

Reduction and Oxidation Potentials

The Standard Electrode Potentials Series.

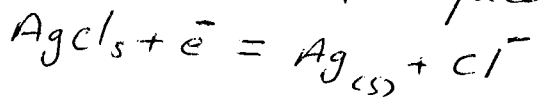
We have seen ~~three~~ ^{four} types of electrode reaction:

1- The reduction of a metal ion to cause it to discharge at an electrode ; $M^{z+} + z e^- = M$

2- The reduction of the ions of an element to form the gaseous element at an ~~inert~~ inert electrode



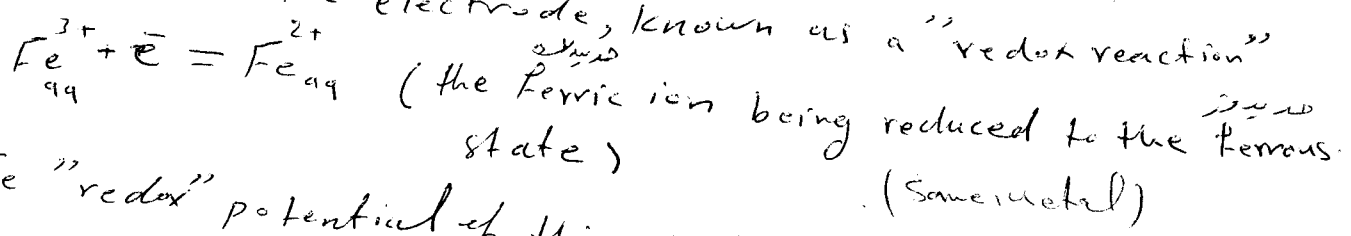
3- The reaction involving a metal, a sparingly soluble salt of the metal and the aqueous solution of the anions of the salt.



All these reactions are reduction reactions; as the species on the left-hand side of the equations are in the "oxidized state" and those on the right-hand side are in the "reduced state"

4- A fourth type of reaction can occur at an electrode, the reduction of an ionic species which remains in the electrolyte while the metal of the electrode remains inert.

The reaction at the electrode, known as a "redox reaction"



⊕ The "redox" potential of this electrode is given by the Nernst equation

$$E = E^{\circ} + \frac{RT}{F} \ln \frac{a_{Fe^{3+}}}{a_{Fe^{2+}}}$$

which can be generalized as:

$$E = E^{\circ} + \frac{RT}{zF} \ln \left[\frac{\text{activity of reacting species in oxidized state}}{\text{activity of reacting species in reduced state}} \right]$$

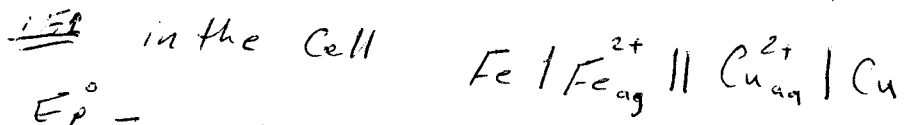
Asst. A "Standard Electrode potential Series"

Electrochemical Series, The value of E_H° against which these potentials are measured, is shown for reference.

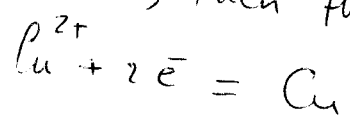
Metal	Electrode reaction	E_M° at 25°C (V)
Au	$Au^{2+} + 2e^- = Au$	+1.43
Hg	$Hg^+ + e^- = Hg$	+0.80
Cu	$Cu^{2+} + 2e^- = Cu$	+0.34
H	$H^+ + e^- = \frac{1}{2} H_2$	0
Pb	$Pb^{2+} + 2e^- = Pb$	-0.13
Sn	$Sn^{2+} + 2e^- = Sn$	-0.14
Ni	$Ni^{2+} + 2e^- = Ni$	-0.25
Fe	$Fe^{2+} + 2e^- = Fe$	-0.44

* Metals with large positive standard Electrode potentials show very little tendency to dissolve in water - and are known as "noble metals"

* Base metals have tendency to dissolve in water or "Corrode" shown by their negative standard Electrode potentials "active metals".



$E_{Fe}^\circ = -0.44V$ and $E_{Cu}^\circ = 0.34$ at 25°C. If Iron and Copper connected by an electronic conductor, were immersed in standard electrolytes in this cell, then the Copper would act as the cathode

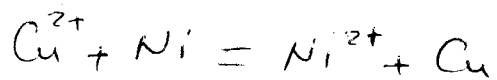


Iron as the anode $Fe = Fe^{2+} + 2e^-$; The result would be a tendency for the iron to dissolve in the electrolyte, and this process is known

as "galvanic corrosion" of the less noble metal in a system containing two metals. The e.m.f of the Corrosion Cell would be

$$E_{cell}^\circ = E_{Cu}^\circ - E_{Fe}^\circ = 0.34 - (-0.44) = 0.78V.$$

* Copper is more noble than nickel, so that, if an aqueous solution containing Cu^{2+} and Ni^{2+} is passed over nickel powder the nickel powder will tend to dissolve anodically, and copper will plate out.



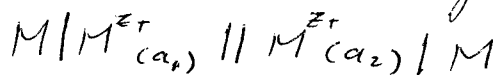
$$E_{\text{cell}}^{\circ} = E_{\text{Cu}}^{\circ} - E_{\text{Ni}}^{\circ} = 0.34 - (-0.25) \\ = 0.59 \text{ V}$$

This process is known as "cementation"

In the same way, Scrap iron can be used to remove Cu^{2+} from aqueous solution and Zinc dust to remove gold from aqueous Cyanide leach solutions.

Concentration Cells

A cell can be constructed of two electrodes of the same metal M dipping into solutions containing ions M^{z+} at different activities a_1 and a_2



The electrode potential of the left-hand electrode, by Nernst equation.

$$E_1 = E_M^{\circ} + \frac{RT}{zF} \ln a_1$$

The electrode potential of the right-hand electrode is

$$E_2 = E_M^{\circ} + \frac{RT}{zF} \ln a_2$$

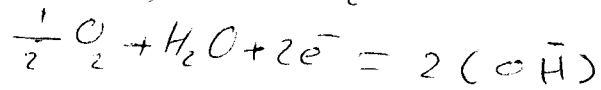
$$E_{\text{cell}} = E_2 - E_1$$

$$= \frac{RT}{zF} \ln \frac{a_2}{a_1}$$

and this depends only on the difference in activities of M^{z+} between the two electrolytes.

*)

The "oxygen electrode" $M|O_{2(aq)}$, a metal in contact with aerated water, has an electrode reaction



This is an important reaction, as it tends to be the cathode reaction in Corrosion Cells set up in aerated aqueous solutions.

The Electrode potential for this electrode is

$$E_{O_2} = E_{O_2}^0 + \frac{RT}{ZF} \ln \left[\frac{P_{O_2}^{1/2}}{a_{(OH^-)}^2} \right]$$

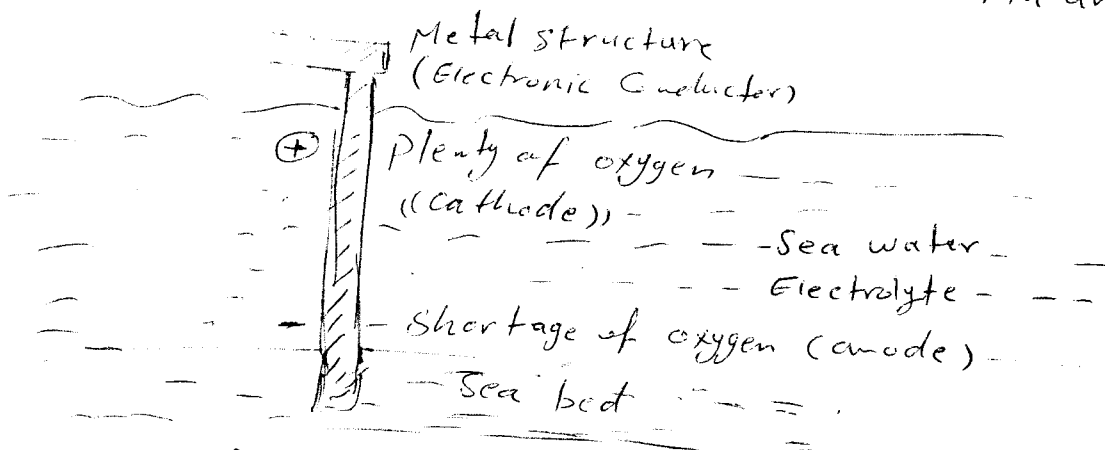
assuming that in aqueous solution $a_{H_2O} = 1$. We can now set up a cell $M|O_{2(aq)}(P_{O_2}^A) || O_{2(aq)}(P_{O_2}^B)|M$, whose e.m.f depends on the relationship

$$E_{cell} = \frac{RT}{ZF} \ln \left(\frac{P_{O_2}^B}{P_{O_2}^A} \right)^{1/2}$$

* IF $P_{O_2}^A$ is less than $P_{O_2}^B$, A will be the anode, B the cathode in the Concentration Cell.

* This is the basis of Corrosion due to differential aeration.

Ex Metal structure may be immersed in large depth of water. The regions close to the surface will be in contact with water of higher oxygen content than those at great depth, and the oxygen-starved metal at great depth will corrode anodically. (The concentration cell will be altered immediately if the metal is iron, because the iron in the anodic region will dissolve whereas the metal in the cathodic region becomes coated with an oxide layer).



Differential aeration causing a Concentration Cell to be set up where a metal structure is partly immersed in large depth of water.