Chapter 4 (Redox)

(49) Find the oxidation # of the indicated element in each thing.

(a) S in $SO_2$

Oxygen must have an O.N. of $-2$ (rule # 3a on page 132)

and the sum of the O.N. in a <u>compound</u> must be zero.

$S + 2(-2) = 0$ $\boxed{S = +4}$

(b) C in $COCl_2$

rule # 3a : oxygen is $-2$ O.N.
rule # 3c : halogens (like Cl) are $-1$ O.N.

$C + (-2) + 2(-1) = 0$
$C - 4 = 0$
$\boxed{C = +4}$

(c) Mn in $KMnO_4 \rightarrow K^{+1}$, $\rightarrow MnO_4^{-1}$ ← The sum of O.N. in a polyatomic ion must be equal to the charge on the ion

$Mn + 4(-2) = -1$
$\boxed{Mn = +7}$

(d) Br in $\overset{}{\underset{+1}{H}}Br\underset{-2}{O}$

$H + Br + O = 0$
$1 + Br + -2 = 0$
$\boxed{Br = +1}$

(e) As in $As_4$

$As_4$ is an element, so the O.N. of $\boxed{\text{As is zero}}$

(f) O in $K_2O_2$

This compound is potassium <u>peroxide</u>; the charges can only balance ~~[illegible]~~ (since K is +1) if the anion is peroxide; $O_2^{-2}$

So each Oxygen has an oxidation number of $-1$

(50) Find the oxidation # of the indicated element in each substance.

(a) Co in $\mathrm{LiCoO_2}$

$\underset{(+1)}{\mathrm{Li}}\,\mathrm{Co}\,\underset{(-2)}{\mathrm{O}_2}$

$1 + Co + 2(-2) = 0$

$\boxed{Co = +3}$

(b) Al in $\mathrm{NaAlH_4}$

sodium aluminum hydride

$Na^{+1}$ $Al^{+3}$ $H^{-1}$

$\boxed{Al = +3}$

(c) C in $\mathrm{CH_3OH}$ (methanol)

$C + 4(H) + \text{Oxygen} = 0$

$C + 4(1) + (-2) = 0$

$\boxed{C = -2}$

(d) N in GaN

Ga +3 , $N^{-3}$ (gallium nitride)

$\boxed{N = -3}$

(e) Cl in $\mathrm{HClO_2}$

$H = +1$

$\text{Oxygen} = -2$

$+1 + \underline{(Cl)} + 2(-2) = 0$

$\boxed{Cl = +3}$

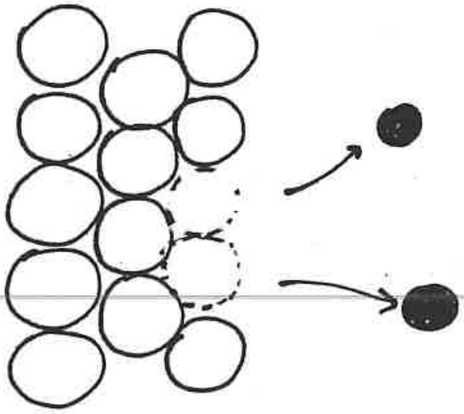
(f) Cr in $\mathrm{BaCrO_4}$

$Ba^{+2}$, $CrO_4^{-2}$

$Cr + 4(-2) = -2$ overall charge on ion

$\boxed{Cr = +6}$

#3



The picture seems to show atoms leaving the electrode, forming ions with a smaller radius than the original atoms, and entering aqueous solution (dissolving).

(a) Since the metal atoms are forming positive ions, oxidation is occurring. the atoms must lose e- to form cations. for example it could be $Ag_{(s)} \rightarrow Ag^{+1}_{(aq)} + 1e^-$

$Fe_{(s)} \rightarrow Fe^{+3}_{(aq)} + 3e^-$

$Cu_{(s)} \rightarrow Cu^{+2}_{(aq)} + 2e^-$

etc.

(c) Since the ions in solution have a smaller radius than the original atoms, the ions must be positively charged.

(anions would have a larger radius than the original atoms, but cations have a smaller radius than the original atoms).

(b) this is the anode since oxidation is occurring.

(#6 is on the next page)

#7 If $E^\circ_{rxn}$ ($E^\circ_{cell}$) is negative, then

(a) $\Delta G^\circ_{rxn}$ will be positive

(b) Keq will be less than one.

(The negative sign for $E^\circ_{rxn}$ shows that the rxn is not spontaneous / is not thermodynamically favored.)

(c) no, an electrochemical cell based on this rxn can not be used to do work on its surroundings. rather, work must be done to cause the rxn to occur.

(although, if we have a very small value of Q, we can make $E_{cell}$ more positive than $E^\circ_{cell}$, so, maybe....)

$\uparrow$ non std conditions

$\uparrow$ standard conditions all solutions are 1 Molar

Chapter 20

#6 given :

| Reduction half-rxn | $E^\circ_{red}$ (Volts) |
|---|---|
| $A^{+1}_{(aq)} + e^- \rightarrow A_{(s)}$ | 1.33 |
| $B^{2+}_{(aq)} + 2e^- \rightarrow B_{(s)}$ | 0.87 |
| $C^{3+}_{(aq)} + e^- \rightarrow C^{2+}_{(s)}$ | -.12 |
| $D^{3+}_{(aq)} + 3e^- \rightarrow D_{(s)}$ | -1.59 |

(a) Which substance is the strongest oxidizing agent, and which is the weakest oxidizing agent?

The strongest oxidizing agent would be the substance most capable of being reduced, so it would be the substance with the most positive $E^\circ_{red}$.

So the strongest oxidizing agent (oxidant) is $\boxed{A^{+1}}$ the weakest oxidizing agent would be $\boxed{D^{+3}}$ (only considering the reactants in the above chart... $C^{2+} + 2e^- \rightarrow C_{(s)}$ could occur but we were not given a voltage for this!)

(b) Which substance is the strongest reducing agent / which is weakest? The strongest reducing agent would be the substance most capable of being oxidized; it would have the most positive $E^\circ_{ox}$.

If we reverse the given reduction half-rxns, we get oxidation half rxns:

$A_{(s)} \rightarrow A^{+1} + 1e^-$ $E^\circ_{ox} = -1.33$ V
$B_{(s)} \rightarrow B^{2+} + 2e^-$ $E^\circ_{ox} = -0.87$ V
$C^{2+} \rightarrow C^{3+} + 1e^-$ $E^\circ_{ox} = +0.12$ V
$D_{(s)} \rightarrow D^{3+} + 3e^-$ $E^\circ_{ox} = +1.59$ V

So D(s) is the strongest reducing agent (reductant) and A(s) is the weakest reducing agent.

(c) Which substance(s) could oxidize $C^{2+}$?

as shown above, $C^{2+}$ has an oxidation potential of 0.12 V

$E^\circ_{rxn} = E^\circ_{ox} + E^\circ_{red} > 0$ ← $E^\circ_{rxn}$ must be ⊕ to occur spontaneously

so we need a substance with $E^\circ_{red} > -.12$ V

So $A^{+1}$ ($E^\circ_{red} = 1.33$V) and $B^{+2}$ ($E^\circ_{red} = 0.87$V) could work.

#13 (a) oxidation = <u>loss of electrons</u>

(or, an <u>increase in oxidation number</u>. This could be due to outright <u>losing</u> electrons, or by becoming covalently bonded to a substance that is very electron-withdrawing, like Oxygen, fluorine, etc).

(b) in an oxidation half-reaction, the free <u>electrons</u> are written on the right (product) side of the equation.

(c) an <u>oxidant</u> (aka "oxidizing agent") is a substance that causes other substances to become oxidized. The <u>oxidant</u> becomes <u>reduced</u> (gains electrons) when this happens; the oxidant takes electrons away from the substance it is reacting with, causing that substance to become oxidized.

(d) see (c). an <u>oxidant</u> is the same thing as an <u>oxidizing agent</u>.

#14 a) Reduction = <u>gain of electrons</u>.

(or, a decrease in oxidation number, which could be due to <u>gaining electrons</u>, or by becoming covalently bonded to an element with low electronegativity)

(b) in a reduction half-reaction, the free electrons are written on the left (reactant) side of the equation.

(c) A <u>reductant</u>, or <u>reducing agent</u>, is a substance that causes other substances to become reduced. In a redox reaction, the reductant itself becomes oxidized; it loses electrons to the substance it is reacting with, allowing that substance to gain electrons and become reduced.

(d) see (c). a <u>reductant</u> is the same thing as a <u>reducing agent</u>.

#21 Complete and balance each half-rxn, and indicate whether it is oxidation or reduction.

(a) $\boxed{Sn^{+2}_{(aq)} \longrightarrow Sn^{+4}_{(aq)} + 2e^-}$ ← I added 2e- to right side to balance charge. this is an oxidation half-rxn.

(acid) (b) $\boxed{2e^- + 4H^{+1}_{(aq)} + TiO_{2(s)} \rightarrow Ti^{+2}_{(aq)} + 2H_2O_{(l)}}$

③ ② then I added $4H^{+1}$ to left to balance hydrogen ① first I added 2 $H_2O$ to balance oxygen

↑ then I added 2e- to left to balance charge. this is reduction.

(acid) (c) $\boxed{6e^- + 6H^{+1}_{(aq)} + ClO_{3\,(aq)}^{-1} \rightarrow Cl^{-1}_{(aq)} + 3H_2O}$

③ ② ①

reduction

(acid) (d) $\boxed{6e^- + 8H^{+1}_{(aq)} + N_{2(g)} \longrightarrow 2NH_{4\,(aq)}^{+1}}$

③ balance charge. reduction. ↑② add H+ to balance hydrogen ↑① need a 2 to balance nitrogen

base (e) $2OH^- + 2OH^{-1}_{(aq)} \longrightarrow O_{2(g)} + 2H_2O + 4e^-$ ③ 2

↑ ① balance oxygen with the 2 ↑ ② add $H_2O$ and $OH^-$ to balance hydrogen

overall: $\boxed{4OH^{-1}_{(aq)} \rightarrow O_{2(g)} + 2H_2O_{(l)} + 4e^-}$ (oxidation)

basic (f) $2OH^{-1}_{(aq)} + H_2O_{(l)} + SO_{3\,(aq)}^{-2} \longrightarrow SO_{4\,(aq)}^{-2} + 2H_2O + 2e^-$

① balance oxygen ② balance Hydrogen ③ balance charge

overall: (oxidation) $\boxed{2OH^{-1}_{(aq)} + SO_{3\,(aq)}^{-2} \rightarrow SO_{4\,(aq)}^{-2} + H_2O_{(l)} + 2e^-}$

(base) (g) $\boxed{6e^- + 6H_2O_{(l)} + N_{2(g)} \longrightarrow 2NH_{3\,(g)} + 6OH^{-1}_{(aq)}}$ (reduction)

③ balance charge ② balance H ① balance N ②

(23) Complete + balance each rxn, and ID oxidizing and reducing agents.

(a) $Cr_2O_7^{-2}{}_{(aq)} + I^{-1}_{(aq)} \rightarrow Cr^{+3}_{(aq)} + IO_3^{-1}{}_{(aq)}$ (acid)

(+6) (-2) (-1) (+3) (+5) (-2)

oxidation half-rxn $3H_2O + I^{-1} \rightarrow IO_3^{-1} + 6H^{+1} + 6e^-$

reduction half-rxn $Cr_2O_7^{-2} + 6e^- + 14H^{+1} \rightarrow 2Cr^{+3} + 7H_2O$

Add up as is since 6e- on each side will cancel

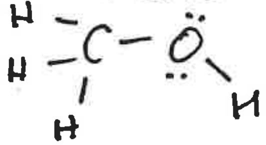
$$\cancel{3H_2O} + I^{-1} + Cr_2O_7^{-2} + \cancel{6e^-} + \underset{8}{\cancel{14}}H^{+1} \rightarrow IO_3^{-1} + \cancel{6H^{+1}} + \cancel{6e^-} + \underset{4}{\cancel{7}}H_2O + 2Cr^{+3}$$

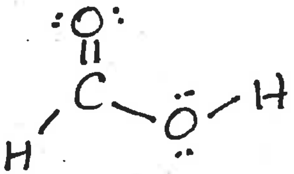
$$\boxed{I^{-1}_{(aq)} + Cr_2O_7^{-2}{}_{(aq)} + 8H^{+1}_{(aq)} \longrightarrow IO_3^{-1}{}_{(aq)} + 2Cr^{+3}_{(aq)} + 4H_2O_{(l)}}$$

↑ reducing agent (becomes oxidized) ↑ oxidizing agent (becomes reduced)

(b) $MnO_4^{-1} + CH_3OH \longrightarrow Mn^{+2} + HCO_2H +$ (acidic soln)

(+7) (-2) (-2) (+1) (-2) (+2) (+1) (+2) (-2)





oxidation half-rxn :

$$(H_2O + CH_3OH \longrightarrow HCO_2H + 4H^{+1} + 4e^-) \times 5$$

reduction half-rxn

$$(8H^{+1} + MnO_4^{-1} + 5e^- \longrightarrow Mn^{+2} + 4H_2O) \times 4$$

$$\left.\begin{matrix} \cancel{5H_2O} + 5CH_3OH \\ + \overset{12}{\cancel{32}}H^{+1} + 4MnO_4^- + \cancel{20e^-} \end{matrix}\right\} \longrightarrow \begin{matrix} 5HCO_2H + \cancel{20H^{+1}} + \cancel{20e^-} \\ + 4Mn^{+2} + \underset{11}{\cancel{16}}H_2O \end{matrix}$$

$$\boxed{5CH_3OH_{(aq)} + 4MnO_4^{-1}{}_{(aq)} + 12H^{+1}_{(aq)} \longrightarrow 5HCO_2H_{(aq)} + 4Mn^{+2}_{(aq)} + 11H_2O_{(l)}}$$

↑ reducing agent (becomes oxidized) ↑ oxidizing agent (becomes reduced)

(#23) (Cont'd)

(c) $I_2 + OCl^{-1} \longrightarrow IO_3^{-1} + Cl^{-1}$ (acidic soln)

(0) (−2)(+1) (+5)(−2) (−1)

oxidation half-rxn :

$$I_{2(s)} + 6H_2O_{(l)} \longrightarrow 2IO^{-1}_{3(aq)} + 12H^{+1}_{(aq)} + 10e^-$$

reduction half-rxn :

$$\left(2e^- + 2H^{+1}_{(aq)} + OCl^{-1}_{(aq)} \longrightarrow Cl^{-1}_{(aq)} + H_2O_{(l)}\right) \times 5$$

Total:

$$I_2 + \overset{1}{\cancel{6}}H_2O + \cancel{10e^-} + \cancel{10H^{+1}} + 5OCl^{-1} \longrightarrow 5Cl^{-1} + \cancel{5H_2O} + 2IO_3^{-1} + \underset{2}{\cancel{12}}H^{+1} + \cancel{10e^-}$$

$$\boxed{I_{2(s)} + H_2O_{(l)} + 5OCl^{-1}_{(aq)} \longrightarrow 5Cl^{-1}_{(aq)} + 2IO^{-1}_{3(aq)} + 2H^{+1}_{(aq)}}$$

reducing agent ↑ ($I_2$) oxidizing agent ↑ ($OCl^{-1}$)

(d) $As_2O_{3(s)} + NO^{-1}_{3(aq)} \longrightarrow H_3AsO_{4(aq)} + N_2O_{3(aq)}$ (acidic soln)

(+3)(−2) (+5)(−2) (+1)(+5)(−2) (+3)(−2)

oxidation half-rxn :

$$5H_2O + As_2O_3 \longrightarrow 2H_3AsO_4 + 4H^{+1} + 4e^-$$

reduction half-rxn

$$6H^{+1} + 2NO_3^{-1} + 4e^- \longrightarrow N_2O_3 + 3H_2O$$

Combined:

$$5H_2O + As_2O_3 + 6H^{+1} + 2NO_3^{-1} + 4e^- \rightarrow 2H_3AsO_4 + 4H^{+1} + 4e^- + N_2O_3 + 3H_2O$$

reducing agent ↓ ($As_2O_3$) oxid. agent ↓ ($NO_3^{-1}$)

$$\boxed{2H_2O_{(l)} + As_2O_{3(s)} + 2H^{+1}_{(aq)} + 2NO^{-1}_{3(aq)} \rightarrow 2H_3AsO_{4(aq)} + N_2O_{3(aq)}}$$

#23 cont'd .....

(e) $MnO_{4\,(aq)}^{-1} + Br^{-1}_{(aq)} \rightarrow MnO_{2(s)} + BrO_{3\,(aq)}^{-1}$ (basic soln)

$+7$ $-2$ $\quad -1 \quad$ $+4$ $-2$ $\quad$ $+5$ $-2$

oxidation half-rxn :

$$\underline{6\,OH^{-1}} + Br^{-1}_{(aq)} + 3H_2O \longrightarrow BrO_{3\,(aq)}^{-1} + \underline{6H_2O} + 6e^-$$

reduction half-rxn :

$$2\times\left(\underline{4H_2O} + MnO_4^{-1} + 3e^- \longrightarrow MnO_{2(s)} + 2H_2O + \underline{4OH^{-1}}\right)$$

Combined :

$$\begin{aligned} &6OH^{-1} + Br^{-1} + 3H_2O && BrO_3^{-1} + 6H_2O + 6e^- \\ &+ 8H_2O + 2MnO_4^{-1} + 6e^- \longrightarrow && + 2MnO_2 + 4H_2O + 8OH^{-1} \end{aligned}$$

$$\boxed{Br^{-1}_{(aq)} + H_2O_{(l)} + 2MnO^{-1}_{4\,(aq)} \longrightarrow BrO^{-1}_{3\,(aq)} + 2MnO_{2\,(s)} + 2OH^{-1}_{(aq)}}$$

↑ reducing agent $\qquad$ ↑ oxidizing agent

(f) $Pb(OH)^{-2}_{4\,(aq)} + ClO^{-1}_{(aq)} \longrightarrow PbO_{2(s)} + Cl^{-1}_{(aq)}$ (basic soln)

$+2$ $\quad$ $+1$ $\quad$ $+4$ $\quad$ $-1$

oxidation :

$$Pb(OH)_4^{-2} \longrightarrow PbO_2 + 2H_2O + 2e^-$$

reduction:

$$2e^- + \underline{2H_2O} + ClO^{-1} \longrightarrow Cl^{-1} + \cancel{H_2O} + \underline{2OH^{-1}}$$

Combined :

$$\begin{aligned} Pb(OH)_4^{-2} + 2e^- + H_2O + ClO^{-1} \rightarrow\ & PbO_2 + 2H_2O + 2e^- \\ & + Cl^{-1} + 2OH^{-1} \end{aligned}$$

$$\boxed{Pb(OH)^{-2}_{4\,(aq)} + ClO^{-1}_{(aq)} \longrightarrow PbO_{2\,(s)} + H_2O_{(l)} + Cl^{-1}_{(aq)} + 2OH^{-1}_{(aq)}}$$

↑ reducing agent $\qquad$ ↑ oxid. agent

Chapter 20

㉔ More redox balancing!

(a) $NO_2^{-1} + Cr_2O_7^{-2} \longrightarrow Cr^{+3} + NO_3^{-1}$ (acidic soln)

+3 -2 +6 -2 +3 +5 -2

oxidation half-rxn

$(H_2O + NO_2^{-1} \longrightarrow NO_3^{-1} + 2H^{+1} + 2e^{-1}) \times 3$

reduction half-rxn:

$6e^- + 14H^{+1} + Cr_2O_7^{-2} \longrightarrow 2Cr^{+3} + 7H_2O$

Combined

$$\begin{array}{lcl} 3H_2O + 3NO_2^{-1} & \longrightarrow & 3NO_3^{-1} + 6H^{+1} + 6e^- \\ + 6e^- + 14H^{+1} + Cr_2O_7^{-2} & & + 2Cr^{+3} + 7H_2O \end{array}$$

$$\boxed{8H^{+1}_{(aq)} + 3NO_{2\,(aq)}^{-1} + Cr_2O_{7\,(aq)}^{-2} \longrightarrow 3NO_{3\,(aq)}^{-1} + 2Cr^{+3}_{(aq)} + 4H_2O_{(l)}}$$

(b) $S_{(s)} + HNO_{3(aq)} \longrightarrow H_2SO_{3(aq)} + N_2O_{(g)}$ (acid)

0 +1 +5 -2 +1 +4 -2 +1 -2

oxidation: $(3H_2O + S \rightarrow H_2SO_3 + 4H^{+1} + 4e^-) \times 2$

reduction: $8e^- + 8H^{+1} + 2HNO_3 \rightarrow N_2O + 5H_2O$

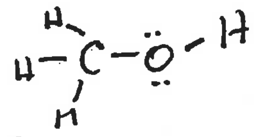
Combined:

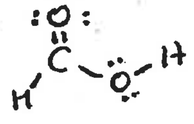
$$\begin{array}{lcl} 6H_2O + 2S & \longrightarrow & 2H_2SO_3 + 8H^{+1} + 8e^- \\ + 8e^- + 8H^{+1} + 2HNO_3 & & + N_2O + 5H_2O \end{array}$$

$$\boxed{H_2O_{(l)} + 2HNO_{3\,(aq)} + 2S_{(s)} \longrightarrow 2H_2SO_{3\,(aq)} + N_2O_{(g)}}$$

(c) $Cr_2O_7^{-2} + CH_3OH \longrightarrow HCO_2H + Cr^{+3}$ (acid)

+6 -2 +2 +3





oxidation: $(CH_3OH + H_2O \longrightarrow HCO_2H + 4H^{+1} + 4e^-) \times 3$

reduction $(14H^{+1}_{(aq)} + Cr_2O_7^{-2} + 6e^- \rightarrow 7H_2O + 2Cr^{+3}) \times 2$

Combined:

$$\begin{array}{lcl} 3CH_3OH + 3H_2O & \longrightarrow & 3HCO_2H + 12H^{+1} + 12e^- \\ + 28H^{+1} + 2Cr_2O_7^{-2} + 12e^- & & + 14H_2O + 4Cr^{+3} \end{array}$$

$$\boxed{3CH_3OH_{(aq)} + 2Cr_2O_{7\,(aq)}^{-2} + 16H^{+1}_{(aq)} \longrightarrow 3HCO_2H_{(aq)} + 4Cr^{+3}_{(aq)} + 11H_2O_{(l)}}$$

㉔ cont'd

(d) $\overset{\textcircled{+5}}{Br}\overset{\textcircled{-2}}{O}{}_{3\,(aq)}^{-1} + \overset{\textcircled{-2}}{N_2}\overset{\textcircled{+1}}{H}{}_{4\,(g)} \longrightarrow \overset{\textcircled{-1}}{Br}{}^{-1}_{(aq)} + \overset{\textcircled{0}}{N}{}_{2\,(g)}$ (acid)

oxidation: $(\; N_2H_4 \longrightarrow N_2 + 4H^{+1} + 4e^- \;) \times 3$

reduction $(\; 6H^{+1} + BrO_3^{-1} + 6e^- \longrightarrow Br^{-1} + 3H_2O \;) \times 2$

Combined: $\begin{bmatrix} 3N_2H_4 \\ + 12H^{+1} + 2BrO_3^- + 12e^- \end{bmatrix} \longrightarrow \begin{bmatrix} 3N_2 + 12H^{+1} + 12e^- \\ + 2Br^{-1} + 6H_2O \end{bmatrix}$

$$\boxed{3\,N_2H_{4\,(g)} + 2\,BrO^{-1}_{3\,(aq)} \longrightarrow 3\,N_{2\,(g)} + 2\,Br^{-1}_{(aq)} + 6\,H_2O_{(l)}}$$

(e) $\underset{\textcircled{+3}\textcircled{-2}}{NO_2^{-1}}{}_{(aq)} + \underset{\textcircled{0}}{Al}{}_{(s)} \longrightarrow \underset{\textcircled{-3}\ \textcircled{+1}}{NH_4^{+1}}{}_{(aq)} + \underset{\textcircled{+3}\ \textcircled{-2}}{AlO_2^{-1}}{}_{(aq)}$ (in $\underline{\text{basic}}$ soln)

$\underline{\text{oxidation}}$: $(\; \underline{4OH^-} + \cancel{2H_2O} + Al \longrightarrow AlO_2^{-1} + \underline{\overset{2}{\cancel{4}}H_2O} + 3e^- \;) \times 2$

$\underline{\text{reduction}}$ $6e^- + NO_2^{-1} + \underline{\overset{6}{\cancel{8}}H_2O} \longrightarrow NH_4^{+1} + \cancel{3H_2O} + \underline{8OH^{-1}}$

Combined: $\begin{bmatrix} 8OH^{-1} + 2Al \\ + 6e^- + NO_2^{-1} + 6H_2O \end{bmatrix} \rightarrow \begin{bmatrix} 2AlO_2^{-1} + 4H_2O + 6e^- \\ + NH_4^{+1} + 8OH^{-1} \end{bmatrix}$

$$\boxed{2\,Al_{(s)} + NO^{-1}_{2\,(aq)} + 2H_2O_{(l)} \longrightarrow 2\,AlO^{-1}_{2\,(aq)} + NH^{+1}_{4\,(aq)}}$$

(f) $\underset{\textcircled{+1}\ \textcircled{-1}}{H_2O_2}{}_{(aq)} + \underset{\textcircled{+4}\textcircled{-2}}{ClO_2}{}_{(aq)} \longrightarrow \underset{\textcircled{+3}\textcircled{-2}}{ClO_2^{-1}}{}_{(aq)} + \underset{\textcircled{0}}{O_2}{}_{(g)}$ (in base)

oxidation: $\underline{2OH^{-1}} + H_2O_2 \longrightarrow O_2 + \underline{2H_2O} + 2e^-$

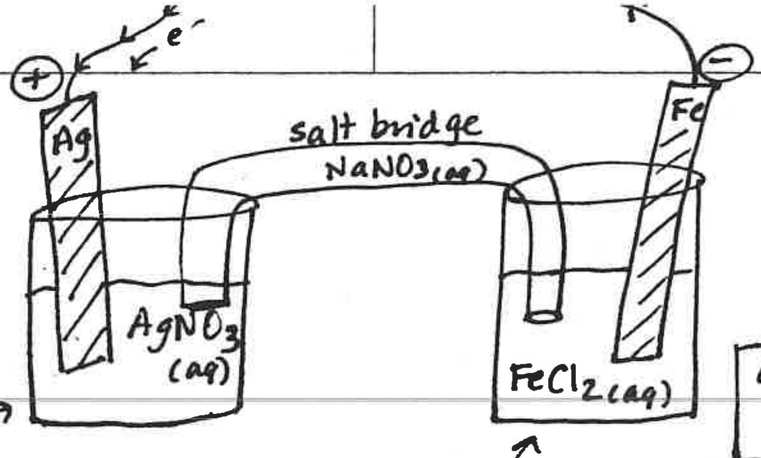
reduction: $(\; e^- + ClO_2 \longrightarrow ClO_2^{-1} \;) \times 2$

Combined: $\begin{matrix} 2OH^{-1} + H_2O_2 \\ + 2e^- + 2ClO_2 \end{matrix} \longrightarrow \begin{matrix} O_2 + 2H_2O + 2e^- \\ + 2ClO_2^{-1} \end{matrix}$

$$\boxed{2OH^{-1} + H_2O_2 + 2\,ClO_2 \longrightarrow O_2 + 2H_2O + 2\,ClO_2^{-1}}$$

#27

Chapter 20



given: overall rxn is

$Fe_{(s)} + 2Ag^{+1}_{(aq)} \rightarrow Fe^{2+}_{(aq)} + 2Ag_{(s)}$

(a) $Fe_{(s)}$ is being oxidized
$Ag^{+1}_{(aq)}$ is being reduced.

(b) Reduction half-rxn:

$Ag^{+1}_{(aq)} + 1e^- \rightarrow Ag_{(s)}$

oxidation half-rxn:

$Fe_{(s)} \rightarrow Fe^{+2}_{(aq)} + 2e^-$

(c) since Fe is oxidized, the Fe electrode is the anode
since $Ag^{+1}$ is reduced, the Ag electrode is the cathode

(d) The Fe electrode is the negative electrode
The Ag electrode is the positive electrode

(e) electrons flow from the Fe electrode to the Ag electrode.

(f) $Na^{+1}$ (or whatever cation is in the salt bridge) will migrate to the left in my picture; toward the Ag side.
$NO_3^{-1}$ (or whatever anion is in the salt bridge) will migrate to the right in my picture; toward the Fe side.

#31 Hydrogen electrode in acidic solution, if it is the cathode of a voltaic cell:

(a) The half reaction will be a reduction half rxn since it is at the cathode:

$$\boxed{2H^{+1}_{(aq)} + 2e^- \longrightarrow H_{2(g)}}$$

(b) the standard hydrogen electrode involves $H^{+1}_{(aq)}$ at a concentration of 1.0 Molar, and $H_{2(g)}$ at a partial pressure of 1.0 atm. (and a temprature of 25°C, usually!)

In general, the standard reduction potentials (Appendix E) involve 1.0 M solutions, and 1 atm.

(c) The Platinum foil provides a surface for the rxn to occur on / a place for $H^{+1}_{(aq)}$ ions to pick up electrons, if the above half-rxn is occurring: or, a place for $H_{2(g)}$ to "drop off" e- if this half rxn occurs: $H_{2(g)} \rightarrow 2H^{+1}_{(aq)} + 2e^-$.
Pt is a good conductor of electricity and a good surface catalyst. If $H^{+1}$ is being reduced, the e- travel from the other half cell and reach $H^{+1}$ through the Pt. If $H_{2(g)}$ is being oxidized, it loses its e- at the Pt surface, and these e- travel through the Pt (and other wire too; probably!) to reach the reduction half of the cell.

#33 b) std reduction potential of a standard hydrogen electrode is zero:

$$2H^{+1}_{(aq)} + 2e^- \rightarrow H_{2(g)} \quad E^\circ_{red} = 0.00\,V$$

(also:

$$H_{2(g)} \longrightarrow 2H^{+1}_{(aq)} + 2e^- \quad E^\circ_{ox} = 0.00\,V)$$

(35) given : voltaic cell rxn with $E^\circ_{rxn}$ of 1.19 V

$$Tl^{3+}_{(aq)} + 2\,Cr^{+2}_{(aq)} \longrightarrow Tl^{+1}_{(aq)} + 2\,Cr^{+3}_{(aq)}$$

(a) oxidation half-rxn (at anode)

$$Cr^{+2}_{(aq)} \longrightarrow Cr^{+3}_{(aq)} + 1e^-$$

reduction half-rxn (at cathode)

$$Tl^{+3}_{(aq)} + 2e^- \longrightarrow Tl^{+1}_{(aq)}$$

(b) calculate $E^\circ_{red}$ for the above Thallium half-rxn

Acc to appendix E (p. 1064)

$Cr^{+3} + e^- \rightarrow Cr^{+2}$ $E^\circ_{red} = -0.41$ V

so, $Cr^{+2} \longrightarrow Cr^{+3} + 1e^-$ $E^\circ_{ox} = +0.41$V

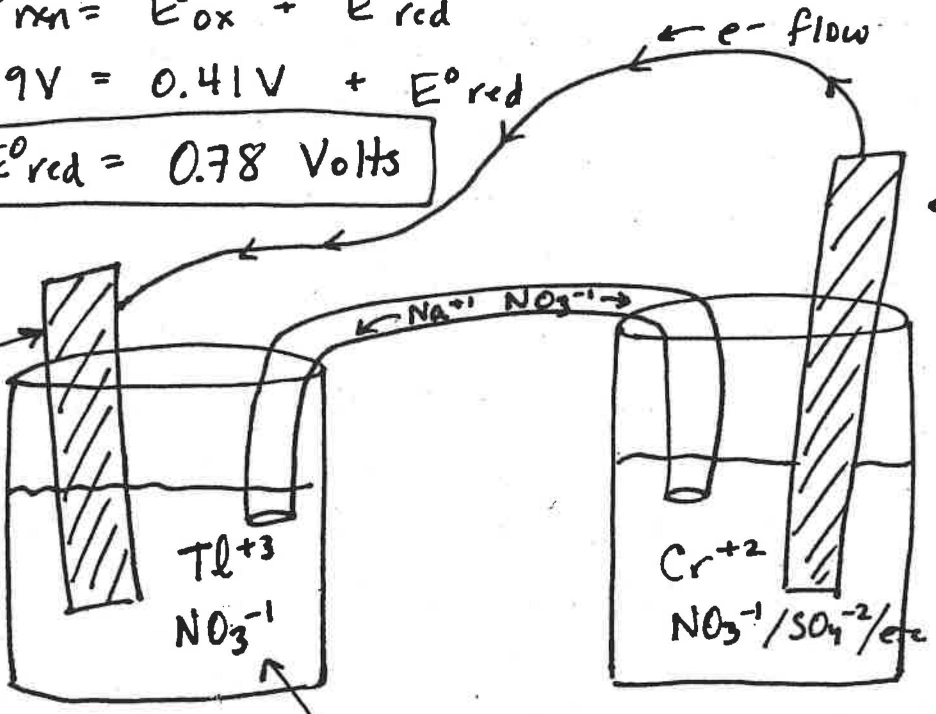
$E^\circ_{rxn} = 1.19$V (given)

$E^\circ_{rxn} = E^\circ_{ox} + E^\circ_{red}$

$1.19V = 0.41V + E^\circ_{red}$

$$\boxed{E^\circ_{red} = 0.78 \text{ Volts}}$$

(c)



graphite or Pt electrode

← Since the rxn involves no metal (solid), we could use graphite or Platinum for the electrodes.

Cr+2 is oxidized at the anode

Tl+3 is reduced at the cathode

or some other anion that won't ppt out or participate in redox rxn...

Chapter 20

#37 Calculate $E^\circ_{rxn}$ and $\Delta G^\circ_{rxn}$

(a) $Cl_{2(g)} + 2I^{-1}_{(aq)} \rightarrow 2Cl^{-1}_{(aq)} + I_{2(s)}$

Acc to Appendix E (p. 1064)

$I_2 + 2e^- \rightarrow 2I^{-1}$ $E^\circ_{red} = 0.536V$

reverse this one and change sign

$Cl_2 + 2e^- \rightarrow 2Cl^{-1}$ $E^\circ_{red} = 1.359V$

$2I^{-1} \rightarrow I_2 + 2e^-$ $E^\circ_{ox} = -.536V$

$$E^\circ_{rxn} = E^\circ_{red} + E^\circ_{ox}$$
$$= 1.359V + (-.536V)$$
$$= \boxed{0.823V} \text{ (a)}$$

$$\Delta G^\circ_{rxn} = -n\mathcal{F}E^\circ$$
$$= -\left(\frac{2 \text{ mole } e^-}{\text{mole rxn}}\right)\left(\frac{96485C}{\text{mole } e^-}\right)\left(\frac{0.823J}{C}\right) = -158814 \text{ J/mole rxn}$$

$$\boxed{\Delta G^\circ = -159 \text{ kJ/mole}}$$

(c) $Fe_{(s)} + 2Fe^{+3}_{(aq)} \rightarrow 3Fe^{+2}_{(aq)}$

$Fe^{+3}_{(aq)} + 1e^- \rightarrow Fe^{+2}_{(aq)}$ $E^\circ_{red} = 0.771V$

$Fe_{(s)} \rightarrow Fe^{+2}_{(aq)} + 2e^-$ $E^\circ_{ox} = +.440V$

acc to App. E
$Fe^{+2} + 2e^- \rightarrow Fe_{(s)}$
$E^\circ_{red} = -.440V$
So I reversed the half-rxn.

$$E^\circ_{rxn} = E^\circ_{red} + E^\circ_{ox}$$
$$= 0.771V + .440V = \boxed{1.211V} \text{ (c)}$$

$$\Delta G^\circ = -n\mathcal{F}E^\circ$$
$$= -\left(\frac{2 \text{ mole } e^-}{\text{mole rxn}}\right)\left(\frac{96485C}{\text{mole } e^-}\right)\left(\frac{1.211J}{C}\right)\left(\frac{1kJ}{1000J}\right) = \boxed{-234 \text{ kJ/mole}}$$

(d) $2NO_{3\,(aq)}^{-1} + 8H^{+1}_{(aq)} + 3Cu_{(s)} \rightarrow 2NO_{(g)} + 4H_2O_{(l)} + 3Cu^{+2}_{(aq)}$

$Cu^{+2} + 2e^- \rightarrow Cu_{(s)}$ $E^\circ_{red} = +0.337V$

reverse: $Cu_{(s)} \rightarrow Cu^{+2} + 2e^-$ $E^\circ_{ox} = -.337V$

$NO_3^{-1} + 4H^{+1} + 3e^- \rightarrow NO_{(g)} + 2H_2O_{(l)}$ $E^\circ_{red} = 0.96V$

$$E^\circ_{rxn} = E^\circ_{ox} + E^\circ_{red} = -.337V + 0.96V = 0.623V$$

$$\boxed{0.62V} \text{ (d)}$$

$$\Delta G^\circ = -n\mathcal{F}E^\circ$$
$$= -\left(\frac{6 \text{ mole } e^-}{\text{mole rxn}}\right)\left(\frac{96485C}{\text{mole } e^-}\right)\left(\frac{0.623J}{C}\right)\left(\frac{1kJ}{1000J}\right) = \boxed{-360 \text{ kJ/mole}}$$

(39) $Ag^{+1} + 1e^- \rightarrow Ag_{(s)}$ $E^\circ_{red} = 0.799\ V$

$Cu^{+2} + 2e^- \rightarrow Cu_{(s)}$ $E^\circ_{red} = 0.337\ V$

$Ni^{+2} + 2e^- \rightarrow Ni_{(s)}$ $E^\circ_{red} = -.28\ V$

$Cr^{+3} + 3e^- \rightarrow Cr_{(s)}$ $E^\circ_{red} = -.74\ V$

(a) Combine the two that would give the largest positive $E^\circ_{rxn}$.

Keep the silver half rxn as is, since it has the largest $E^\circ_{red}$
Reverse the $Cr^{+3}$ rxn since it has the most negative $E^\circ_{red}$

$Ag^{+1} + 1e^- \rightarrow Ag$ $E^\circ_{red} = .799\ V$

$Cr_{(s)} \longrightarrow Cr^{+3}_{(aq)} + 3e^-$ $E^\circ_{ox} = +0.74\ V$

$E^\circ_{rxn} = .799\ V + .74\ V = 1.539\ V \rightarrow \boxed{1.54\ V}$

overall: $\boxed{3\,Ag^{+1}_{(aq)} + Cr_{(s)} \rightarrow Cr^{+3}_{(aq)} + 3\,Ag_{(s)}}$

---

(41) 1 M $Cu(NO_3)_{2(aq)}$ w/ strip of $Cu_{(s)}$
1 M $SnSO_{4(aq)}$ w/ strip of $Sn_{(s)}$
> connected w/ salt bridge, voltmeter between electrodes

look up half rxns: $Cu^{+2}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$ $E^\circ_{red} = 0.337\ V$

$Sn^{+2}_{(aq)} + 2e^- \rightarrow Sn_{(s)}$ $E^\circ_{red} = -.136\ V$

one of the half-rxns must be reversed.
reverse the <u>Tin</u> half rxn so that the overall cell voltage comes out positive (spontaneous rxn)

$Sn \rightarrow Sn^{+2} + 2e^-$ $E^\circ_{ox} = +.136\ V$

$Cu^{+2} + 2e^- \rightarrow Cu$ $E^\circ_{red} = .337\ V$

$\boxed{Sn_{(s)} + Cu^{+2}_{(aq)} \rightarrow Sn^{+2}_{(aq)} + Cu_{(s)}}$ (c)

(d) $E^\circ_{rxn} = E^\circ_{ox} + E^\circ_{red} = 0.136\ V + 0.337\ V = \boxed{0.473\ V}$ (d)

(a) The Tin is oxidized so the solid <u>Sn electrode is the anode</u>.
The $Cu^{+2}$ is reduced so the <u>$Cu_{(s)}$ is the cathode.</u>

(b) The <u>$Cu_{(s)}$ electrode will gain mass</u> since $Cu_{(s)}$ is produced in the overall rxn.
The <u>$Sn_{(s)}$ electrode will lose mass</u> since $Sn_{(s)}$ is a reactant in the overall rxn.

Chapter 20

(43) Determine the stronger ~~reducing agent~~ in each pair. (use App. E)
(a) $Fe_{(s)}$ or $Mg_{(s)}$ (b) $Ca_{(s)}$ or $Al_{(s)}$

The stronger reducing agent would be the substance more "capable" of being oxidized, or the substance with the more positive $E^\circ_{oxidation}$

<u>from Appendix E</u>

reverse these to get <u>oxidation</u> half-rxns:

$Fe^{+2}_{(aq)} + 2e^- \rightarrow Fe_{(s)}$ $E^\circ_{red} = -.440V$
$Mg^{+2} + 2e^- \rightarrow Mg_{(s)}$ $E^\circ_{red} = -2.37V$

$Fe_{(s)} \rightarrow Fe^{+2}_{(aq)} + 2e^-$ $E^\circ_{ox} = +.440$
$Mg \rightarrow Mg^{+2} + 2e^-$ $E^\circ_{ox} = +2.37V$

$Ca^{+2}_{(aq)} + 2e^- \rightarrow Ca_{(s)}$ $E^\circ_{red} = -2.87V$
$Al^{+3}_{(aq)} + 3e^- \rightarrow Al_{(s)}$ $E^\circ_{red} = -1.66V$

$Ca \rightarrow Ca^{+2} + 2e^-$ $E^\circ_{ox} = +2.87V$
$Al \rightarrow Al^{+3} + 3e^-$ $E^\circ_{ox} = +1.66V$

(a) $Mg_{(s)}$ is a stronger reducing agent than $Fe_{(s)}$
since $2.37V > 0.440V$

(b) $Ca_{(s)}$ is a stronger reducing agent than $Al_{(s)}$
since $2.87V > 1.66V$

note that this is consistent with our <u>activity series of metals</u>! Metals at the <u>top</u> of the series are more reactive; more capable of being oxidized to form a cation!
for example Mg is higher than Fe
Ca is higher than Al.

K
Ca
Na
Mg
Al
Zn
Cr
Fe
Sn
Cu

(44) Determine the stronger oxidizing agent in each pair.
This would be the substance more "capable" of being <u>reduced</u>; the substance with the more positive $E^\circ_{reduction}$!

(a) $Cl_{2(g)}$ or $Br_{2(l)}$

$Cl_{2(g)} + 2e^- \rightarrow 2Cl^{-1}_{(aq)}$ $E^\circ_{red} = 1.359V$
$Br_{2(l)} + 2e^- \rightarrow 2Br^{-1}_{(aq)}$ $E^\circ_{red} = 1.065V$

$\boxed{Cl_2}$ is the stronger oxidizing agent, since $1.359V > 1.065V$.
(also, remember the halogen activity series! $F_2 > Cl_2 > Br_2 > I_2$)

(b) $Zn^{+2}_{(aq)}$ or $Cd^{+2}_{(aq)}$

$Zn^{+2}_{(aq)} + 2e^- \rightarrow Zn_{(s)}$ $E^\circ_{red} = -0.763V$
$Cd^{+2}_{(aq)} + 2e^- \rightarrow Cd_{(s)}$ $E^\circ_{red} = -0.403V$

$\boxed{Cd^{+2}}$ is the stronger oxidant, since $-.403 > -.763$

Chapter 20

(55) Calculate Keq for each rxn @ 298 K

(a) $Fe_{(s)} + Ni^{+2}_{(aq)} \longrightarrow Fe^{+2}_{(aq)} + Ni_{(s)}$

$Ni^{+2} + 2e^- \rightarrow Ni_{(s)} \quad E^\circ_{red} = -0.28\ V$

$Fe^{+2} + 2e^- \rightarrow Fe_{(s)} \quad E^\circ_{red} = -.440\ V$ reverse rxn

$Fe_{(s)} \rightarrow Fe^{+2} + 2e^- \quad E^\circ_{ox} = +.440\ V$

$E^\circ_{rxn} = E^\circ_{red} + E^\circ_{ox} = (-0.28\ V) + (.440\ V) = \underline{0.16\ Volts}$

$\Delta G^\circ = -n\mathcal{F}E^\circ = -\left(\frac{2\ mole\ e^-}{mole\ rxn}\right)\left(\frac{96485 C}{mole\ e^-}\right)\left(\frac{.16\ J}{C}\right) = -30875 \underline{\frac{J}{mole}}$

$\Delta G^\circ = -RT \ln Keq$

$Keq = e^{-\frac{\Delta G^\circ}{RT}} = e^{\frac{+30875\ J/mole}{(8.314\ J/mol.K)(298\ K)}} = e^{12.46188} = \boxed{2.6\times10^5}$

---

(b) $Co_{(s)} + 2H^{+1}_{(aq)} \longrightarrow Co^{+2}_{(aq)} + H_{2(g)}$

$Co_{(s)} \longrightarrow Co^{+2} + 2e^- \quad E^\circ_{ox} = -(-.277\ V) = .277\ V$

$2H^{+1}_{(aq)} + 2e^- \longrightarrow H_{2(g)} \quad E^\circ_{red} = 0.000\ V$ (std hydrogen electrode)

$E^\circ_{rxn} = E^\circ_{ox} + E^\circ_{red} = 0.277\ V + 0.000\ V = \boxed{0.277\ V}$

$\Delta G^\circ = -n\mathcal{F}E^\circ = -RT \ln Keq$

$Keq = e^{\frac{n\mathcal{F}E^\circ}{RT}} = exp\left(\frac{\left(\frac{2\ mole\ e^-}{mole\ rxn}\right)\left(\frac{96485\ C}{mole\ e^-}\right)\left(\frac{.277\ J}{C}\right)}{(8.314\ J/mol.K)(298\ K)}\right)$

$Keq = e^{21.57} = 2.343\times10^9 \rightarrow \boxed{2.34\times10^9}$

---

(c) $10\ Br^{-1}_{(aq)} + 2MnO_4{}^{-1}_{(aq)} + 16H^{+1}_{(aq)} \longrightarrow 2Mn^{+2}_{(aq)} + 8H_2O_{(l)} + 5Br_{2(l)}$

$Br_{2(l)} + 2e^- \rightarrow 2Br^{-1}_{(aq)} \quad E^\circ_{red} = 1.065\ V$ reverse

$2Br^{-1}_{(aq)} \rightarrow Br_{2(l)} + 2e^- \quad E^\circ_{ox} = -1.065\ V$

$MnO_4{}^{-1}_{(aq)} + 8H^{+1}_{(aq)} + 5e^- \rightarrow 4H_2O_{(l)} + Mn^{+2}_{(aq)} \quad E^\circ_{red} = 1.51\ Volts$

$E^\circ_{rxn} = E^\circ_{red} + E^\circ_{ox} = 1.51\ V + (-1.065\ V) = 0.44(5)\ Volts$

$Keq = exp\left(\frac{n\mathcal{F}E^\circ}{RT}\right) = exp\left(\frac{\left(\frac{10\ mole\ e^-}{mole\ rxn}\right)\left(\frac{96485\ C}{mole\ e^-}\right)\left(\frac{0.44(5)\ J}{C}\right)}{(8.314\ J/mol.K)(298\ K)}\right)$

$Keq = e^{173.298} = \boxed{1.8\times10^{75}}$

(59) Voltaic cell rxn: $Sn_{(s)} + I_{2(s)} \rightarrow Sn^{+2}_{(aq)} + 2\,I^{-1}_{(aq)}$

What is the max electrical work (in Joules) that can be done by rxn if 75.0 g Sn are consumed?

$Sn^{+2}_{(aq)} + 2e^- \rightarrow Sn_{(s)}$ $E^\circ_{red} = -0.136\text{ V}$

reverse this, and change sign of potential

$Sn_{(s)} \rightarrow Sn^{+2}_{(aq)} + 2e^-$ $E^\circ_{ox} = -(-.136\text{ V}) = +0.136\text{ V}$

$\underline{I_{2(s)} + 2e^- \rightarrow 2\,I^{-1}_{(aq)}}$ $\underline{E^\circ_{red} = 0.536\text{ V}}$

$E^\circ_{rxn} = E^\circ_{ox} + E^\circ_{red} = .136\text{ V} + .536\text{ V} = 0.672\text{ V}$

$E^\circ_{rxn} = 0.672\text{ V}$ or $\underline{\underline{0.672\text{ Joules/Coulomb}}}$

$$\left(75.0\text{ g Sn}\right)\left(\frac{1\text{ mole}}{118.710\text{ g}}\right)\left(\frac{2\text{ mole }e^-}{\text{mole Sn}}\right)\left(\frac{96485\text{ C}}{\text{mole }e^-}\right)\left(\frac{0.672\text{ J}}{\text{C}}\right) \doteq 81928\text{ J}$$

The max work that can be done is $\boxed{81900\text{J}}$ (or 81.9 kJ)

**#63** $Zn_{(s)} + 2H^{+1}_{(aq)} \longrightarrow Zn^{+2}_{(aq)} + H_{2(g)}$

How will the cell emf be affected by the following changes?

Note: $E_{cell} = E^\circ - \frac{RT}{n\mathcal{F}} \ln Q$ so as Q increases, Ecell decreases.

$Q = \frac{[Zn^{+2}][H_2]}{[H^+]^2}$

(a) pressure of $H_{2(gas)}$ increases

This would increase Q, so Ecell will decrease.

(b) Zinc nitrate is added to the anode half cell

This will increase $[Zn^{+2}]$, which will increase Q, causing Ecell to decrease

(c) NaOH is added to the cathode half-cell, decreasing $[H^+]$. This will cause Q to increase, so Ecell will decrease.

(d) Increase the surface area of anode.

this will not affect Q, so Ecell is not affected.

---

**#66** $3\,Ce^{+4}_{(aq)} + Cr_{(s)} \longrightarrow 3\,Ce^{+3}_{(aq)} + Cr^{+3}_{(aq)}$

(a) Find standard emf ($E^\circ_{cell}$)

$Ce^{+4} + 1e^- \rightarrow Ce^{+3}$ $E^\circ_{red} = 1.61V$

$Cr_{(s)} \longrightarrow Cr^{+3} + 3e^-$ $E^\circ_{ox} = +0.74V$

$E^\circ_{rxn} = E^\circ_{red} + E^\circ_{ox} = 1.61V + 0.74V = \boxed{2.35V}$

(b) calculate $E_{cell}$ if $[Ce^{+4}] = 3.0\,M$, $[Ce^{+3}] = 0.10\,M$, $[Cr^{+3}] = .010\,M$

(at 298 K)

$Q = \frac{[Ce^{+3}]^3[Cr^{+3}]}{[Ce^{+4}]^3} = \frac{(.10)^3(.010)}{(3.0)^3} = 3.7(04) \times 10^{-7}$

$E = E^\circ - \frac{RT}{n\mathcal{F}} \ln Q = 2.35V - \frac{(8.314\frac{J}{mol \cdot K})(298K)}{(\frac{3\,mole\,e^-}{mole\,rxn})(\frac{96485C}{mole\,e^-})} \ln(3.704 \times 10^{-7})$

$= 2.35V - (-.12675) = \boxed{2.48\ V}$

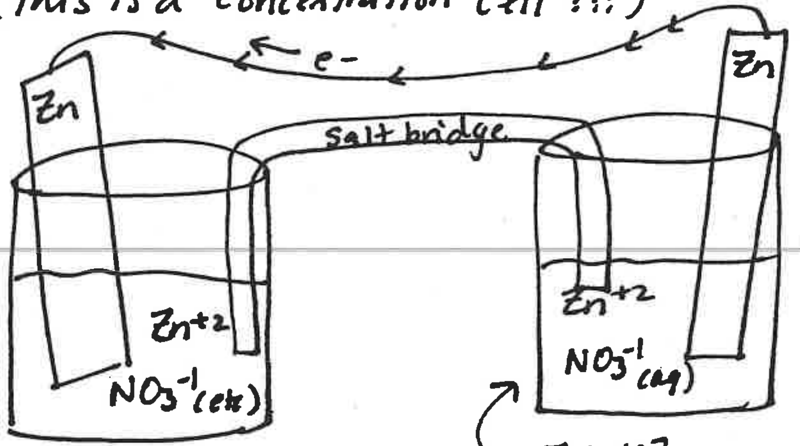
(c) Calculate $E_{cell}$ if $[Ce^{+4}] = .010M$, $[Ce^{+3}] = 2.0M$, $[Cr^{+3}] = 1.5M$

$E = E^\circ - \frac{RT}{n\mathcal{F}} \ln Q = 2.35V - \frac{(8.314\,J/mol \cdot K)(298\,K)}{(\frac{3\,mole\,e^-}{mole\,rxn})(\frac{96485\,C}{mole\,e^-})} \ln(1.2 \times 10^7)$

$Q = \frac{(2.0)^3(1.5)}{(.010)^3} = 1.2 \times 10^7$

$= 2.35V - (.1395\,V) = \boxed{2.21\ V}$

(69) Voltaic cell with two $Zn^{+2}/Zn$ electrodes.
(This is a concentration cell !!!)



$[Zn^{+2}] = 1.8$ M

$Zn^{+2} + 2e^- \longrightarrow Zn_{(s)}$

$Zn^{+2}$ will be reduced on the left (1.8 M) side since the left cell contains $Zn^{+2}$ at a higher concentration

$[Zn^{+2}] = 0.0100$ M

$Zn_{(s)} \longrightarrow Zn^{+2}_{(aq)} + 2e^-$

$Zn_{(s)}$ will be oxidized to form $Zn^{+2}_{(aq)}$ Since the right (.0100 M) cell contains $Zn^{+2}$ at the lower concentration

(a) The 1.8 M side is the cathode since reduction occurs here.

the .0100 M side is the anode since oxidation occurs here.

$Zn^{+2}_{(aq)}$ concentrated $+ 2e^- \longrightarrow Zn_{(s)}$

$Zn_{(s)} \longrightarrow 2e^- + Zn^{+2}_{(dilute)}$

$Zn^{+2}_{(aq)}$ conc'd $\longrightarrow Zn^{+2}_{(aq)}$ dilute

(b) $E^\circ_{rxn} = E^\circ_{ox} + E^\circ_{red}$

$= .763\text{ V} + -.763\text{ V} = 0$ Volts

$\boxed{E^\circ_{rxn} = E^\circ_{cell} = 0 \text{ Volts}}$ (b)

(c) $E = E^\circ - \frac{RT}{n\mathcal{F}} \ln Q$

$Q = \frac{[Zn^{+2}]_{dilute}}{[Zn^{+2}]_{conc'd}} = \frac{(.0100)}{(1.8)} = .0055(56)$

$E = 0 - \frac{(8.314 \frac{J}{mol \cdot K})(298\,K)}{\left(\frac{2 \text{ mole } e^-}{\text{mole rxn}}\right)\left(\frac{96485\,C}{\text{mole}}\right)} \ln(.005556) = \boxed{0.067 \text{ Volts}}$ (c)

(d) $[Zn^{+2}]$ will decrease on the cathode (1.8 M) side, and $[Zn^{+2}]$ will increase on the anode (.0100 M) side,
The "rxn" will proceed until the concentrations are equal!
once concns are equal, Q will equal one,
So $E = E^\circ - \frac{RT}{n\mathcal{F}} \ln(1) = E^\circ = 0$ !

Chapter 20

(72) $Sn^{+2}_{(aq)} + Pb_{(s)} \longrightarrow Sn_{(s)} + Pb^{+2}_{(aq)}$ (Voltaic cell)

(a) If cell emf ($E_{cell}$) $= +0.22\text{ V}$ when $[Sn^{+2}] = 1.0\text{ M}$, what is $[Pb^{+2}]$ ?

$Sn^{+2} + 2e^- \rightarrow Sn$ $E^\circ_{red} = -.136\text{ V}$

$Pb \rightarrow Pb^{+2} + 2e^-$ $E^\circ_{ox} = -(-.126\text{ V})$
$= .126\text{ V}$

$E^\circ_{rxn} = E^\circ_{red} + E^\circ_{ox}$

$= -.136\text{ V} + (.126\text{ V}) = -.010\text{ V}$

$E^\circ_{cell} = -.010\text{ V}$

If both $[Sn^{+2}]$ and $[Pb^{+2}]$ were 1.0 M, Ecell would be $-.010$V, which would indicate a nonspontaneous rxn, which would be an electrolytic cell, not a voltaic cell.
<u>but</u>, the $[Pb^{+2}]$ is <u>not</u> 1.0 M!

$E = E^\circ - \frac{RT}{n\mathcal{F}} \ln Q$

$.22\text{ V} = -.010\text{ V} - \frac{RT}{n\mathcal{F}} \ln Q$

$.23\text{ V} = \frac{-RT}{n\mathcal{F}} \ln Q = -\frac{(8.314)(298)}{(2)(96485)} \ln Q$

$\ln Q = -17.914$

$Q = e^{-17.914} = 1.6599 \times 10^{-8}$

$Q = \frac{[Pb^{+2}]}{[Sn^{+2}]}$ $1.6599 \times 10^{-8} = \frac{[Pb^{+2}]}{1.0\text{ M}}$ so $[Pb^{+2}] = 1.6599 \times 10^{-8}\text{ M}$

(a) $\boxed{[Pb^{+2}] = 1.7 \times 10^{-8}\text{ M}}$

(b) if $[SO_4^{-2}] = 1.0\text{ M}$ in the anode (lead) half-cell, find Ksp of $PbSO_4$.

$PbSO_{4(s)} \rightleftarrows Pb^{+2}_{(aq)} + SO_4^{-2}{}_{(aq)}$

$K_{sp} = [Pb^{+2}][SO_4^{-2}] = (1.6599 \times 10^{-8})(1.0) = \boxed{1.7 \times 10^{-8}}$ (b)

Chapter 20

(89) (a) Electrolysis is when a power supply (or "voltage source") does work in order to cause a nonspontaneous reaction to occur.

If a rxn has a positive $\Delta G^\circ_{rxn}$ (and a negative $E^\circ_{rxn}$) then the rxn can not occur spontaneously, but it can be "forced" to occur by doing work on the reactants. the power supply "pumps" electrons from the substance being oxidized to the substance being reduced.

(b) no. Electrolysis rxns are not thermodynamically favored / spontaneous. they have a positive $\Delta G^\circ_{rxn}$
a negative $E^\circ_{cell}$
and a $K_{eq}$ value of less than one.

(c) In electrolysis of molten NaCl, which process occurs at the anode?

$Na^{+1} + 1e^- \rightarrow Na$ reduction

$2Cl^{-1} \longrightarrow Cl_2 + 2e^-$ oxidation

oxidation occurs at the anode; $\boxed{2Cl^{-1}_{(l)} \rightarrow Cl_{2(g)} + 2e^-}$

(d) In electrolysis of aqueous NaCl, why is sodium metal not obtained?

$Na^{+1}_{(aq)} + 1e^- \rightarrow Na_{(s)}$ $E^\circ_{red} = -2.71\ V$

$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^{-1}_{(aq)}$ $E^\circ_{red} = -0.83\ V$

In aqueous NaCl, $H_2O_{(l)}$ is present. (!) $H_2O_{(l)}$ has a more positive reduction potential than $Na^{+1}_{(aq)}$ ($-.83\ V > -.2.71\ V$)
So $H_2O_{(l)}$ is reduced (to hydrogen gas!) instead of the $Na^{+1}$ when the voltage is applied.

Chapter 20

(91) Electrolysis of a solution containing $Cr^{+3}_{(aq)}$

(a) What mass of $Cr_{(s)}$ plates out after 2.00 days, if current is 7.60 A?

$$(2.00\,\text{day})\left(\frac{24\,\text{hr}}{\text{day}}\right)\left(\frac{3600\,\text{s}}{\text{hr}}\right)\left(\frac{7.60\,\text{C}}{\text{s}}\right)\left(\frac{1\,\text{mole e}^-}{96485\,\text{C}}\right)\left(\frac{1\,\text{mole Cr}}{3\,\text{mole e}^-}\right)\left(\frac{51.996\,\text{g}}{\text{mole}}\right)$$

$$= \boxed{236 \text{ grams chromium}}$$

(b) What amperage (current) is needed to plate 0.250 mole Cr (from $Cr^{+3}_{(aq)}$) in 8.00 hr?

$$\text{current} = \frac{\text{charge}}{\text{time}} = \frac{(.250\,\text{mole Cr})\left(\frac{3\,\text{mole e}^-}{\text{mole Cr}}\right)\left(\frac{96485\,\text{C}}{\text{mole e}^-}\right)}{(8.00\,\text{hr})(3600\,\text{s}/\text{hr})} = \frac{72364\,\text{C}}{28800\,\text{s}}$$

$$= 2.513\ \text{C/s} \longrightarrow \boxed{2.51\ \text{A}}$$

(97) is on next page and (102) is after that

(108) using a solution containing $CrO_4^{-2}$ (chromate ion) to electroplate a bumper with chromium metal!

Density of Cr = 7.20 g/cm3
thickness of $Cr_{(s)}$ layer = 0.25 mm (or 0.025 cm thick)
area of bumper = 0.32 m²

(a) how many Coulombs needed?

$$\text{mass of } Cr_{(s)} = V \cdot D = A \cdot t \cdot D$$

$$m = (.32\,\text{m}^2)\left(\frac{100\,\text{cm}}{\text{m}}\right)^2(.025\,\text{cm})\left(\frac{7.20\,\text{g}}{\text{cm}^3}\right) = 576 \text{ grams}$$

$$(576\,\text{g Cr})\left(\frac{1\,\text{mole Cr}}{51.996\,\text{g}}\right)\overset{*}{\left(\frac{6\,\text{mole e}^-}{\text{mole Cr}}\right)}\left(\frac{96485\,\text{C}}{\text{mole e}^-}\right) = \boxed{6.4\times10^6 \text{ Coulombs}}$$

(b) What current is needed if only 10.0 seconds needed?!

$$\text{current} = \frac{\text{charge}}{\text{time}} = \frac{6.41 \times 10^6\,\text{C}}{10.0\,\text{s}} = \boxed{6.4\times10^5 \text{ Amps}}$$

* to get the $\left(\frac{6\,\text{mole e}^-}{\text{mole Cr}}\right)$ I just used the fact that the oxidation # of Cr is ⑥ (+6) in $CrO_4^{-2}$ and zero in $Cr_{(s)}$. but you could write the half-rxn!

$$CrO_{4\,(aq)}^{-2} + \underline{\underline{6e^-}} + 4H_2O \rightarrow Cr_{(s)} + 8OH^{-1}$$

Chapter 20

#97 Disproportionation rxns : the same element is oxidized and reduced in the rxn. complete / balance.

(a) $Ni^{+1} \longrightarrow Ni^{+2} + Ni$

oxidation : $Ni^{+1} \rightarrow Ni^{+2} + 1e^-$

reduction : $Ni^{+1} + 1e^- \rightarrow Ni$

combined (!) $\boxed{2Ni^{+1}_{(aq)} \longrightarrow Ni^{+2}_{(aq)} + Ni_{(s)}}$

(b) $\overset{+6}{MnO_4^{-2}} \longrightarrow \overset{+7}{MnO_4^{-1}} + \overset{+4}{MnO_{2(s)}}$ (in base)

manganate ion — permanganate ion — manganese (IV) oxide (aka "manganese dioxide")

oxidation :

$(MnO_4^{-2} \longrightarrow MnO_4^{-1} + 1e^-) \times 2$

reduction : $2e^- + \underline{\overset{2}{\cancel{4}}H_2O} + MnO_4^{-2} \longrightarrow MnO_2 + \cancel{2H_2O} + \underline{4OH^-}$

combined :

$2MnO_{4\,(aq)}^{-2} + 2H_2O_{(l)} + MnO_{4\,(aq)}^{-2} \longrightarrow 2MnO_{4\,(aq)}^{-1} + MnO_{2(s)} + 4OH^{-1}_{(aq)}$

$\boxed{3MnO_{4\,(aq)}^{-2} + 2H_2O_{(l)} \longrightarrow 2MnO_{4\,(aq)}^{-1} + MnO_{2(s)} + 4OH^{-1}_{(aq)}}$

(d) $\overset{0}{Cl_{2(g)}} \longrightarrow \overset{-1}{Cl^{-1}_{(aq)}} + \overset{+1}{ClO^{-1}_{(aq)}}$ (in base)

oxidation : $\underline{4OH^{-1}} + \cancel{2H_2O} + Cl_2 \longrightarrow 2ClO^{-1} + \underline{\overset{2}{\cancel{4}}H_2O} + 2e^-$

reduction : $Cl_2 + 2e^- \longrightarrow 2Cl^{-1}$

combined : $4OH^{-1} + Cl_2 + Cl_2 + 2e^- \rightarrow 2ClO^{-1} + 2Cl^{-1} + 2H_2O + 2e^-$

divide all by 2 :

$\boxed{2OH^{-1} + Cl_2 \longrightarrow ClO^{-1} + Cl^{-1} + H_2O}$

(102) Voltaic cell with $Ni^{+2}/Ni$ and $Ag^{+1}/Ag$.

$Ag^{+1} + 1e^- \rightarrow Ag$ $E^\circ_{red} = +.799\ V$

$Ni^{+2} + 2e^- \rightarrow Ni$ $E^\circ_{red} = -.28\ V$

reverse the Nickel half-rxn so that the overall cell voltage comes out positive (voltaic cell).

$$\left.\begin{array}{ll} 2\times(Ag^{+1} + 1e^- \rightarrow Ag) & E^\circ_{red} = .799V \\ Ni \rightarrow Ni^{+2} + 2e^- & E^\circ_{ox} = +.28V \end{array}\right]$$

$$2Ag^{+1}_{(aq)} + Ni_{(s)} \rightarrow Ni^{+2}_{(aq)} + 2Ag_{(s)}$$

(a) $E^\circ_{cell} = E^\circ_{red} + E^\circ_{ox}$

$= .799V + .28V$

$E^\circ_{cell} = 1.07(9)$ Volts

$\boxed{1.08\ V}$ (a)

(b) as the cell operates, $[Ni^{+2}]$ will <u>increase</u>. $Ni^{+2}$ is produced in the rxn.

(c) The initial $[Ni^{+2}] = .0100M$, and the initial $E_{cell}$ is 1.12 V. Find initial $[Ag^{+1}]$.

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

$$1.12\ V = 1.08V - \frac{(8.314\frac{J}{mol \cdot K})(298K)}{(2\frac{mol\ e^-}{mol\ rxn})(96485\frac{C}{mol\ e^-})}\ln Q$$

$$\ln Q = \frac{.04V\ (2mol\ e^-/mol\ rxn)(96485\ C/mol\ e^-)}{-(8.314\ J/mol \cdot K)(298\ K)}$$

$$\ln Q = -3.11547$$

$$Q = e^{-3.11547} = 0.04436$$

$$Q = \frac{[Ni^{+2}]}{[Ag^{+1}]^2}$$

$$.04436 = \frac{(.0100)}{[Ag^{+1}]^2}$$

$[Ag^+] = 0.47\ M$

$\boxed{0.5\ M}$

(#108 is on the same page as #91 a couple pages back)