

Balancing redox reactions by half-reaction method: in acid



1) Write the oxidation half reaction

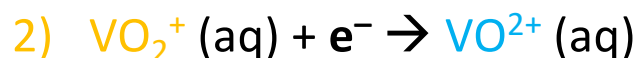
2) Write the reduction half reaction

3) Balance all elements except H/O

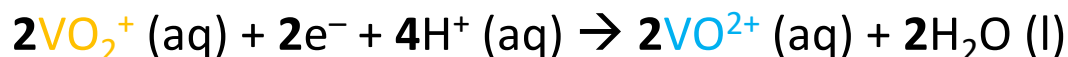
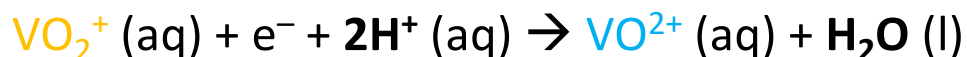
4) Balance **H/O with H⁺/H₂O**

5) Multiply (least common multiple) to make # of electrons same in both half reactions

6) Combine half reactions, check that both mass and charge are balanced



3) Here, Zn and V are already balanced



Balancing redox reaction in base

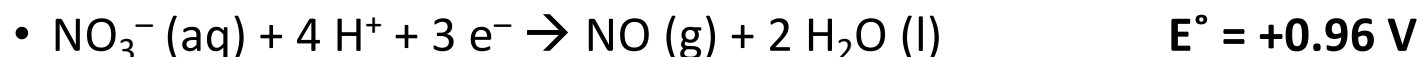
- $$\overset{0}{\text{Al}} (\text{s}) + \overset{+1}{\text{H}_2\text{O}} (\text{l}) \rightarrow [\overset{+3}{\text{Al}}(\text{OH})_4]^- (\text{aq}) + \overset{0}{\text{H}_2} (\text{g})$$
- Oxidation
 - $\text{Al} (\text{s}) \rightarrow [\text{Al}(\text{OH})_4]^- (\text{aq}) + 3 \text{e}^-$
 - $\text{Al} (\text{s}) + 4 \text{H}_2\text{O} (\text{l}) \rightarrow [\text{Al}(\text{OH})_4]^- (\text{aq}) + 4 \text{H}^+ (\text{aq}) + 3 \text{e}^-$
- Reduction
 - $\text{H}_2\text{O} (\text{l}) + 2 \text{e}^- \rightarrow \text{H}_2 (\text{g})$
 - $\text{H}_2\text{O} (\text{l}) + 2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{H}_2 (\text{g}) + \text{H}_2\text{O} (\text{l})$
- LCM: 6
 - $2 \text{Al} (\text{s}) + 8 \text{H}_2\text{O} (\text{l}) \rightarrow 2 [\text{Al}(\text{OH})_4]^- (\text{aq}) + 8 \text{H}^+ (\text{aq}) + 6 \text{e}^-$
 - $3 \text{H}_2\text{O} (\text{l}) + 6 \text{H}^+ + 6 \text{e}^- \rightarrow 3 \text{H}_2 (\text{g}) + 3 \text{H}_2\text{O} (\text{l})$
- Combine
 - $2 \text{Al} (\text{s}) + 8 \text{H}_2\text{O} (\text{l}) \rightarrow 2 [\text{Al}(\text{OH})_4]^- (\text{aq}) + 2 \text{H}^+ (\text{aq}) + 3 \text{H}_2 (\text{g})$
- Neutralize H^+ with OH^-
 - $2 \text{Al} (\text{s}) + 8 \text{H}_2\text{O} (\text{l}) + 2 \text{OH}^- (\text{aq}) \rightarrow 2 [\text{Al}(\text{OH})_4]^- (\text{aq}) + 2 \text{H}_2\text{O} (\text{l}) + 3 \text{H}_2 (\text{g})$
 - $2 \text{Al} (\text{s}) + 6 \text{H}_2\text{O} (\text{l}) + 2 \text{OH}^- (\text{aq}) \rightarrow 2 [\text{Al}(\text{OH})_4]^- (\text{aq}) + 3 \text{H}_2 (\text{g})$

Sample problem

Using standard reduction potentials, calculate the E°_{cell} for the reaction



- N is reduced



- Cu is oxidized



- So for oxidation



- $E^\circ_{\text{cell}} = +0.96 \text{ V} - 0.337 \text{ V} = 0.62 \text{ V}$

Sample problem

Rank the halogens in order of their strength as oxidizing agents

- $\text{F}_2 (\text{g}) + 2 \text{e}^- \rightarrow 2 \text{F}^- (\text{aq})$ $E^\circ = +2.87 \text{ V}$
- $\text{Cl}_2 (\text{g}) + 2 \text{e}^- \rightarrow 2 \text{Cl}^- (\text{aq})$ $E^\circ = +1.36 \text{ V}$
- $\text{Br}_2 (\text{l}) + 2 \text{e}^- \rightarrow 2 \text{Br}^- (\text{aq})$ $E^\circ = +1.08 \text{ V}$
- $\text{I}_2 (\text{s}) + 2 \text{e}^- \rightarrow 2 \text{I}^- (\text{aq})$ $E^\circ = +0.535 \text{ V}$
- F_2 is most readily reduced, so it is the best oxidizing agent
- I_2 is least readily reduced, so it is the poorest oxidizing agent
- $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$

Sample problem

Decide which of the halogens is capable of oxidizing gold metal to $\text{Au}^{3+}(\text{aq})$

- $\text{Au}^{3+}(\text{aq}) + 3 \text{e}^{-} \rightarrow \text{Au}(\text{s}) \quad E^{\circ} = +1.50 \text{ V}$
- So the **oxidation potential** of Au is **-1.50 V**
- To **oxidize Au**, the halogen will need to get **reduced**. The sum of the **standard reduction potential** of the halogen and the **oxidation potential of Au** needs to be **positive** for the reaction to be **product favored**.
- The only halogen with a high enough E° for this to hold is F_2 ($+2.87 \text{ V}$)
 - $2.87 \text{ V} - 1.50 \text{ V} = 1.37 \text{ V}$

Sample problem

A voltaic cell is set up at 25 °C with the half-cells Al^{3+} (0.0010 M) | Al and Ni^{2+} (0.50 M) | Ni. Write an equation for the reaction that occurs when the cell generates an electric current and determine the cell potential.

- $\text{Al}^{3+} (\text{aq}) + 3 \text{e}^{-} \rightarrow \text{Al} (\text{s}) \quad E^{\circ} = -1.66 \text{ V}$
- $\text{Ni}^{2+} (\text{aq}) + 2 \text{e}^{-} \rightarrow \text{Ni} (\text{s}) \quad E^{\circ} = -0.25 \text{ V}$
- Ni^{2+} is more readily reduced than Al^{3+} (less negative standard reduction potential), so Al must be oxidized to Al^{3+} ($E^{\circ} = +1.66 \text{ V}$)

Sample problem

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- Oxidation HR: $\text{Al (s)} \rightarrow \text{Al}^{3+} \text{ (aq)} + 3 \text{ e}^{-}$
- Reduction HR: $\text{Ni}^{2+} \text{ (aq)} + 2 \text{ e}^{-} \rightarrow \text{Ni (s)}$
- LCM: 6
 - $2 \text{ Al (s)} \rightarrow 2 \text{ Al}^{3+} \text{ (aq)} + 6 \text{ e}^{-}$
 - $3 \text{ Ni}^{2+} \text{ (aq)} + 6 \text{ e}^{-} \rightarrow 3 \text{ Ni (s)}$
- Combine
 - $2 \text{ Al (s)} + 3 \text{ Ni}^{2+} \text{ (aq)} \rightarrow 2 \text{ Al}^{3+} \text{ (aq)} + 3 \text{ Ni (s)}$
 - $Q = \frac{[\text{Al}^{3+}]^2}{[\text{Ni}^{2+}]^3}$

$$E^{\circ}_{\text{cell}} = -0.25 \text{ V} + 1.66 \text{ V} = +1.41 \text{ V}$$

Sample problem

A voltaic cell is set up at 25 °C with the half-cells Al^{3+} (0.0010 M) | Al and Ni^{2+} (0.50 M) | Ni. Write an equation for the reaction that occurs when the cell generates an electric current and determine the cell potential.

$$\begin{aligned} \bullet E &= E^\circ - \frac{0.0257}{n} \ln Q = +1.41 \text{ V} - \frac{0.0257}{6} \ln \frac{[\text{Al}^{3+}]^2}{[\text{Ni}^{2+}]^3} = \\ &+1.41 \text{ V} - \frac{0.0257}{6} \ln \frac{[0.0010 \text{ M}]^2}{[0.50 \text{ M}]^3} = \mathbf{1.46 \text{ V}} \end{aligned}$$

Sample problem

A voltaic cell is set up with copper and hydrogen half-cells. Standard conditions are employed in the copper half-cell, $\text{Cu}^{2+} (\text{aq}, 1.00 \text{ M}) | \text{Cu} (\text{s})$. The hydrogen gas pressure is 1.00 bar and $[\text{H}^+ (\text{aq})]$ in the hydrogen half-cell is unknown. A value of 0.490 V is recorded for E_{cell} at 298 K. Determine the pH of the solution

- $\text{Cu}^{2+} (\text{aq}) + 2 \text{e}^- \rightarrow 2 \text{Cu} (\text{s})$ $E^\circ = +0.337 \text{ V}$
- $2 \text{H}^+ (\text{aq}) + 2 \text{e}^- \rightarrow \text{H}_2 (\text{g})$ $E^\circ = 0.00 \text{ V}$
- Cu^{2+} is reduced and H_2 is oxidized
- $\text{Cu}^{2+} (\text{aq}) + \text{H}_2 (\text{g}) \rightarrow 2 \text{Cu} (\text{s}) + 2 \text{H}^+ (\text{aq})$ $E^\circ_{\text{cell}} = 0.337 \text{ V}$
- $Q = \frac{[\text{H}^+]^2}{[\text{Cu}^{2+}]}$

Sample problem

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$$\begin{aligned} \bullet E &= E^{\circ} - \frac{0.0257}{n} \ln Q \rightarrow 0.490 \text{ V} = 0.337 \text{ V} - \frac{0.0257}{2} \ln Q \rightarrow \\ \ln Q &= -11.9 \rightarrow Q = 6.75 \times 10^{-6} = \frac{[\text{H}^+]^2}{[\text{Cu}^{2+}]} \\ [\text{H}^+]^2 &= 6.75 \times 10^{-6} \\ [\text{H}^+] &= 2.60 \times 10^{-3} \\ \text{pH} &= 2.6 \end{aligned}$$

Sample problem

Predict how products of electrolysis of aqueous solutions of NaF, NaBr and NaI are likely to be different and predict E°_{cell} for each electrolysis.

- Reduction potentials needed:
 - $2 \text{H}_2\text{O} (\text{l}) + 2 \text{e}^- \rightarrow \text{H}_2 (\text{g}) + 2 \text{OH}^- (\text{aq})$ $E^\circ = -0.8277 \text{ V}$
 - $\text{Na}^+ (\text{aq}) + \text{e}^- \rightarrow \text{Na} (\text{s})$ $E^\circ = -2.714 \text{ V}$
- Oxidation potentials needed:
 - $2 \text{H}_2\text{O} (\text{l}) \rightarrow \text{O}_2 (\text{g}) + 2 \text{e}^- + 4 \text{H}^+$ $E^\circ_{\text{ox}} = -1.229 \text{ V}$
 - $2 \text{F}^- (\text{aq}) \rightarrow \text{F}_2 (\text{g}) + 2 \text{e}^-$ $E^\circ_{\text{ox}} = -2.87 \text{ V}$
 - $2 \text{Br}^- (\text{aq}) \rightarrow \text{Br}_2 (\text{l}) + 2 \text{e}^-$ $E^\circ_{\text{ox}} = -1.08 \text{ V}$
 - $2 \text{I}^- (\text{aq}) \rightarrow \text{I}_2 (\text{s}) + 2 \text{e}^-$ $E^\circ_{\text{ox}} = -0.535 \text{ V}$
- For all four electrolyses, the product formed at the cathode is $\text{H}_2 (\text{g})$.
- For electrolysis of NaF (aq), the product formed at the anode is $\text{O}_2 (\text{g})$
 - F^- has a more negative oxidation potential than O^{2-} in H_2O
- For electrolysis of NaBr (aq), the product formed at the anode is $\text{Br}_2 (\text{l})$
- For electrolysis of NaI (aq), the product formed at the anode is $\text{I}_2 (\text{s})$
 - Br^- and I^- have less negative oxidation potentials than O^{2-} in H_2O

Sample problem

A current of 2.40 A is passed through a solution containing Cu^{2+} (aq) for 30.0 min with Cu metal being deposited at the cathode. What mass of Cu, in grams, is deposited

$$\begin{aligned} & 30.0 \text{ min} \times \frac{60 \text{ s}}{1 \text{ min}} \times \frac{2.40 \text{ C}}{1 \text{ s}} \times \frac{1 e^-}{1.60 \times 10^{-19} \text{ C}} \times \frac{1 \text{ atom Cu}}{2 e^-} \\ & \times \frac{1 \text{ mole Cu}}{6.022 \times 10^{23} \text{ atoms Cu}} \times \frac{63.546 \text{ g Cu}}{1 \text{ mole Cu}} = \mathbf{1.42 \text{ g Cu}} \end{aligned}$$