Determination of Electrode Potentials

- Electrode potentials can be determined by measurements versus the standard H-electrode or other electrodes with known potentials

Example: E^o_{cell} = **+0.46 V** for the reaction:

$$\mathbf{Cu(s) + 2Ag^+ \rightarrow Cu^{2+} + 2Ag(s)}$$

If E^o = **+0.34 V** for the Cu^{2+}/Cu redox couple, what is E^o for the Ag^+/Ag redox couple?

→ Split into half-reactions:

$\mathbf{Cu(s) \rightarrow Cu^{2+} + 2e^-}$ $\quad E^o_{Cu} = +0.34$ V (anode, ox)

$\mathbf{Ag^+ + e^- \rightarrow Ag(s)}$ $\quad E^o_{Ag} = ???$ V (cathode, red)

$E^o_{cell} = E^o_{Ag} - E^o_{Cu} = E^o_{Ag} - (+0.34) = +0.46$

$\Rightarrow E^o_{Ag} = +0.46 + (+0.34) =$ **+0.80 V**

Using Cell Potentials in Calculations

- Cell potentials are **additive**
  - If two reactions are added, their potentials are added too
- Cell potentials are **intensive properties** – remain independent of the system size
  - If a reaction (or a half-reaction) is multiplied by a number, its potential remains the same

Example:

$\mathbf{Cu(s) + 2Ag^+ \rightarrow Cu^{2+} + 2Ag(s)}$ $(\times 3)$ $\quad E^o_{cell} = +0.46$ V

$\mathbf{3Ag(s) + Au^{3+} \rightarrow 3Ag^+ + Au(s)}$ $(\times 2)$ $\quad E^o_{cell} = +0.70$ V

$\mathbf{3Cu(s) + 2Au^{3+} \rightarrow 3Cu^{2+} + 2Au(s)}$

$E^o_{cell} = +0.46 + 0.70 = \mathbf{+1.16\ V}$

Strengths of Oxidizing and Reducing Agents

- E^o values are always tabulated for **reduction**

$$\mathbf{Ox + ne^- \rightarrow Red} \qquad (E^o)$$

  - **Ox** is an oxidizing agent; **Red** is a reducing agent
- E^o is a measure for the tendency of the half-reaction to undergo reduction

⇒**Higher** (more positive) E^o means
  - Greater tendency for reduction
  - Lower tendency for oxidation

⇒**Higher** (more positive) E^o means
  - **Stronger oxidizing agent (Ox)** ← Ox is reduced
  - **Weaker reducing agent (Red)** ← Red is oxidized

- **Electrochemical series** – an arrangement of the redox couples in order of decreasing reduction potentials (E^o) → Appendix D
  - The most positive E^os are at the top of the table
  - The most negative E^os are at the bottom of the table

⇒The **strongest oxidizing agents** (Ox) are **at the top** of the table **as reactants**

⇒The **strongest reducing agents** (Red) are **at the bottom** of the table **as products**

- Every redox reaction is a sum of two half-reactions, one occurring as oxidation and another as reduction

$$\mathbf{Red_1 \rightarrow Ox_1 + ne^-} \qquad \mathbf{Ox_2 + ne^- \rightarrow Red_2}$$

$$\mathbf{Red_1 + Ox_2 \rightarrow Ox_1 + Red_2}$$

- In a **spontaneous redox reaction**, the stronger oxidizing and reducing agents react to produce the weaker oxidizing and reducing agents

Stronger Red_1 + Stronger Ox_2 → Weaker Ox_1 + Weaker Red_2

Example: Given the following half-reactions:

Appendix D

$\mathbf{Cl_2(g) + 2e^- \rightarrow 2Cl^-}$	$E^o = +1.36$ V
$\mathbf{O_2(g) + 4H^+ + 4e^- \rightarrow 2H_2O(l)}$	$E^o = +1.23$ V
$\mathbf{Fe^{3+} + e^- \rightarrow Fe^{2+}}$	$E^o = +0.77$ V
$\mathbf{Fe^{2+} + 2e^- \rightarrow Fe(s)}$	$E^o = -0.44$ V

a) Rank the oxidizing and reducing agents by strength

→ Ox agents on the left; Red agents on the right

Oxidizing → (Top) $\mathbf{Cl_2 > O_2 > Fe^{3+} > Fe^{2+}}$ (Bottom)

Reducing → (Bottom) $\mathbf{Fe > Fe^{2+} > H_2O > Cl^-}$ (Top)

b) Can $\mathbf{Cl_2}$ oxidize $\mathbf{H_2O}$ to $\mathbf{O_2}$ in acidic solution?

→ $\mathbf{Cl_2/Cl^-}$ has higher E^o (Cl_2/Cl^- is above O_2,H^+/H_2O)

⇒ $\mathbf{Cl_2}$ is a stronger oxidizing agent than $\mathbf{O_2}$

⇒ $\mathbf{Cl_2}$ can oxidize $\mathbf{H_2O}$ to $\mathbf{O_2}$ at standard conditions

c) Write the spontaneous reaction between the $\mathbf{Cl_2/Cl^-}$ and $\mathbf{Fe^{3+}/Fe^{2+}}$ redox couples and calculate its E^o_{cell}

→ $\mathbf{Cl_2/Cl^-}$ has the higher reduction potential (E^o)

⇒ $\mathbf{Cl_2/Cl^-}$ undergoes **reduction**

⇒ $\mathbf{Fe^{3+}/Fe^{2+}}$ undergoes **oxidation** (reverse equation)

$\mathbf{Cl_2(g) + 2e^- \rightarrow 2Cl^-}$ (reduction) $E^o = +1.36$ V

$\mathbf{Fe^{2+} \rightarrow Fe^{3+} + e^-}$ ×2 (oxidation) $E^o = +0.77$ V

$\mathbf{Cl_2(g) + \cancel{2e^-} + 2Fe^{2+} \rightarrow 2Cl^- + 2Fe^{3+} + \cancel{2e^-}}$

$E^o_{cell} = E^o_{cath} - E^o_{anod} = +1.36 - (+0.77) = \mathbf{+0.59\ V}$

d) Is the reaction of disproportionation (simultaneous oxidation and reduction) of $\mathbf{Fe^{2+}}$ to $\mathbf{Fe^{3+}}$ and $\mathbf{Fe(s)}$ spontaneous at standard conditions?

→ Need the sign of E^o_{cell}

⇒ $\mathbf{Fe^{2+}/Fe(s)}$ undergoes **reduction**

⇒ $\mathbf{Fe^{3+}/Fe^{2+}}$ undergoes **oxidation** (reverse equation)

$\mathbf{Fe^{2+} + 2e^- \rightarrow Fe(s)}$ (reduction) $E^o = -0.44$ V

$\mathbf{Fe^{2+} \rightarrow Fe^{3+} + e^-}$ ×2 (oxidation) $E^o = +0.77$ V

$\mathbf{3Fe^{2+} + \cancel{2e^-} \rightarrow Fe(s) + 2Fe^{3+} + \cancel{2e^-}}$

$E^o_{cell} = E^o_{cath} - E^o_{anod} = -0.44 - (+0.77) = \mathbf{-1.21\ V}$

⇒ $E^o_{cell} < 0$ → the reaction is **non-spontaneous** at standard conditions

Relative Reactivity of Metals

- The **activity series** of metals – ranks metals based on their ability to displace H_2 from acids or water or displace each other's ions in solution
- **Metals that can displace H_2 from acids**
  - The reduction of H^+ from acids to H_2 is given by the standard hydrogen half-reaction

$$\mathbf{2H^+ + 2e^- \rightarrow H_2(g)} \qquad E^o = \mathbf{0\ V}$$

  - In order for this half-reaction to proceed as written, the metal must have lower reduction potential (**the metal must be below H_2/H^+** in Appendix D)

⇒ If $E^o_{metal} < 0$, the metal **can** displace H_2 from acids

⇒ If $E^o_{metal} > 0$, the metal **cannot** displace H_2

Example: Can **Fe** and **Cu** be dissolved in HCl(aq)?

→ $\mathbf{Fe^{2+}/Fe}$ is below and $\mathbf{Cu^{2+}/Cu}$ is above $\mathbf{H_2/H^+}$

$$\oplus \begin{array}{lll} \mathbf{2H^+ + 2e^- \rightarrow H_2(g)} & \text{(reduction)} & E^o = 0.00\ \text{V} \\ \mathbf{Fe(s) \rightarrow Fe^{2+} + 2e^-} & \text{(oxidation)} & E^o = -0.44\ \text{V} \end{array}$$

$$\mathbf{2H^+ + \cancel{2e^-} + Fe(s) \rightarrow H_2(g) + Fe^{2+} + \cancel{2e^-}}$$

$$E^o_{cell} = E^o_{cath} - E^o_{anod} = 0.00 - (-0.44) = \mathbf{+0.44\ V}$$

$\Rightarrow E^o_{cell} > 0 \rightarrow$ spontaneous (Fe dissolves in HCl)

$$\oplus \begin{array}{lll} \mathbf{2H^+ + 2e^- \rightarrow H_2(g)} & \text{(reduction)} & E^o = 0.00\ \text{V} \\ \mathbf{Cu(s) \rightarrow Cu^{2+} + 2e^-} & \text{(oxidation)} & E^o = +0.34\ \text{V} \end{array}$$

$$\mathbf{2H^+ + \cancel{2e^-} + Cu(s) \rightarrow H_2(g) + Cu^{2+} + \cancel{2e^-}}$$

$$E^o_{cell} = E^o_{cath} - E^o_{anod} = 0.00 - (+0.34) = \mathbf{-0.34\ V}$$

$\Rightarrow E^o_{cell} < 0 \rightarrow$ non-spontaneous (Cu doesn't dissolve)

- **Metals that can displace $\mathbf{H_2}$ from water**
  - The reduction of H_2O to H_2 is given by:

$$\mathbf{2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-} \qquad E = \mathbf{-0.42\ V}$$

  - The value of E is for $pH = 7$ (nonstandard state)

$\Rightarrow$ Metals that are **below** $\mathbf{H_2O/H_2,OH^-}$ in Appendix D can displace H_2 from water at standard conditions

$\Rightarrow$ Metals that have $E^o_{metal} < \mathbf{-0.42}$ can displace H_2 from water at $pH = 7$

Example: Potassium, **K**, dissolves readily in water

$$\begin{array}{llll} \mathbf{2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-} & & \text{(reduction)} & E = -0.42\ \text{V} \\ \mathbf{K(s) \rightarrow K^+ + e^-} & \times 2 & \text{(oxidation)} & E^o = -2.93\ \text{V} \end{array}$$

$$\mathbf{2H_2O(l) + \cancel{2e^-} + 2K(s) \rightarrow H_2(g) + 2OH^- + 2K^+ + \cancel{2e^-}}$$

$$E^o_{cell} = -0.42 - (-2.93) = \mathbf{+2.51\ V > 0\ (spontaneous)}$$