Construction of a Pourbaix Diagram

A Pourbaix diagram plots the equilibrium potential ($E_{e\,:}$) between a metal and its various oxidised species as a function of pH.
The extent of half-cell reactions that describe the dissolution of metal

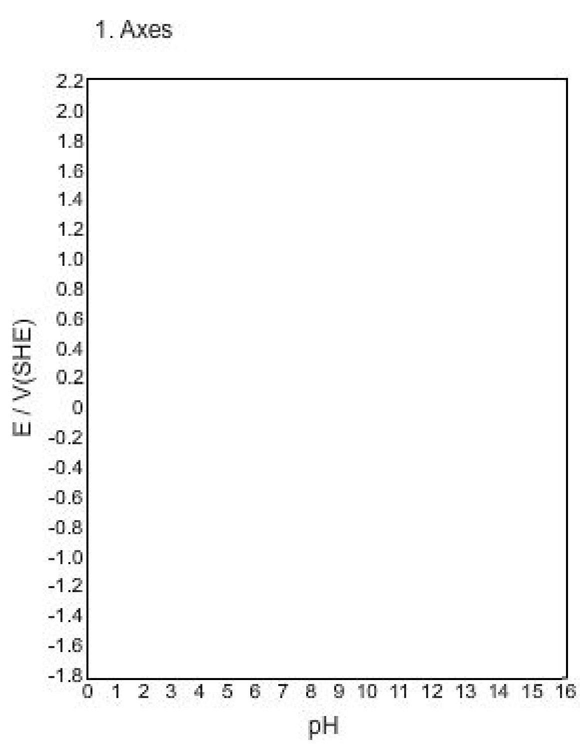
$M = M^{z+} + ze^{-}$

depend on various factors, including the potential, *E*, pH and the concentration of the oxidised species, M^{z+}. The Pourbaix diagram can be thought of as analogous to a phase diagram of an alloy, which plots the lines of equilibrium between different phases as temperature and composition are varied.
To plot a Pourbaix diagram the relevant Nernst equations are used. As the Nernst equation is derived entirely from thermodynamics, the Pourbaix diagram can be used to determine which species is *thermodynamically* stable at a given *E* and pH. It gives no information about the *kinetics* of the corrosion process.

Constructing a Pourbaix Diagram :

The following steps illustrates how a Pourbaix diagram is constructed from first principles, using the example of Zinc.

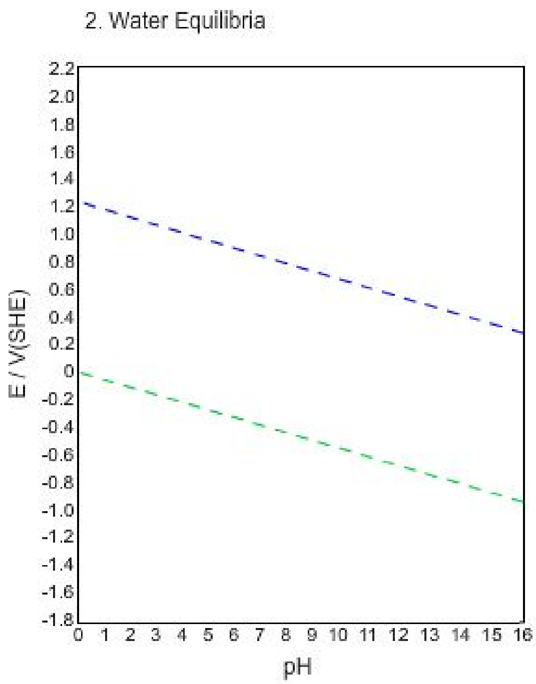
Step 1 :



pH is plotted on the **x-axis.**

Potential is plotted on the **y-axis** in units of volts relative to the standard hydrogen electrode (SHE). Potential can be though of as the oxidising power of the solution.

Step 2 :



For corrosion to occur a cathodic reactior (consumes e^-) must take place to balance the anodic reaction (produces e^-) of meta dissolving.
In pure water there are two possible cathodic reactions*:

1. $O_2 + 4H^+ + 4e^- = 2H_2O$
Oxygen dissolved in water is in equilibriu with water.

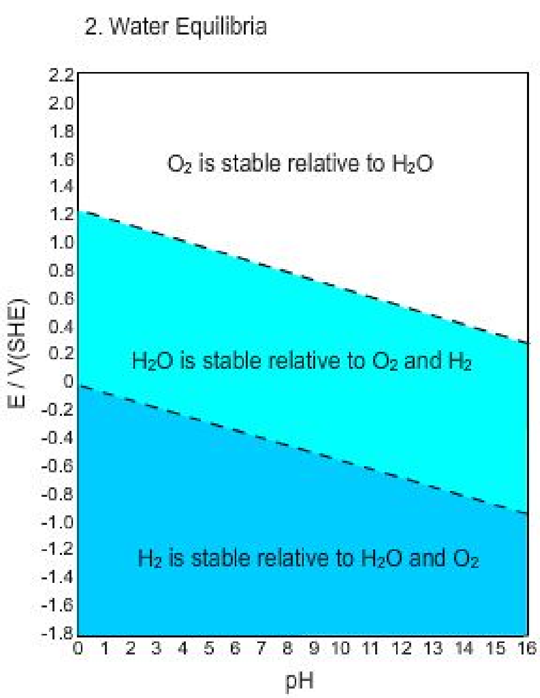
$$E_e = 1.223 - 0.0591pH$$

2. $2H^+ + 2e^- = H_2$
Water is in equilibrium with gaseous hydrogen.

$$E_e = - 0.0591pH$$

* others may be possible if the water contains oxidating species such as CrO_4^{2-}, NO^{3-}, etc

Step 3 :



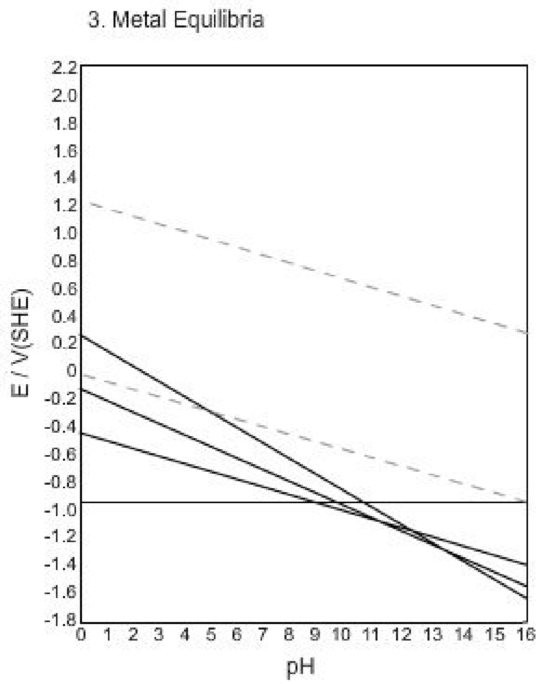
Above the line the oxidised species is stable, below the line it can be reduced if a suitable anode is available.

The lines representing these reactions have the same positions on all Pourbaix Diagrams.

1. $O_2 + 4H^+ + 4e^- = 2H_2O$

2. $2H^+ + 2e^- = H_2$

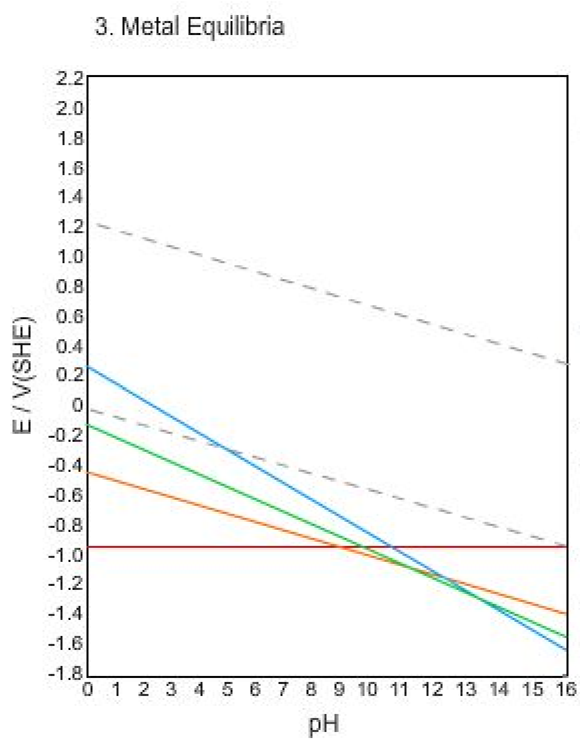
Step 4 :



Zinc can oxidise in four different ways. The four stable oxidation products are Zn^{2+}, $Zn(OH)_2$, $HZnO_2^-$ and ZnO_2^{2-}.

Appropriate Nernst equations are written for each of these (at an arbitrarily chosen concentration of 10^{-6} mol dm^{-3}) in equilibrium with solid zinc.

Step 5:



1. $Zn^{2+} + 2e^- = Zn$

$E_e = -0.763 + 0.0295 \log [Zn^{2+}]$

2. $Zn(OH)_2 + 2H^+ + 2e^- = Zn + 2H_2O$

$E_e = -0.439 - 0.0591\ pH$

3. $HZnO_2^- + 3H^+ + 2e^- = Zn + 2H_2O$

$E_e = 0.054 - 0.0886\ pH + 0.0295 \log [HZnO_2^-]$

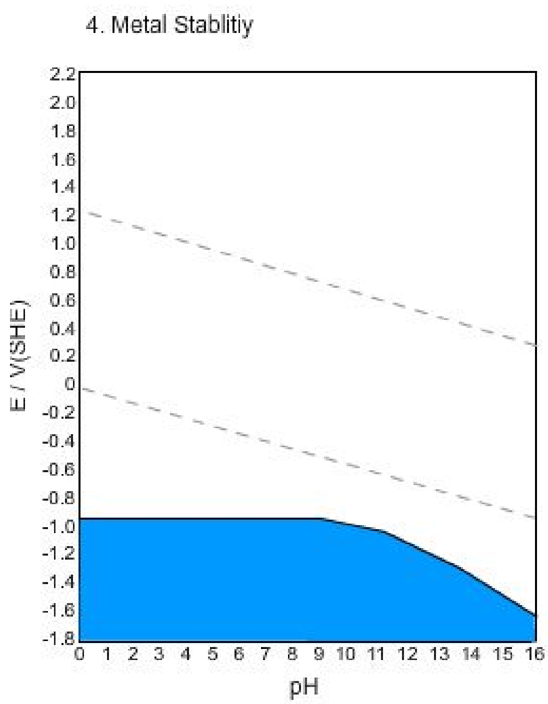
4. $ZnO_2^{2-} + 4H+ + 2e- = Zn + 2H_2O$

$E_e = 0.441 – 0.1182\ pH + 0.0295 \log [ZnO_2^{2-}]$

The Nernst equation for reaction 1 shows that it is independent of pH, it is therefore horizontal when plotted.

The other reactions all vary linearly with pH, so they are plotted as straight lines with negative gradients.

Step 6:



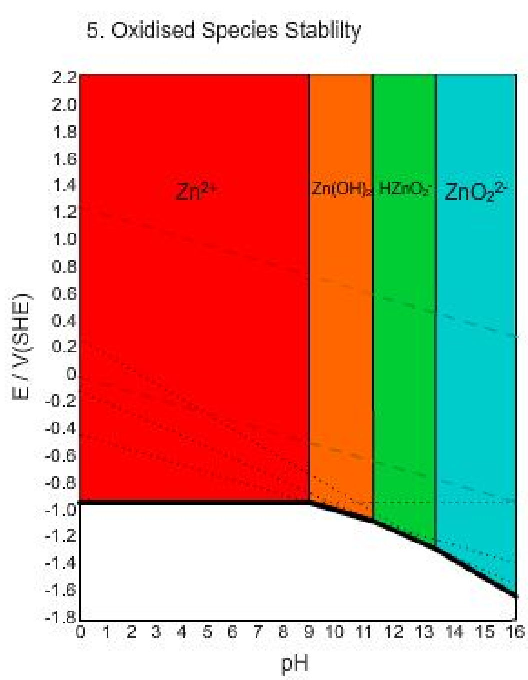
Above an anodic line the oxidised product is stable.

Below an anodic equilibrium line solid zinc is stable relative to the oxidised product.

Therefore if zinc is in conditions that correspond to a position on the Pourbaix diagram that is below* all the anodic reaction equilibrium lines the zinc is said to be **immune** to corrosion: it cannot be dissolved.

*However, a piece of zinc in water cannot lie in this region without an externally applied potential because there is no anodic reaction.

Step 7 :

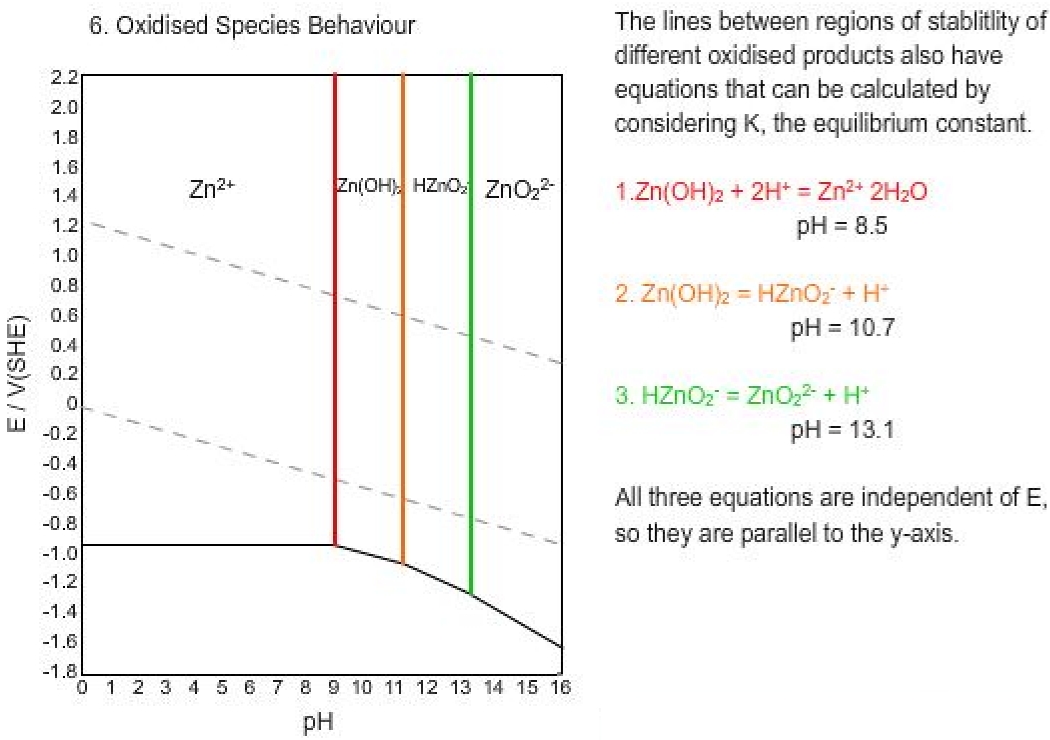


Above an anodic line the oxidised product is stable.

If zinc is under conditions that correspond to a position above more than one anodic line the oxidised product stable at the lowest E_e is the one present.

The Pourbaix diagram can be divided into four regions, corresponding to different oxidation products being stable.

Step 8:



Source : http://www.doitpoms.ac.uk/tlplib/pourbaix/pourbaix_construction.php