Fundamental of Electrochemistry
Redox reaction

- **Redox** = reduction and oxidation
  - The reaction involves electron transfer from one reactant to another – the oxidation state of the elements has to be changed.

- **Cu^{2+} + Zn → Cu + Zn^{2+}**
  - Cu^{2+} gaining two electrons is oxidizing agent, being reduced.
  - Zn losing two electrons is reducing agent, being oxidized.

- **Faraday constant:**
  - The unit of electric charge is coulombs (C).
  - One electron has 1.602 x 10^{-19} C
  - One mole of electron has 96500 C of charge
    \[ F = 96500 \text{C/mol} \]
Chemistry and electricity

- \( \text{Cu}^{2+} + \text{Zn} \rightarrow \text{Cu} + \text{Zn}^{2+} \)
  - If \( \text{Cu}^{2+} \) is mixed with \( \text{Zn} \), the electron will be transferred and chemical energy will become heat. \( \Delta G = \Delta H - T \Delta S < 0 \).
  - If the reaction is separated into two *Half Reactions*
    - \( \text{Cu}^{2+} + 2e^{-} \rightarrow \text{Cu} \)
    - \( \text{Zn} \rightarrow \text{Zn}^{2+} + 2e^{-} \)
    - Electrons flow from \( \text{Zn} \) electrode to \( \text{Cu} \) electrode
      - Current (?) flows from \( \text{Cu} \) to \( \text{Zn} \)
      - \( \text{Cu} \) is positive electrode
      - \( \text{Zn} \) is negative electrode
The driving force of electron flow

- Second Law of thermodynamic: For spontaneous reaction, $\Delta G<0$.
- $\text{Cu}^{2+} + 2e^{-} \rightarrow \text{Cu} \quad \Delta G_1$
- $\text{Zn}^{2+} + 2e^{-} \rightarrow \text{Zn} \quad \Delta G_2$
  \[ \Delta G = \Delta G_1 - \Delta G_2 < 0 \]
- $\Delta G = -\text{work}$
  so the electron flow from Zn to Cu through the load e.g. a radio to do the work, instead of generating heat.
Redox reactions

• Redox reaction always happen in couple of oxidation and reduction and can not happen alone.

• For example the reaction can not happen:

Electrons can not be created.
Electric current

- Current is resulted from the movement of the charged species e.g. electron or ions in the solution.
- The direction of electric current is the direction of the movement of positive charges.
- Current flows from high potential to low potential, while electron flow from low potential to high potential.
- The unit of current is Ampere (A): the quantity of charge flowing each second through a circuit.
  \[ 1 \text{ A} = 1\text{C/s} \]
Terminologies

- **Redox** (short for Oxidation/Reduction) reactions:
  - electrons, ne-, are transferred between reactants
  - A substance which loses electrons is **oxidized**, the substance is **reductant**. A reductant (reducing agent) is a substance causing **reduction**.
  - A substance which gains electrons is **reduced**, the substance is **oxidant**. An oxidant (oxidizing agent) is a substance causing **oxidation**.
- Reactions involving oxidation of A to B and reduction of C to D:
  - \( aA + cC \leftrightarrow bB + dD \)
  - Separated into two **half-reactions** with equal but opposite e-transfer:
    - \( aA + ne- \rightarrow bB \) (cathode)
    - and \( cC - ne- \rightarrow dD \) (anode)
Chemistry and electricity

- \( \text{Cu}^{2+} + \text{Zn} \rightarrow \text{Cu} + \text{Zn}^{2+} \)
  - If \( \text{Cu}^{2+} \) is mixed with \( \text{Zn} \), the electron will transferred and chemical energy will become heat. \( \Delta G = \Delta H - T \Delta S < 0 \).
  - If the reaction is separated in two **Half Reactions**
    - \( \text{Cu}^{2+} + 2e^- \rightarrow \text{Cu} \)
    - \( \text{Zn} \rightarrow \text{Zn}^{2+} + 2e^- \)
  - Electrons flow from \( \text{Zn} \) electrode to \( \text{Cu} \) electrode
  - Current flows from \( \text{Cu} \) to \( \text{Zn} \)
  - \( \text{Cu} \) is positive electrode
  - \( \text{Zn} \) is negative electrode
Electrochemical Potential

- Electrode potentials express the driving force for oxidation or reduction
  - A negative electrode potential describes a material easier to oxidize compared to chemical species with a more positive potential
  - A positive electrode potential describes a material easier to reduce.
- This is given by electromotive force or potential, “E” with units of volts
- Electrochemical potential express the possibility of the redox reaction, but does not express the kinetic of the reaction!
Electrode potential

- Redox reaction energy creates measurable electrochemical potential determined by the thermodynamics & related equilibria of the reaction.
- Requires complete circuit to compare the voltage between electrodes.
- Can not measure the voltage of half a cell, requires 2 electrodes.
- Placed in an electrolytic medium. For ex., voltmeter reads 0.46 V in: Cu | CuSO4(0.1 M) | AgSO4(0.1 M) | Ag
Electric potential

- Moving charges from one potential to another needs to do work:
  \[ \text{Work} = \text{Potential difference} \times \text{charge} \]

- \( \Delta G = -\text{work} = -\text{Potential difference} \times \text{charge} \)

Relationship between free energy and potential difference.

- Units: potential (E): Volt (V)
  work (W): Joule = one coulomb of charge moves between the points of 1 Volt

\[ \Delta G = -nFE \]
Terminologies

• Resistance:
  – Ohm’s law: \( R = \frac{E}{I} \)

• Power: work done in the unit time
  – \( P = \frac{\text{work}}{s} = \frac{Eq}{s} = E \times \frac{q}{s} \)
  – Unit Watt (W)
Critical Relationships

• Charge and moles
  – \( Q \ (C) = n \ (\text{moles}) \times F \) (Faraday constant 96500)

• Work and voltage
  – Work (J) = E (V) \times Q \ (C)

• Free energy and potential
  – \( \Delta G \ (J) = -n(\text{mole}) \times F \ (96500\text{C/mol}) \times E \ (V) \)

• Ohm’s law
  – \( I \ (A) = E \ (V) / R \ (\text{ohm}) \)

• Power
  – \( P \ (\text{watt}) = \text{work} \ (J) / S = E \ (V) \times I \ (A) \)
Galvanic Cells

- Converting chemical energy into electric energy by using spontaneous chemical reaction.
- Reduction - cathode:
  \[ 2\text{AgCl (s)} + 2e \rightleftharpoons 2\text{Ag (s)} + 2\text{Cl}^- (aq) \]
- Oxidation - Anode:
  \[ \text{Cd (s)} \rightleftharpoons \text{Cd}^{2+} (aq) + 2e \]
- Total reaction:
  \[ \text{Cd (s)} + 2\text{AgCl} \rightleftharpoons \text{Cd}^{2+} (aq) + 2\text{Ag (s)} + 2\text{Cl}^- (aq) \]
Separation of Redox Reactions

Cathode: $2\text{Ag}^+(aq) + 2e \rightleftharpoons 2\text{Ag}(s)$

Anode: $\text{Cd} (s) \rightleftharpoons \text{Cd}^{2+} (aq) + 2e$

Total: $\text{Cd} (s) + 2\text{Ag}^+(aq) \rightleftharpoons \text{Cd}^{2+}(aq) + 2\text{Ag}(s)$
Salt Bridge

• Electronic conductivity Vs ionic conductivity
  – Electronic conductivity: movement of electrons
  – Ionic conductivity: movement of ions
  – Both are under potential difference or in the electric field.

• Salt bridge: connecting two half reactions with ionic conductive salt
Notation of electrochemical reactions

- | phase boundary; || salt bridge (two phases)
- \( \text{Cd (s)} | \text{CdCl}_2(aq) | \text{AgCl (s)} | \text{Ag(s)} \)
- \( \text{Cd(s)} | \text{Cd(NO}_3)_2(aq) || \text{AgNO}_3(aq) | \text{Ag(s)} \)

How about without salt bridge?
Standard Electrode Potentials

- Standard electrode potential, "E°", when each of the chemical species participating in a redox process are at standard state and unit activity
  - No absolute point of reference about for an electrode potential scale
  - One half-cell has been arbitrarily defined as E ≡ 0.0000 volt. Reference is a hydrogen-platinum half-cell containing unit activities, called the "Standard Hydrogen Electrode"
  - All other electrode or rest potentials are reported compared to SHE
Standard Potential

- "Standard Hydrogen Electrode": Pt, H2 (pressure = 1 atm) | H+ (activity = 1) (the "SHE" or Normal Hydrogen Potential “NHE”) SHE describes:
  \[2\text{H}^+ (\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2 (\text{gas})\]
  \[E^\circ = 0 \text{ V}\]

- All other electrode or rest potentials are reported compared to SHE

  e.g.

  \[\text{Ag}^+ + \text{e} \rightarrow \text{Ag} \quad E^\circ = 0.799 \text{ V}\]
# Oxidation/reduction power

## Table 14-1: Ordered redox potentials

<table>
<thead>
<tr>
<th>Oxidizing agent</th>
<th>Reducing agent</th>
<th>$E^\circ$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_2(g) + 2e^- \rightleftharpoons 2F^-$</td>
<td></td>
<td>2.890</td>
</tr>
<tr>
<td>$O_3(g) + 2H^+ + 2e^- \rightleftharpoons O_2(g) + H_2O$</td>
<td></td>
<td>2.075</td>
</tr>
<tr>
<td>$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$</td>
<td></td>
<td>1.507</td>
</tr>
<tr>
<td>$Ag^+ + e^- \rightleftharpoons Ag(s)$</td>
<td></td>
<td>0.799</td>
</tr>
<tr>
<td>$Cu^{2+} + 2e^- \rightleftharpoons Cu(s)$</td>
<td></td>
<td>0.339</td>
</tr>
<tr>
<td>$2H^+ + 2e^- \rightleftharpoons H_2(g)$</td>
<td></td>
<td>0.000</td>
</tr>
<tr>
<td>$Cd^{2+} + 2e^- \rightleftharpoons Cd(s)$</td>
<td></td>
<td>-0.402</td>
</tr>
<tr>
<td>$K^+ + e^- \rightleftharpoons K(s)$</td>
<td></td>
<td>-2.936</td>
</tr>
<tr>
<td>$Li^+ + e^- \rightleftharpoons Li(s)$</td>
<td></td>
<td>-3.040</td>
</tr>
</tbody>
</table>

Oxidizing power increases from top to bottom, reducing power increases from left to right.

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Properties of Umass Boston