard conditions

If the element is not under standard conditions, you need to use the extended version of Nernst's law, i.e.

$$E = E_{\text{right}} - E_{\text{left}}$$

In this we insert the formula for a half cell, i.e.

$$E = E^{\circ} - \frac{R \cdot T}{z \cdot F} \cdot \ln(Q)$$

The result is that for the cell we now have:

$$E = E^{\circ}_{\text{right}} - E^{\circ}_{\text{left}} - \frac{R \cdot T}{z \cdot F} \cdot \ln(Q)$$

E = EMF for the cell

E° = the standard electrode potential for the half cell, i.e. E at 1 M and 25 °C

R = the gas constant

T = temperature in degrees Kelvin

z = the number of electrons to be transferred

F = Faraday's constant

Q = the reaction quotient

The formula makes more sense what you have tried using it, so let's have a look at an example. The formula has two critical points

1. The number of electrons
2. How the reaction quotient look

where you need to be a bit cautious about what you are doing, but otherwise the formula is quite simple to use.

For the Daniell cell at 25 °C



the reaction that goes with it is



and

$$T = 298 \text{ K}$$

$$z = 2$$

$$Q = \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

Inserted in the EMF formula (E° values found by looking them up) we now have

$$E = E^\circ(\text{Cu}/\text{Cu}^{2+}) - E^\circ(\text{Zn}/\text{Zn}^{2+}) - \frac{R \cdot T}{z \cdot F} \cdot \ln \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

$$E = 0.340 \text{ V} - (-0.762 \text{ V}) - \frac{8.31451 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} \cdot 298 \text{ K}}{2 \cdot 9.65 \cdot 10^4 \text{ C}\cdot\text{mol}^{-1}} \cdot \ln \frac{1.0 \text{ M}}{0.5 \text{ M}}$$

$$E = 1.093 \text{ V}$$

As seen, the EMF for the Daniell cell decreases when $[\text{Cu}^{2+}]$ decreases, and we are now getting to the interesting aspects of the formula. Now we can start making equations and inequations, e.g. what the ratio for $[\text{Cu}^{2+}]$ and $[\text{Zn}^{2+}]$ should be to get a 1.5 V EMF, or would it be possible to have a $[\text{Cu}^{2+}]$ low enough to make the reaction that produces a current go in the opposite direction of what we just saw in the last example.