Balancing redox reactions by half-reaction method: in acid

$\overset{+5}{VO_2^+}(aq) + \overset{0}{Zn}(s) \rightarrow \overset{+4}{VO^{2+}}(aq) + \overset{+2}{Zn^{2+}}(aq)$

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^+/H_2O
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

1) $Zn(s) \rightarrow Zn^{2+}(aq) + \mathbf{2e^-}$
2) $VO_2^+(aq) + \mathbf{e^-} \rightarrow VO^{2+}(aq)$
3) Here, Zn and V are already balanced
4) $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

   $VO_2^+(aq) + e^- + \mathbf{2H^+}(aq) \rightarrow VO^{2+}(aq) + \mathbf{H_2O}(l)$
5) $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

   $\mathbf{2}VO_2^+(aq) + \mathbf{2}e^- + \mathbf{4}H^+(aq) \rightarrow \mathbf{2}VO^{2+}(aq) + \mathbf{2}H_2O(l)$

$$Zn(s) + 2\,VO_2^+(aq) + 4\,H^+(aq) \rightarrow Zn^{2+}(aq) + 2\,VO^{2+}(aq) + 2\,H_2O(l)$$

Balancing redox reaction in base

- $\overset{0}{Al}\ (s) + \overset{+1}{H}_2O\ (l) \rightarrow [\overset{+3}{Al}(OH)_4]^-\ (aq) + \overset{0}{H_2}\ (g)$
- Oxidation
  - $Al\ (s) \rightarrow [Al(OH)_4]^-\ (aq) + \mathbf{3\ e^-}$
  - $Al\ (s) + \mathbf{4\ H_2O\ (l)} \rightarrow [Al(OH)_4]^-\ (aq) + \mathbf{4\ H^+\ (aq)} + 3\ e^-$
- Reduction
  - $H_2O\ (l) + \mathbf{2\ e^-} \rightarrow H_2\ (g)$
  - $H_2O\ (l) + \mathbf{2\ H^+} + 2\ e^- \rightarrow H_2\ (g) + \mathbf{H_2O\ (l)}$
- LCM: 6
  - $\mathbf{2}\ Al\ (s) + \mathbf{8}\ H_2O\ (l) \rightarrow \mathbf{2}\ [Al(OH)_4]^-\ (aq) + \mathbf{8}\ H^+\ (aq) + \mathbf{6}\ e^-$
  - $\mathbf{3}\ H_2O\ (l) + \mathbf{6}\ H^+ + \mathbf{6}\ e^- \rightarrow \mathbf{3}\ H_2\ (g) + \mathbf{3}\ H_2O\ (l)$
- Combine
  - $2\ Al\ (s) + 8\ H_2O\ (l) \rightarrow 2\ [Al(OH)_4]^-\ (aq) + \mathbf{2\ H^+}\ (aq) + 3\ H_2\ (g)$
- Neutralize H^+ with OH^-
  - $2\ Al\ (s) + 8\ H_2O\ (l) + \mathbf{2\ OH^-\ (aq)} \rightarrow 2\ [Al(OH)_4]^-\ (aq) + \mathbf{2\ H_2O}\ (l) + 3\ H_2\ (g)$
  - $\mathbf{2\ Al\ (s) + 6\ H_2O\ (l) + 2\ OH^-\ (aq) \rightarrow 2\ [Al(OH)_4]^-\ (aq) + 3\ H_2\ (g)}$

Sample problem

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

$2\ NO_3^- (aq) + 8\ H^+ (aq) + 3\ Cu (s) \rightarrow 2\ NO (g) + 4\ H_2O (l) + 3\ Cu^{2+} (aq)$

- N is reduced
  - $NO_3^- (aq) + 4\ H^+ + 3\ e^- \rightarrow NO (g) + 2\ H_2O (l)$ **$E^\circ = +0.96$ V**
- Cu is oxidized
  - $Cu^{2+} (aq) + 2\ e^- \rightarrow Cu (s)$ $E^\circ = +0.337$ V
  - So for oxidation
  - $Cu (s) \rightarrow Cu^{2+} (aq) + 2\ e^-$ **$E^\circ_{ox} = -0.337$ V**
- $E^\circ_{cell} = +0.96\ V - 0.337\ V = 0.62\ V$

Sample problem

Rank the halogens in order of their strength as oxidizing agents

- F_2 (g) + 2 e^- → 2 F^- (aq) E° = +2.87 V
- Cl_2 (g) + 2 e^- → 2 Cl^- (aq) E° = +1.36 V
- Br_2 (l) + 2 e^- → 2 Br^- (aq) E° = +1.08 V
- I_2 (s) + 2 e^- → 2 I^- (aq) E° = +0.535 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
- $F_2 > Cl_2 > Br_2 > I_2$

Sample problem

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

- Au^{3+} (aq) + 3 e^- → Au (s)   E° = +1.50 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 V)
  - 2.87 V – 1.50 V = 1.37 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.

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

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- Oxidation HR: Al (s) → Al^{3+} (aq) + 3 e^-
- Reduction HR: Ni^{2+} (aq) + 2 e^- → Ni (s)
- LCM: 6
  - 2 Al (s) → 2 Al^{3+} (aq) + 6 e^-
  - 3 Ni^{2+} (aq) + 6 e^- → 3 Ni (s)
- Combine
  - 2 Al (s) + 3 Ni^{2+} (aq) → 2 Al^{3+} (aq) + 3 Ni (s) E°_{cell} = –0.25 V +1.66 V = +1.41 V
  - $Q = \frac{[Al^{3+}]^2}{[Ni^{2+}]^3}$

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- $E = E^{\circ} - \frac{0.0257}{n} lnQ = +1.41\ V - \frac{0.0257}{6} ln \frac{[Al^{3+}]^2}{[Ni^{2+}]^3} =$

$$+1.41\ V - \frac{0.0257}{6} ln \frac{[0.0010\ M]^2}{[0.50\ M]^3} = \mathbf{1.46\ V}$$

Sample problem

A voltaic cell is set up with copper and hydrogen half-cells. Standard conditions are employed in the copper half-cell, Cu^{2+} (aq, 1.00 M)|Cu (s). The hydrogen gas pressure is 1.00 bar and [H^+ (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

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

Sample problem

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- $E = E^{\circ} - \frac{0.0257}{n} lnQ \rightarrow 0.490\ V = 0.337\ V - \frac{0.0257}{2} lnQ \rightarrow$

$$lnQ = -11.9 \rightarrow Q = 6.75\times10^{-6} = \frac{[H^+]^2}{[Cu^{2+}]}$$

$$[H^+]^2 = 6.75\times10^{-6}$$

$$[H^+] = 2.60\times10^{-3}$$

$$\mathbf{pH = 2.6}$$

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:
  - $2\ H_2O\ (l) + 2\ e^- \rightarrow H_2\ (g) + 2\ OH^-\ (aq)$ $E^\circ = -0.8277\ V$
  - $Na^+\ (aq) + e^- \rightarrow Na\ (s)$ $E^\circ = -2.714\ V$
- Oxidation potentials needed:
  - $2\ H_2O\ (l) \rightarrow O_2\ (g) + 2\ e^- + 4\ H^+$ $E^\circ_{ox} = -1.229\ V$
  - $2\ F^-\ (aq) \rightarrow F_2\ (g) + 2\ e^-$ $E^\circ_{ox} = -2.87\ V$
  - $2\ Br^-\ (aq) \rightarrow Br_2\ (l) + 2\ e^-$ $E^\circ_{ox} = -1.08\ V$
  - $2\ I^-\ (aq) \rightarrow I_2\ (s) + 2\ e^-$ $E^\circ_{ox} = -0.535\ V$
- For all four electrolyses, the product formed at the cathode is H_2 (g).
- For electrolysis of NaF (aq), the product formed at the anode is O_2 (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 Br_2 (l)
- For electrolysis of NaI (aq), the product formed at the anode is I_2 (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

$$30.0\ min \times \frac{60\ s}{1\ min} \times \frac{2.40\ C}{1\ s} \times \frac{1\ e^-}{1.60 \times 10^{-19} C} \times \frac{1\ atom\ Cu}{2\ e^-}$$

$$\times \frac{1\ mole\ Cu}{6.022 \times 10^{23}\ atoms\ Cu} \times \frac{63.546\ g\ Cu}{1\ mole\ Cu} = \mathbf{1.42\ g\ Cu}$$