

# The Nernst equation

The Nernst equation links the equilibrium potential of an electrode,  $E_e$ , to its standard potential,  $E^0$ , and the concentrations or pressures of the reacting components at a given temperature. It describes the value of  $E_e$  for a given reaction as a function of the concentrations (or pressures) of all participating chemical species.

In its most fundamental forms, the **Nernst equation for an electrode** is written as:

$$E_e = E^0 - \frac{2.303RT}{zF} \log \frac{[reduced]}{[oxidised]} \text{ or}$$

$$E_e = E^0 - \frac{RT}{zF} \ln \frac{[reduced]}{[oxidised]}$$

$R$  is the universal gas constant ( $8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$ )

$T$  is the absolute temperature

$z$  is the number of moles of electrons involved in the reaction as written

$F$  is the Faraday constant ( $96\,485 \text{ C per mole of electrons}$ )

The notation  $[reduced]$  represents the product of the concentrations (or pressures where gases are involved) of all the species that appear on the reduced side of the electrode reaction, raised to the power of their stoichiometric coefficients. The notation  $[oxidised]$  represents the same for the oxidised side of the electrode reaction.

## Explanation of Activity :

### Example 1 :

In the reaction  $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- = 2\text{H}_2\text{O}$

water is the reduced species and the oxygen gas is the oxidised species. By convention, electrochemical half-equations are written as

Oxidised State +  $ne^- \rightleftharpoons$  Reduced State

Taking into account the stoichiometric coefficients of the species, the log term of the Nernst equation for this reaction appears as

$$\log \frac{[\text{H}_2\text{O}]^2}{p_{\text{O}_2} [\text{H}^+]^4}$$

Some of the species that take part in electrode reactions are pure solid compounds. The standard state for these compounds is unit mole fraction, and as they are pure, and are in their standard states. In dilute aqueous solutions, water has an overwhelming concentration, so it may be considered pure. The standard state for a gas is taken as 1 atm (or 1 bar) and the standard state for solutes (such as ions) is taken as 1 mol dm<sup>-3</sup>. The log term of the Nernst equation can now be reduced to

$$\log \frac{1}{p_{O_2}[H^+]^4}$$

The Nernst Equation under standard conditions:

At 298.15 K (25 °C), the numeric values of the constants can be combined to give a simpler form of the **Nernst equation for an electrode under standard conditions**:

$$E_e = E^0 - \frac{0.0591}{z} \log \frac{[reduced]}{[oxidised]}$$

This equation can be applied both to the potentials of individual electrodes and the potential differences across a pair of half-cells. However, it is generally more convenient to apply the Nernst equation to one electrode at a time.

### Example 2 :

The reaction  $Al = Al^{3+} + 3e^-$  has a Nernst equation of

$$E_e = E^0_{Al/Al^{3+}} - \frac{2.303RT}{3F} \log \frac{[Al]}{[Al^{3+}]}$$

$$= -1.66 + 0.0197 \log[Al^{3+}]$$

at 298 K, as  $E^0$  is -1.66 V(SHE) and the activity of pure aluminium is 1. In this simple reaction, the resulting equilibrium potential is independent of  $pH$ .

### General expression of the Nernst Equation :

Taking the general equation for a half-cell reaction as,



the Nernst equation becomes

$$E_e = E^0 + \frac{0.0591}{z} \log \frac{[A]^a}{[B]^b} - \frac{m}{z} 0.0591 pH$$

Source : <http://www.doitpoms.ac.uk/tlplib/pourbaix/nernst.php>