Determining Oxidation Number (State)

Determine the oxidation states of the elements in each of the following:

a.) P_2O_5 $O = -2$, $P = +5$ $-2 \times 5 = -10$ $-10 + 2P = 0$ (+10 / +10) $\frac{2P}{2} = \frac{10}{2}$ $P = +5$

b.) NaH $Na = +1$, $H = -1$ $+1 + H = 0$ (−1 / −1) $H = -1$

c.) $Cr_2O_7^{2-}$ $O = -2$, $Cr = +6$ $-2 \times 7 = -14$ $-14 + 2Cr = -2$ (+14 / +14) $\frac{2Cr}{2} = +\frac{12}{2}$ $Cr = +6$

d.) $SnBr_4$ $Br = -1$, $Sn = +4$ $-1 \times 4 = -4$ $-4 + Sn = 0$ (+4 / +4) $Sn = +4$

e.) NO_2^- $O = -2$, $N = +3$ $-2 \times 2 = -4$ $-4 + N = -1$ (+4 / +4) $N = +3$

f.) ClO_3^- $O = -2$, $Cl = +5$ $-2 \times 3 = -6$ $-6 + Cl = -1$ (+6 / +6) $Cl = +5$

Oxidizing & Reducing Agents

OH^- ↳ causes something to happen

Indicate which is the oxidizing agent and which is the reducing agent in the following reaction:

$$\overset{0}{Cd}(s) + \overset{+4\ -2}{NiO_2}(s) + 2\overset{+1\ -2}{H_2O}(l) \rightarrow \overset{+2\ -2+1}{Cd(OH)_2}(s) + \overset{+2\ \overset{-1}{-2+1}}{Ni(OH)_2}(s)$$

Cd 0 → +2 → oxidized → cause reduced → reducing agent

Ni +4 → +2 → reduced → cause oxidation → oxidizing agent

Balancing Redox Reactions in Acidic Solution

Complete and balance the following equation. The reaction occurs in acidic solution.

$Mn^{2+}(aq) + BiO_3^-(s) \rightarrow Bi^{3+}(aq) + MnO_4^-(aq)$

$Mn^{2+} \rightarrow MnO_4^-$

$BiO_3^- \rightarrow Bi^{3+}$

Add H_2O to balance O.

$Mn^{2+} + 4H_2O \rightarrow MnO_4^-$

$BiO_3^- \rightarrow Bi^{3+} + 3H_2O$

Add H^+ to balance H

$Mn^{2+} + 4H_2O \rightarrow MnO_4^- + 8H^+$

$BiO_3^- + 6H^+ \rightarrow Bi^{3+} + 3H_2O$

add e- $\times 2$ $[Mn^{2+} + 4H_2O \rightarrow MnO_4^- + 8H^+ + 5e^-]$ $[BiO_3^- + 6H^+ + 2e^- \rightarrow Bi^{3+} + 3H_2O] \times 5$

$2Mn^{2+} + 8H_2O \rightarrow 2MnO_4^- + 16H^+ + 10e^-$

$+ 5BiO_3^- + 30H^+ + 10e^- \rightarrow 5Bi^{3+} + 15H_2O$

$2Mn^{2+} + 5BiO_3^- + 14H^+ \rightarrow 2MnO_4^- + 5Bi^{3+} + 7H_2O$

A: $2Mn^{2+}(aq) + 5BiO_3^-(s) + 14H^+(aq) \rightarrow 5Bi^{3+}(aq) + 2MnO_4^-(aq) + 7H_2O(l)$

Balancing Redox Reactions in Basic Solution

Complete and balance the following equation. The reaction occurs in basic solution.

$$NO_2^-(aq) + Al(s) \rightarrow NH_3(aq) + Al(OH)_4^-(aq)$$

$NO_2^- \rightarrow NH_3$ $\qquad$ $Al \rightarrow Al(OH)_4^-$

$NO_2^- \rightarrow NH_3 + 2H_2O$ $\qquad$ $Al + 4H_2O \rightarrow Al(OH)_4^-$

$NO_2^- + 7H^+ \rightarrow NH_3 + 2H_2O$ $\qquad$ $Al + 4H_2O + 4H^+ \rightarrow Al(OH)_4^- + 8H^+$

$NO_2^- + 7H^+ + 6e^- \rightarrow NH_3 + 2H_2O$ $\qquad$ $[Al + 4H_2O \rightarrow Al(OH)_4^- + 4H^+ + 3e^-] \times 2$

$$2Al + 6H_2O \rightarrow 2Al(OH)_4^- + 8H^+ + 6e^-$$

Add OH^- to eliminate H^+

$$OH^- + NO_2^- + 2Al + 5H_2O \rightarrow 2Al(OH)_4^- + NH_3 + H_2O$$

$$NO_2^- + 2Al + 5H_2O + OH^- \rightarrow 2Al(OH)_4^- + NH_3$$

A: $NO_2^-(aq) + 2Al(s) + 5H_2O(l) + OH^-(aq) \rightarrow NH_3(aq) + 2Al(OH)_4^-(aq)$

Galvanic Cells

A voltaic cell is constructed with one compartment consisting of an aluminum strip placed in a solution of $Al(NO_3)_3$, and the other has a nickel strip placed in a solution of $NiSO_4$. The overall cell reaction is:

$$2Al(s) + 3Ni^{2+}(aq) \rightarrow 2Al^{3+}(aq) + 3Ni(s)$$

a.) What is being oxidized & what is being reduced?

Al: 0 → +3 = oxidized Ni: +2 → 0 = reduced

b.) Write the half reactions that occur in the two electrode compartments.

Anode (oxidation): $Al(s) \rightarrow Al^{3+}(aq) + 3e^-$

Cathode (reduction): $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$

c.) Indicate the signs of the electrodes.

Anode → negative $Al(s)|Al^{3+}(aq)$ Cathode - positive $Ni^{2+}(aq)|Ni(s)$

d.) In which direction do the electrons flow?

toward cathode → toward $Ni^{2+}(aq)|Ni(s)$

e.) In which directions do the cations and anions migrate through the solution?

Anions → toward anode - $Al(s)|Al^{3+}(aq)$

Cations → toward cathode - $Ni^{2+}(aq)|Ni(s)$

f.) Give the cell diagram for this voltaic cell.

Anode $Al(s)|Al^{3+}(aq)||Ni^{2+}(aq)|Ni(s)$ Cathode

Cell Potentials (E°_{cell})

1.) Using data in Table 19.1 p673, calculate the standard emf for a cell that employs the following overall cell reaction:

$$2\overset{0}{Al}(s) + 3\overset{0}{I_2}(s) \rightarrow 2Al^{3+}(aq) + 6I^-(aq)$$

A: 2.19V

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

$E^\circ_{cell} = +0.53V \ominus (-1.66V)$

$= +2.19V$

cathode → reduction - I $\quad I_2 + 2e^- \rightarrow 2I^- \quad +0.53V$

anode → oxidation - Al $\quad Al^{3+} + 3e^- \rightarrow Al \quad -1.66V$

2.) A voltaic cell is based on a Co/Co^{2+} half-cell and an $\overset{0}{Ag}/\overset{+1}{AgCl}$ half-cell.

(a) Write the half-cell reaction for each electrode.

(b) What is the standard cell potential (use Table 19.1)?

$Co^{2+}_{(aq)} + 2e^- \rightarrow Co_{(s)}$

$-0.28V$

Anode

$AgCl(s) + e^- \rightarrow Ag$

$+0.22V$

Cathode

$E^\circ_{cell} = +0.22V \ominus (-0.28V) = +0.50V$

A: $Co^{2+}(aq) + 2e^- \rightarrow Co(s)$

$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$

0.50V

Cell Potentials (E°_{cell})

3.) Will $Br_2(l)$ spontaneously oxidize $Fe^{2+}(aq)$?

red ↙ ↙ OX

↳ E°_{cell} positive

$Br_2(l) + Fe^{2+}_{(aq)} \longrightarrow Fe^{3+}_{(aq)} + 2Br^-$

$Br_2(l) + 2e^- \rightarrow 2Br^-$ +1.07 V (cathode)

$Fe^{3+}_{(aq)} + 1e^- \rightarrow Fe^{2+}_{(aq)}$ +0.77 V (anode)

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

$= 1.07V - 0.77V = +0.30V$ → spontaneous (pos)

4.) Will I^- spontaneously reduce $Cr^{3+}(aq)$ to the free metal?

$2I^- + Cr^{3+} \longrightarrow I_2 + Cr$

$Cr^{3+}_{(aq)} + 3e^- \rightarrow Cr_{(s)}$ −0.74V cathode

$I_2 + 2e^- \rightarrow 2I^-$ +0.53V anode

$E^\circ_{cell} = -0.74V - 0.53V = -1.27V$

↳ not spontaneous (neg)

Cell Diagrams

1.) Write the balanced equation for the given cell:

Anode catalyst $Pt(s)|Sn^{2+}(aq)|Sn^{4+}(aq)||Ag^{+}(aq)|Ag(s)$ cathode

A: $Sn^{2+}(aq) + 2Ag^{+}(aq) \rightarrow Sn^{4+}(aq) + 2Ag(s)$

$Sn^{2+} \rightarrow Sn^{4+} + 2e^-$

$2\,[Ag^+ + e^- \rightarrow Ag]$

$2Ag^+ + 2e^- \rightarrow 2Ag$

$Sn^{2+}_{(aq)} + 2Ag^+_{(aq)} \xrightarrow{Pt} Sn^{4+}_{(aq)} + 2Ag_{(s)}$

2.) Give the shorthand notation for the following cell reaction with a graphite (carbon) cathode:

$\overset{0}{Cu}(s) + \overset{0}{Cl_2}(g) \rightarrow Cu^{2+}(aq) + 2Cl^-(aq)$

A: $Cu(s)|Cu^{2+}(aq)||Cl_2(g)|Cl^-(aq)|C(s)$

Anode - ox $Cu \rightarrow Cu^{2+} + 2e^-$

Cathode - red $Cl_2(g) + 2e^- \rightarrow 2Cl^-$

Anode $Cu(s)|Cu^{2+}_{(aq)}||Cl_2(g)|Cl^-_{(aq)}|C(s)$ Cathode

Cell Potential & Redox

1.) Which of the following pairs of substances is the stronger reducing agent?

A: (a) Mg(s)
(b) Cr(s)

(a) Fe(s) or Mg(s)

(b) Cr(s) or Co(s)

More positive E° = easier to reduce = stronger oxidizing agent

More negative E° = easier to oxidize = stronger reducing agent

(a) Fe(s) vs **Mg(s)**

$Fe^{2+} + 2e^- \rightarrow Fe(s)$ $\quad -0.44V$

$Mg^{2+} + 2e^- \rightarrow Mg(s)$ $\quad -2.37V$

(b) **Cr(s)** vs Co(s)

$Cr^{3+} + 3e^- \rightarrow Cr(s)$ $\quad -0.74V$ ↑

$Co^{2+} + 2e^- \rightarrow Co(s)$ $\quad -0.28V$

Thermodynamics of Redox Reactions

1. What is the equilibrium constant at 25°C for the reaction:

$$Sn(s) + 2Cu^{2+}(aq) \longrightarrow Sn^{2+}(aq) + 2Cu^{+}(aq)?$$

$$E^\circ = \frac{RT}{nF} \ln K$$

$E^\circ_{cell} = E^\circ_{cathode}(red) - E^\circ_{anode}(ox)$

Cath: $Cu^{2+} + e^- \rightarrow Cu^+ + 0.15V$

Anode $Sn \rightarrow Sn^{2+} + 2e^- - 0.14V$

$E^\circ = 0.15V - (-0.14V) = 0.29V$

$R = 8.314\ J/mol\,K$

$T = 25°C + 273.15 = 298.15\ K$

$n = 2$

$F = 96{,}485\ J/V \cdot mol$

$$0.29V = \frac{(8.314\ J/mol\,K)(298.15\ K)}{(2)(96{,}485\ J/V \cdot mol)} \ln K$$

$$\frac{0.29V}{0.0128456V} = \frac{0.0128456V \times \ln K}{0.0128456V}$$

$\ln K = 22.5758$

$K = e^{22.5758}$

$K = 6.376 \times 10^9 \rightarrow \boxed{6.4 \times 10^9}$

A: 6.4×10^9

Thermodynamics of Redox Reactions

2.) If the equilibrium constant for a two electron redox reaction at 298K is 1.5×10^{-4}, calculate the corresponding ΔG° and E°_{red}.

$$E^\circ = \frac{RT}{nF} \ln K$$

$$\Delta G^\circ = -nFE^\circ$$

$R = 8.314\ J/mol\,K$

$T = 298\,K$

$n = 2$

$F = 96{,}485\ J/V \cdot mol$

$$E^\circ_{red} = \frac{(8.314\ J/mol\,K)(298\,K)}{(2)(96{,}485\ J/V \cdot mol)} \ln(1.5 \times 10^{-4})$$

$$E^\circ_{red} = (0.02839\,V)(\ln(1.5 \times 10^{-4}))$$

$$E^\circ_{red} = (0.02839\,V)(-8.805)$$

$$E^\circ_{red} = -0.113\,V \rightarrow \boxed{-0.11\,V}$$

$$\Delta G^\circ = -(2)(96{,}485\ J/V \cdot mol)(-0.113\,V)$$

$$\Delta G^\circ = 2.18 \times 10^4\ J/mol$$

A: 2.2×10^4 J/mol;-0.11V

The Nernst Equation

1. A voltaic cell utilizes the following reaction:

$2Al(s) + 3I_2(s) \rightarrow 2Al^{3+}(aq) + 6I^-(aq)$

(a) What is the E_{cell} under standard conditions?

(b) What is the E_{cell} when $[Al^{3+}] = 4.0 \times 10^{-3} M$ & $[I^-] = 0.010 M$ (still at 298K)

$$E = E^\circ_{cell} - \left(\frac{RT}{nF}\right) \ln Q$$

cathode - red - $I_2 + 2e^- \rightarrow 2I^-$ $+0.53V$

anode - ox - $Al^{3+} + 3e^- \rightarrow Al(s)$ $-1.66V$

(a) $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

$= 0.53V - (-1.66V) = 2.19V$

$E^\circ_{cell} = 2.19V$

$R = 8.314\ J/mol$

$T = 298K$

$n = 6$

$F = 96,485\ J/V \cdot mol$

(b) $E = 2.19V - \left(\frac{8.314\ J/mol \cdot K \times 298K}{6 \times 96,485\ J/V \cdot mol}\right) \ln(1.6 \times 10^{-17})$

$Q = [Al^{3+}]^2 [I^-]^6$

$= [4.0 \times 10^{-3} M]^2 [0.010]^6$

$= 1.6 \times 10^{-17}$

$E = 2.19V - [4.2797 \times 10^{-3} V][-38.674]$

$E = 2.19V + 0.1655V$

$\boxed{E = 2.36V}$

Concentration Cells

1. A concentration cell is constructed at 298K with two $Zn(s)$-$Zn^{2+}(aq)$ half cells. One half-cell has a Zn^{2+} concentration of 1.35M, and the other has a Zn^{2+} concentration of 3.75×10^{-4}M. What is the cell potential?

Nernst Eq = $E_{cell} = E^\circ_{cell} - \left[\frac{RT}{nF} \ln Q\right]$

$E_{cell} = 0 - \frac{(8.314\ J/mol\ K)(298\ K)}{(2)(96{,}485\ J/V \cdot mol)} \ln\left(\frac{3.75 \times 10^{-4}}{1.35M}\right)$

$E_{cell} = -0.012839V (\ln 2.7778 \times 10^{-4})$

$E_{cell} = (-0.012839V)(-8.18868)$

$E_{cell} = +0.105V$

$Zn^{2+} + 2e^- \rightarrow Zn(s) \quad -0.76V$

$E^\circ_{cell} = -0.76V - (-0.76V) = 0$

high conc → low conc

$Q = \frac{\text{low conc}}{\text{high conc}}$

$R = 8.314\ J/mol\ K$

$T = 298K$

$n = 2$

$F = 96{,}485\ J/V \cdot mol$

Electrolysis

1.) A 1M aqueous solution of iron (III) chloride is electrolyzed. What are the products? Fe(s), $O_2(g)$, $H^+(aq)$

Red $Fe^{3+} + 3e^- \rightarrow Fe(s)$ $+0.77V$ ← more pos
$2H_2O(\ell) + 2e^- \rightarrow H_2(g) + 2OH^-$ $-0.83V$
} Fe(s)

Fe(s), $O_2(g)$, $H^+(aq)$

Ox $2Cl^- \rightarrow Cl_2 + 2e^-$ $E_{ox} = -1.36V$
$2H_2O(\ell) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$ $E_{ox} = -1.23V$ ← more pos / less negative value
} $Cl_2(g)$ + $H^+(aq)$

2.) A 1M solution of potassium iodide (KI) is electrolyzed under acidic (H^+) conditions. What are the products? $H_2(g)$, $I_2(s)$

Red: $K^+ + e^- \rightarrow K(s)$ $E_{red} = -2.93V$
$2H^+ + 2e^- \rightarrow H_2(g)$ $E_{red} = 0.00V$ ← more pos
} $H_2(g)$

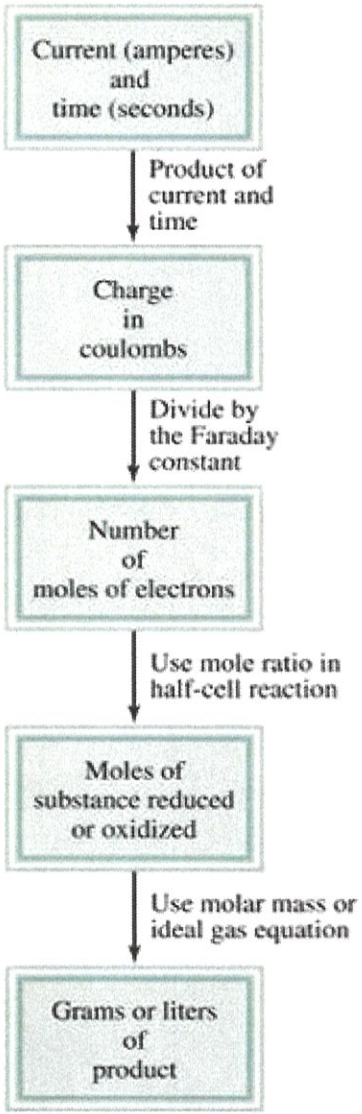
$H_2(g)$, $I_2(s)$

Ox: $2I^- \rightarrow I_2(s) + 2e^-$ $E_{ox} = -0.53V$ ← more pos
$2H_2O(\ell) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$ $E_{ox} = -1.23V$
} $I_2(s)$

Producing Products by Electrolysis

1.) How many grams of Ca(s) will be produced in an electrolytic cell of molten $CaCl_2$ if a current of 0.452 A is passed through the cell for 1.5 hours?

A: 0.51g



$nF = At$ n = # moles = specific # moles of e^-

$F = 96{,}485\ C/mol$ Coulomb = current × time = $A \times t$

$96{,}485 \frac{A \times s}{mol}$ $t = s$

$A = 0.452\ A$

t = time (s) $1.5\ hrs \left(\frac{60\ min}{1\ hr}\right)\left(\frac{60\ s}{1\ min}\right) = 5400\ s$

$n = \frac{At}{F} = \frac{(0.452\ A)(5400\ s)}{96{,}485 \frac{A \times s}{mol}}$ $Ca^{2+} + 2e^- \rightarrow Ca(s)$

$n = 0.025297\ mol\ e^- \left(\frac{1\ mol\ Ca(s)}{2\ mol\ e^-}\right) = 0.012649\ mol\ Ca \left(\frac{40.078\ g}{mol}\right)$

$= 0.50693\ g\ Ca$

↳ 0.51 g Ca

Producing Products by Electrolysis

2.) Water is electrolyzed in a cell at 25mA for 15 minutes. How many mL of oxygen gas are produced at 1.0 atm and 25°C?

$2H_2O(\ell) \rightarrow O_2(g) + 4e^- + 4H^+$

A: 1.4mL

$n = \frac{At}{F}$

$A = 25mA\left(\frac{1A}{1000mA}\right) = 0.025A$

$t = 15min\left(\frac{60s}{1min}\right) = 900s$

$F = 96{,}485\frac{A \cdot s}{mol}$

$25°C + 273.15 = 298.15K$

$n = \frac{(0.025A)(900s)}{96{,}485 A{\cdot}s/mol} = 2.332 \times 10^{-4} mole^- \left(\frac{1 mol\ O_2}{4 mole^-}\right) = 5.83 \times 10^{-5} mol\ O_2$

$PV = nRT \quad (1.0atm)(V) = (5.83 \times 10^{-5} mol)\left(0.0821 \frac{L{\cdot}atm}{mol{\cdot}K}\right)(298.15K)$

$\frac{(1.0\ atm)(V)}{1.0 atm} = \frac{0.001427\ L \cdot atm}{1.0 atm}$

$V = 0.001427L\left(\frac{1000mL}{L}\right) = 1.427mL \rightarrow \boxed{1.4mL}$

Producing Products by Electrolysis

3.) How many minutes are needed to plate out 25.00g Mg from molten $MgCl_2$ using 3.50 A of current? A: 945 min

$nF = A(t)$ $\quad t = \frac{nF}{A}$

$A = 3.50\ A$

$F = 96{,}485\ \frac{A \cdot s}{mol}$

$Mg^{2+} + 2e^- \rightarrow Mg(s)$

$n = 25.00g\ Mg\left(\frac{1\ mol}{24.305g}\right)$

$= 1.0286\ mol\ Mg\left(\frac{2\ mol\ e^-}{1\ mol\ Mg}\right) = 2.057\ mol\ e^-$

$$t = \frac{(2.057\ \cancel{mol})(96{,}485\ \frac{A \cdot s}{\cancel{mol}})}{3.50\ \cancel{A}}$$

$t = 56{,}706\ sec\left(\frac{1\ min}{60s}\right) = \boxed{945\ min}$

Electrical Work

1.) Consider the voltaic cell which is based on the cell reaction: $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$
Under standard conditions, what is the maximum electrical work, in Joules, that the cell can accomplish if 50.0g of copper is plated out?

A: -1.67×10^5 J

$W_{max} = -nFE$

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

Cathode: $Cu^{2+} + 2e^- \Rightarrow Cu(s) + 0.34V$

Anode: $Zn^{2+} + 2e^- \Rightarrow Zn(s) \quad -0.76V$

$E^\circ_{cell} = +0.34V - (-0.76V)$

$= 1.10V = E$

$n = 50.0g\,Cu\left(\frac{1mol}{63.546g}\right) = 0.78683\,mol\,Cu\left(\frac{2\,mole^-}{mol\,Cu}\right)$

$= 1.57366\,mole^-$

$F = 96{,}485\,\frac{A \cdot S}{mol}\left[\frac{J}{V \cdot mol}\right]$

$W_{max} = -(1.57366\,mol)(96{,}485\,J/mol)(1.10V)$

$W_{max} = -1.67 \times 10^5\,J$