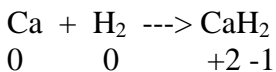
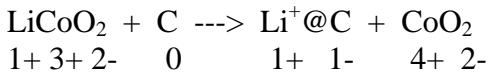
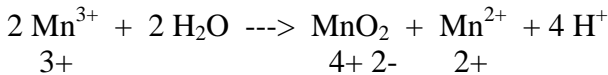
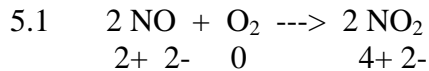


Section 2 Solutions (from Shriver and Atkins questions)



5.2 There are many potential answers, I'll just suggest one each here:
 (a) $\text{Cr}_2\text{O}_7^{2-}$ (b) Fe (c) Al (d) Al

5.3 (a) $2 \text{Cr}^{2+} + 2 \text{H}^+ \rightarrow 2 \text{Cr}^{3+} + \text{H}_2$
 (b) no reaction
 (c) no reaction
 (d) $2 \text{HClO} \rightarrow 2 \text{Cl}^- + \text{O}_2 + 2 \text{H}^+$
 (e) $\text{Zn} + 2 \text{H}^+ \rightarrow \text{Zn}^{2+} + \text{H}_2$

5.6 $2 \text{MnO}_4^- + 5 \text{H}_2\text{SO}_3 + \text{H}^+ \rightarrow 2 \text{Mn}^{2+} + 5 \text{HSO}_4^- + 3 \text{H}_2\text{O}$
 because the H^+ is in the reactants, it is on the bottom in Q in the Nernst equation; Q becomes larger (as does $\ln Q$), therefore the $(0.0592/n)\ln Q$ term becomes larger (more negative), so the E° will become more negative.

5.7 (a) $E_{pH=x}^\circ = E^\circ - \frac{0.0592}{n} \log \frac{1}{P_{\text{O}_2} [\text{H}^+]^4}$

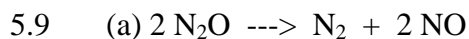
Assuming a $P_{\text{O}_2} = 1$ atm and knowing that $\log(1/x)^n = -n \log x$,

$$E_{pH}^\circ = E^\circ - \frac{4(0.0592)}{n} \text{pH}$$

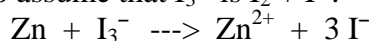
(b) by the same argument, $E_{pH}^\circ = E^\circ - \frac{6(0.0592)}{n} \text{pH}$

$$E_{pH=x}^\circ = E^\circ - \frac{0.0592}{n} \log \frac{1}{P_{\text{O}_2} [\text{H}^+]^4} = 1.23 - \frac{0.0592}{4} \log \frac{1}{(0.2)(1 \times 10^{-7})^4} = 0.805 \text{V}$$

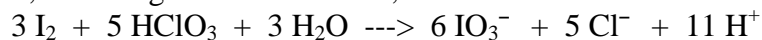
5.8 (a) disproportionation to Cl^- and ClO^-
 (b) nothing (although Cl_2 will react with water, but we can't see that from Fig. 5.18)
 (c) kinetic



(b) since the question does not specify, we'll have to assume standard (acidic) conditions; also we'll have to assume that I_3^- is $\text{I}_2 + \text{I}^-$.

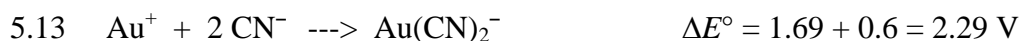
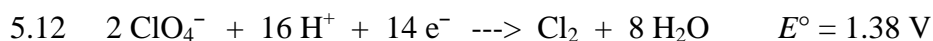


(c) again, assuming acidic conditions,



5.10 Because the pH is 14, the $[\text{OH}^-] = 1 \text{ M}$, therefore, the effective $[\text{Ni}^{2+}] = k_{\text{sp}}/[\text{OH}^-] = 1.5 \times 10^{-16}$

$$E^\circ_{14} = E^\circ - \frac{0.0592}{n} \log \frac{1}{[\text{Ni}^{2+}]} = 0.26 - \frac{0.0592}{2} \log \frac{1}{1.5 \times 10^{-16}} = -0.21$$



$$\Delta G^\circ = -nF\Delta E^\circ = -2(96485)(2.29) = -442\,000 \text{ J/mol}$$

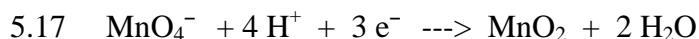
$$\Delta G^\circ = -RT \ln K \quad \text{or} \quad \ln K = \Delta G^\circ / (-RT) \quad (\text{use } R = 8.314 \text{ and } T = 298 \text{ K})$$

$$K = 3.0 \times 10^{77}$$

5.14 The potential is between 0.5 and 0.7 V for an aerated lake (use "surface water, lake/stream). Therefore, the stable species of the elements of interest would likely be Fe^{2+} , Mn^{2+} , and HSO_4^- .

5.15 We don't care about the Frost diagram.

$$E^\circ = [(0.16)(2) + (0.40)(2) + (0.60)(2)] / 6 = 0.39 \text{ V}$$



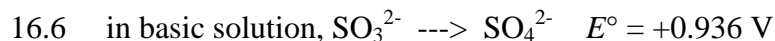
$$E^\circ = 1.69 - (4/3)(0.0592)(9) = 0.98 \text{ V}$$

5.p2 $\Delta H^\circ_{\text{rxn}} = 0 + 6(-230) - (-1908.7) - 3(-285.8) = +1383.7 \text{ kJ mol}^{-1}$

$$\Delta S^\circ_{\text{rxn}} = 34.76 + 6(-10.75) - 77.0 - 3(69.91) = -316.47 \text{ J mol}^{-1} \text{ K}^{-1}$$

therefore, $\Delta G^\circ = 1383.7 - 298(-0.31647) = 1478 \text{ kJ/mol}$

$$\Delta G^\circ = -nF\Delta E^\circ \quad \text{or} \quad \Delta E^\circ = \Delta G^\circ / (-nF) = -1478000 / (6 \cdot 96485) = -2.55 \text{ V}$$



This has the power to reduce all basic Mn species (see Resource Section 3) except $\text{Mn}(\text{OH})_2$

16.8 The following will disproportionate in acidic solution: $\text{S}_2\text{O}_6^{2-}$ and $\text{S}_2\text{O}_3^{2-}$



The following have reduction potentials greater than 0.40 V (and will therefore oxidize thiosulfate):

