

OXIDATION-REDUCTION AND ELECTROCHEMISTRY

1. Definitions:

oxidation - loss of electrons

reduction - gain of electrons

oxidizing agent or *oxidant* - is the substance being reduced

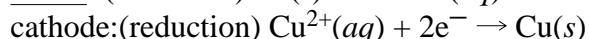
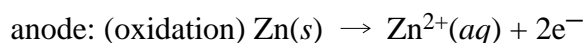
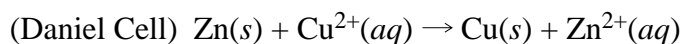
reducing agent or *reductant* - is the substance being oxidized

2. Balancing Redox equations:

a. In acidic solution (H^+ and H_2O are added) **SEE LECTURE NOTES OR TEXT**

b. In basic solution (OH^- and H_2O are added) **SEE LECTURE NOTES OR TEXT**

3. Voltaic cells - convert chemical energy into electrical energy.



Cell representation: $\ominus Zn(s)|Zn^{2+}(1M)||Cu^{2+}(1M)|Cu(s) \oplus$

Standard EMF - at $25^\circ C$; all reactants and products in their standard states (i.e. solids or liquids as a pure substance; gas and solutions at *ideal unit activity* ($a = \gamma c = 1$)).
HOWEVER IN ALL OF OUR CALCULATIONS AT THE FIRST YEAR LEVEL WE SHALL USE FOR A GAS a pressure of 1 atm and for a SOLUTION a concentration of 1 M.

4. Electrode potentials - values are assigned to half-reactions using the standard hydrogen electrode as the reference. This half-reaction is given the value of $\epsilon^\circ = 0.00$ volts and therefore all electrode potentials are on a relative scale and **not** an absolute scale.



Therefore from this series we can make the following statements:

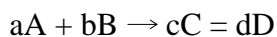
$Li^+(aq)$ is the weakest oxidizing agent

$Li(s)$ is the strongest reducing agent

$F_2(g)$ is the strongest oxidizing agent

$F^-(aq)$ is the weakest reducing agent

5. Nernst equation - used when concentrations are not at standard conditions.



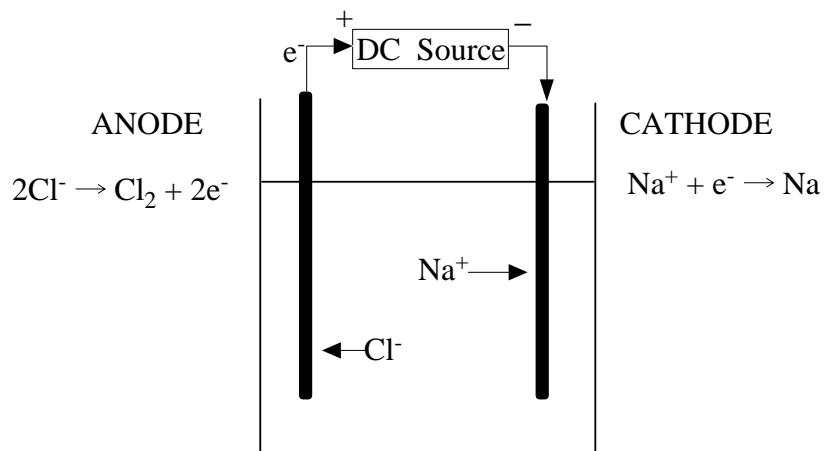
$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$\epsilon = \epsilon^\circ - \frac{0.05916}{n} \log Q \quad (\text{at } 25^\circ C)$$

where n is the number of electrons transferred in the reaction.

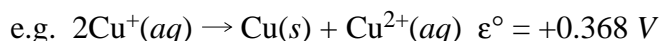
NOTE: If all substances are in their standard states $Q = 1$ and therefore $\epsilon = \epsilon^\circ$.

6. Electrolytic cells - use electric current to bring about chemical changes.



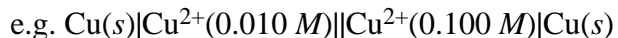
Electrolysis of molten sodium chloride

7. Disproportionation - an oxidation reduction reaction in which the same chemical species is both oxidized and reduced.



Therefore $\text{Cu}^+(\text{aq})$ disproportionates to $\text{Cu}(\text{s})$ and $\text{Cu}^{2+}(\text{aq})$.

8. Concentration cell - a voltaic cell constructed from two-half-cells that are composed of the same substances but that differ in the concentration of the ions.



$$\varepsilon = 0.00 - \frac{0.05916}{2} \log (0.010/0.100) = + 0.030 \text{ V}$$

9. Corrosion
- Passivation.
 - Protective films of Zn or Sn on iron.
 - Cathodic protection.
10. Commercial cells
- Dry cell.
 - Mercury battery.
 - Lead-storage cell.
 - Ni-Cd storage cell.
11. Fuel cells