

A portion of the Frost diagram for nitrogen is shown in the figure above. The points connected with the bold lines are for basic solution, and the other points are for acid solution.

- **S5.14** The possibility of finding Fe_2O_3 in a waterlogged soil? According to Figure 5.12, a typical waterlogged soil (organic rich and oxygen depleted) has a pH of about 4 and a potential of about -0.1 V. If you find the point on the Pourbaix diagram for naturally occurring iron species, Figure 5.11, you see that Fe_2O_3 is not stable and $Fe^{2^+}(aq)$ will be the predominant species. In fact, as long as the potential remained at -0.1 V, Fe^{2^+} remains the predominant species below pH = 8. Above pH = 8, Fe^{2^+} is oxidized to Fe_2O_3 at this potential. Note that for a potential of -0.1 V and a pH below 2, Fe^{2^+} is still the predominant iron species in solution, but water is reduced to H_2 .
- S5.15 The minimum temperature for reduction of MgO by carbon? According to the Ellingham diagram shown in Figure 5.16, at about 1800°C the line for the reducing agent (C) dips below the MgO line, which means that the reactions $2Mg(1) + O_2(g) \rightarrow 2MgO(s)$ and $2C(s) + O_2(g) \rightarrow 2CO(g)$ have the same free energy change at that temperature. Thus, coupling the two reactions (i.e., subtracting the first from the second) yields the overall reaction MgO(s) + C(s) \rightarrow Mg(1) + CO(g) with $\Delta G = 0$. At 1800°C or above, MgO can be conveniently reduced to Mg by carbon.
- 5.1 Suggest chemical reagents for redox transformations? (a) Oxidation of HCl to Cl₂? Assume that all of these transformations are occurring in acid solution (pH 0). Referring to Resource Section 3, you will find that the oxidation potential (not the reduction potential) for the Cl⁻/Cl₂ couple is -1.358 V. To oxidize Cl⁻ to Cl₂, you need a couple with a reduction potential more positive than 1.358 V, because then the net potential will be positive and DG will be negative. Examples include the S₂O₈²⁻/SO₄²⁻ couple ($E^{\circ} = 1.96$ V), the H₂O₂/H₂O couple ($E^{\circ} = 1.763$ V), and the α -PbO₂/Pb²⁺ couple ($E^{\circ} = 1.468$ V). Therefore, since the *oxidized* form of the couple will get *reduced* by *oxidizing* Cl⁻, you would want to use either S₂O₈²⁻, H₂O₂, or α -PbO₂ to oxidize Cl⁻ to Cl₂.

(b) Reducing $Cr^{3+}(aq)$ to $Cr^{2+}(aq)$? In this case, the reduction potential is -0.424 V. Therefore, to have a net $E^{\circ} > 0$, you need a couple with an oxidation potential more positive than 0.424 V (or a couple with a reduction potential more negative than -0.424 V). Examples include Mn^{2+}/Mn ($E^{\circ} = -1.18$ V), Zn^{2+}/Zn ($E^{\circ} = -0.7626$ V), and NH_3OH^+/N_2 ($E^{\circ} = -1.87$ V). Remember that it is the reduced form of the couple that you want to use to reduce Cr^{3+} to Cr^{2+} , so in this case you would choose metallic manganese, metallic zinc, or NH_3OH^+ .

(c) Reducing $Ag^+(aq)$ to Ag(s)? The reduction potential is 0.799 V. As above, the reduced form of any couple with a reduction potential less than (i.e., less positive than) 0.799 V will reduce Ag^+ to silver metal.

(d) Reducing I₂ to I? The reduction potential is 0.535 V. As above, the reduced form of any couple with a reduction potential less than 0.535 V will reduce iodine to iodide.

5.2 Write balanced equations, if a reaction occurs, for the following species in aerated aqueous acid? (a) Cr^{2+} ? For all of these species, you must determine whether they can be oxidized by O₂. The standard potential for the reduction O₂ + 4 H⁺ + 4 e⁻ \rightarrow 2 H₂O is 1.23 V. Therefore, only redox couples with a reduction potential less positive than 1.23 V will be driven to completion to the oxidized member of the couple by the reduction of O₂ to H₂O. Since the Cr³⁺/Cr²⁺ couple has $E^{\circ} = -0.424$ V, Cr²⁺ will be oxidized to Cr³⁺ by O₂. The balanced equation is:

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$$4Cr^{2+}(aq) + O_2(g) + 4H^+(aq) \rightarrow 4Cr^{3+}(aq) + 2H_2O(l)$$
 $E^{\circ} = 1.65 \text{ V}$

(b) Fe^{2+} ? Since the Fe^{3+}/Fe^{2+} couple has $E^{\circ} = 0.771$ V, Fe^{2+} will be oxidized to Fe^{3+} by O₂. The balanced equation is:

$$4Fe^{2^{+}}(aq) + O_{2}(g) + 4H^{+}(aq) \rightarrow 4Fe^{3^{+}}(aq) + 2H_{2}O(l) \qquad E^{6} = 0.46 V$$

(c) CI⁻? Both of the following couples have E° values, shown in parentheses, more positive than 1.23 V, so there will be no reaction when O_2 is mixed with aqueous chloride ion in acid solution: CIO_4^{-}/CI^{-} (1.287 V); CI_2/CI^{-} (1.358 V). The appropriate equation is $CI^{-}(aq) + O_2(g) \rightarrow NR$ (NR = no reaction).

(d) HOCI? Since the HClO₂/HClO couple has $E^{\circ} = 1.701$ V, HClO will not be oxidized to HClO₂ by O₂. The standard potential for the oxidation of HOCl by O₂ is -0.47 V.

(e) Zn(s)? Since the Zn^{2+}/Zn couple has $E^{\circ} = -0.763$ V, metallic zinc will be oxidized to Zn^{2+} by O₂. The balanced equation is:

 $2Zn(s) + O_2(g) + 4H^+(aq) \rightarrow 2Zn^{2+}(aq) + 2H_2(1)$ $E^{\circ} = 1.99 V$

A competing reaction is $Zn(s) + 2H^{+}(aq) \rightarrow Zn^{2+}(aq) + H_{2}(g) (E^{\circ} = 0.763 \text{ V}).$

5.3 Balanced equations for redox reactions? (a) Fe^{2+} ? When a chemical species is dissolved in aerated acidic aqueous solution, you need to think about four possible redox reactions. These are: (i) the species might oxidize water to O₂, (ii) the species might reduce water (hydronium ions) to H₂, (iii) the species might be oxidized by O₂, and (iv) the species might undergo disproportionation. In the case of Fe^{2+} , the two couples of interest are Fe^{3+}/Fe^{2+} ($E^{\circ} = 0.77$ V) and Fe^{2+}/Fe ($E^{\circ} = -0.44$ V). Consider the four possible reactions (refer to Resource Section 2 for the potentials you need): (i) The O₂/H₂O couple has $E^{\circ} = 1.229$ V, so the oxidation of water would only occur if the Fe^{2+}/Fe potential were greater than positive 1.229 V. In other words, the net reaction below is not spontaneous because the net E° is less than zero:

$$2Fe^{2*} + 4e^{-} \rightarrow 2Fe \qquad E^{\circ} = -0.44 V$$

$$2H_2O \rightarrow O_2 + 4H^{+} + 4e^{-} \qquad E^{\circ} = -1.67 V$$

$$2Fe^{2+} + 2H_2O \rightarrow 2Fe + O_2 + 4H^{+} \qquad E^{\circ} = -1.67 V$$

Therefore, Fe^{2^+} will not oxidize water. (ii) The H₂O/H₂ couple has $E^0 = 0$ V (by definition), so the reduction of water would only occur if the potential for the oxidation of Fe^{2^+} to Fe^{3^+} was positive, and it is -0.77 V (note that it is the *reduction* potential for the Fe^{3^+}/Fe^{2^+} couple that is *positive* 0.77 V). Therefore, Fe^{2^+} will not reduce water. (iii) Since the O₂/H₂O has $E^0 = 1.229$ V, the reduction of O₂ would occur as long as the potential for the oxidation of Fe^{2^+} to Fe^{3^+} was less negative than -1.229 V. Since it is only -0.77 V (see above), Fe^{2^+} will reduce O₂ and in doing so will be oxidized to Fe^{3^+} . (iv) The disproportionation of a chemical species will occur if it can act as its own oxidizing agent and reducing agent, which will occur when the potential for reduction minus the potential for oxidation is *positive*. For the Latimer diagram for iron in acidic solution (see Resource Section 3), the difference (-0.44 V) - (0.771 V) = -1.21 V, so disproportionation will not occur.

(b) Ru^{2+} ? Consider the $\operatorname{Ru}^{3+}/\operatorname{Ru}^{2+}$ ($E^{\circ} = 0.249 \text{ V}$) and $\operatorname{Ru}^{2+}/\operatorname{Ru}$ ($E^{\circ} = 0.81 \text{ V}$) couples. Since the $\operatorname{Ru}^{2+}/\operatorname{Ru}$ couple has a potential that is not more positive than 1.229 V, Ru^{2+} will not oxidize water. Also, since the $\operatorname{Ru}^{3+}/\operatorname{Ru}^{2+}$ couple has a positive potential, Ru^{2+} will not reduce water. However, since the potential for the oxidation of Ru^{2+} to Ru^{3+} , -0.249 V, is less negative than -1.229 V, Ru^{2+} will reduce O_2 and in doing so will be oxidized to Ru^{3+} . Finally, since the difference (0.81 V) – (0.249 V) is positive, Ru^{2+} will disproportionate in aqueous acid to Ru^{3+} and metallic ruthenium. It is not possible to tell from the potentials whether the reduction of O_2 by Ru^{2+} or the disproportionation of Ru^{2+} will be the faster process.

(c) HClO₂? Consider the ClO₃⁻/HClO₂ ($E^{\circ} = 1.181$ V) and HClO₂/HClO ($E^{\circ} = 1.674$ V) couples. Since the HClO₂/HClO couple has a potential that is more positive than 1.229 V, HClO₂ will oxidize water. However, since the ClO₃⁻/HClO₂ couple has a positive potential, HClO₂ will not reduce water. Since the potential for the oxidation of HClO₂ to ClO₃⁻, -1.181 V, is less negative than -1.229 V, HClO₂ will reduce O₂ and in doing so will be oxidized to ClO₃⁻. Finally, since the difference (1.674 V) – (1.181 V) is positive, HClO₂ will disproportionate in aqueous acid to ClO₃⁻ and HClO. As above, it is not possible to tell from the potentials whether the reduction of O₂ by HClO₂ or the disproportionation of HClO₂ will be the faster process.

(d) Br_2 ? Consider the Br_2/Br^- ($E^\circ = 1.065$ V) and $HBrO/Br_2$ ($E^\circ = 1.604$ V) couples. Since the Br_2/Br^- couple has a potential that is less positive than 1.229 V, Br_2 will not oxidize water. Also, since the $HBrO/Br_2$ couple has a positive potential, Br_2 will not reduce water. Since the potential for the oxidation of Br_2 to HBrO,

-1.604 V, is more negative than -1.229 V, Br₂ will not reduce O₂. Finally, since the difference (1.065 V) - (1.604 V) is negative, Br₂ will not disproportionate in aqueous acid to Br⁻ and HBrO. In fact, the equilibrium constant for the following reaction is 7.2×10^{-9} .

 $Br_2(aq) + H_2O(l) \Leftrightarrow Br(aq) + HBrO(aq) + H^+(aq)$

Write the Nernst equation for (a) The reduction of O_2 ? In general terms, the Nernst equation is given by the formula: $E = E^\circ - (RT/nF)(\ln Q)$ where Q is the reaction quotient.

For the reduction of oxygen, $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(1)$,

$$Q = 1/(p(O_2)[H^+]^4)$$
 and $E = E^\circ - [(0.059 \text{ V})/4][\log(1/(p(O_2)[H^+]^4)]$

Therefore, the potential for O_2 reduction at pH = 7 and $p(O_2) = 0.20$ bar is:

E = 1.229 V - 0.42 V = 0.81 V

(b) The reduction of Fe₂O₃(s)? For the reduction of solid iron(III) oxide, Fe₂O₃(s) + $6H^+(aq) + 6e^- \rightarrow 2$ Fe(s) + $3H_2O(1)$, we have:

 $Q = 1/[H^+]^6$ and $E = E^\circ - (RT/nF)(13.8 \text{ pH})$

since
$$pH = -\log[H^+] = -2.3 \ln[H^+]$$
 and $\log[H^+]^6 = 6 \log[H^+]$.

5.5 Calculate E, ΔG° , and K for the reduction of $\operatorname{CrO}_4^{2-}$ and $[\operatorname{Cu}(\operatorname{NH}_3)_4]^+$ by H_2 in basic solution? You must recognize that although the two values of E° are similar, the two reactions involve different numbers of electrons, n, and the expressions for ΔG° and K involve n whereas E does not:

 $\Delta G^{\circ} = -nFE$ and $\Delta G^{\circ} = -RTlnK$

For the reduction of chromate ion:

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$$\Delta G^{\circ} = -nFE = -(3)(9.65 \times 10^4 \text{ C mol}^{-1})(-0.11 \text{ V}) = 31.8 \text{ kJ mol}^{-1}$$

(recall that 1 V = 1 J C⁻¹) and, since RT = 2.48 kJ mol⁻¹ at 25°C,

$$K = \exp((-31.8 \text{ kJ mol}^{-1})/(2.48 \text{ kJ mol}^{-1}) = 2.70 \times 10^{-6}$$

For the reduction of $[Cu(NH_3)_4]^+$:

 $\Delta G^{\circ} = -nFE = -(1)(9.65 \times 10^4 \text{ C mol}^{-1})(-0.10 \text{ V}) = 9.65 \text{ kJ mol}^{-1}$

 $K = \exp((-9.65 \text{ kJ mol}^{-1})/(2.48 \text{ kJ mol}^{-1}) = 2.04 \times 10^{-2}$

So, because the reductions differ by the number of electrons required (3 versus 1), the equilibrium constants are different by a factor of about 8000.

5.6 Using Frost diagrams? (a) What happens when Cl₂ is dissolved in aqueous basic solution? The Frost diagram for chlorine in basic solution is shown below. If the points for Cl⁻ and ClO₄⁻ are connected by a straight line, Cl₂ lies above it. Therefore, Cl₂ is thermodynamically susceptible to disproportionation to Cl⁻ and ClO₄⁻ when it is dissolved in aqueous base. In practice, the oxidation of ClO⁻ is slow, so a solution of Cl⁻ and ClO⁻ is formed when Cl₂ is dissolved in aqueous base.

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(b) What happens when Cl_2 is dissolved in aqueous acid solution? The Frost diagram for chlorine in acidic solution is shown in Figure 6.16. If the points for Cl^- and any positive oxidation state of chlorine are connected by a straight line, the point for Cl_2 lies below it (if only slightly). Therefore, Cl_2 will not disproportionate. However, E° for the Cl_2/Cl^- couple, 1.36 V, is more positive than E° for the O_2/H_2O couple, 1.23 V. Therefore, Cl_2 is thermodynamically capable of oxidizing water as follows, although the reaction is very slow:

$$Cl_2(aq) + H_2O(l) \rightarrow 2Cl^-(aq) + 2H^+(aq) + \frac{1}{2}O_2(g)$$
 $E = 0.13 V$

(c) Should HClO₃ disproportionate in aqueous acid solution? The point for ClO_3^- in acidic solution on the Frost diagram lies above the single straight line connecting the points for Cl_2 and ClO_4^- . Therefore, since ClO_3^- is thermodynamically unstable with respect to disproportionation in acidic solution (i.e., it *should* disproportionate), the failure of it to exhibit any observable disproportionation must be due to a kinetic barrier.

5.7 Write equations for the following reactions: (a) N₂O is bubbled into aqueous NaOH solution? The Frost diagram for nitrogen in basic solution, showing some pertinent species, is shown below:



Inspection of the diagram shows that N_2O lies above the line connecting N_2 and NO_3^- . Therefore, N_2O is thermodynamically susceptible to disproportionation to N_2 and NO_3^- in basic solution:

 $5N_2O(aq) + 2OH(aq) \rightarrow 2NO_3(aq) + 4N_2(g) + H_2O(l)$

However, the redox reactions of nitrogen oxides and oxyanions are generally slow. In practice, N_2O has been found to be inert.

(b) Zinc metal is added to aqueous acidic sodium triiodide? The overall reaction is:

$$Zn(s) + I_3(aq) \rightarrow Zn^{2+}(aq) + 3I(aq)$$

Since E° values for the Zn^{2+}/Zn and I_3^{-}/I^{-} couples are -0.76 V and 0.54 V, respectively (these potentials are given in Resource Section 3), E° for the net reaction above is 0.54 V + 0.76 V = 1.30 V. Since the net potential is positive, this is a favorable reaction, and it should be kinetically facile if the zinc metal is finely divided and thus well exposed to the solution.

(c) I_2 is added to excess aqueous acidic HClO₃? Since E° values for the I_2/I^- and ClO_3^-/ClO_4^- couples are 0.54 V and -1.20 V, respectively (see Resource Section 2), the net reaction involving the reduction of I_2 to I^- and the oxidation of ClO_3^- to ClO_4^- will have a net negative potential, $E^\circ = 0.54$ V + (-1.20 V) = -0.66 V. Therefore, this net reaction will not occur. However, since E° values for the IO_3^-/I_2 and ClO_3^-/Cl^- couples are 1.19 V and 1.47 V, respectively, the following net reaction will occur, with a net $E^\circ = 0.28$ V:

$$5 [ClO_{3}^{-}(aq) + 6H^{+}(aq) + 6e^{-} \rightarrow Cl^{-}(aq) + 3H_{2}O(l)]$$
reduction

$$3 [I_{2}(s) + 6H_{2}O(l) \rightarrow 2IO_{3}^{-}(aq) + 12H^{+}(aq) + 10e^{-}]$$
oxidation

 $3I_2(s) + 5CIO_3^-(aq) + 3H_2O(l) \rightarrow 6IO_3^-(aq) + 5Cl^-(aq) + 6H_1(aq)$

Will acid or base most favor the following half-reactions? (a) $Mn^{2+} \rightarrow MnO_4^{-?}$ You can answer questions such as this by applying Le Chatelier's principle to the complete, balanced half-reaction, which in this case is:

 $Mn^{2+}(aq) + 4H_2O(l) \rightarrow MnO_4^{-}(aq) + 8H^{+}(aq) + 5e^{-1}$

Since hydrogen ions are produced by this oxidation half-reaction, raising the pH will favor the reaction. (Alternatively, you could come to the same conclusion by using the Nernst equation.) Thus this reaction is favored in basic solution. At a sufficiently high pH, Mn^{2+} will precipitate as $Mn(OH)_2$. The rate of oxidation for this solid will be slower than for dissolved species.

(b) $CIO_4^- \rightarrow CIO_3^-$? The balanced half-reaction is:

 $ClO_4^-(aq) + 2H^+(aq) + 2e^- \rightarrow ClO_3^-(aq) + H_2O(l)$

Since hydrogen ions are consumed by this reduction half-reaction, lowering the pH will favor the reaction. Thus this reaction is favored in acidic solution. This is the reason that perchloric acid is a dangerous oxidizing agent, even though salts of the perchlorate ion are frequently stable in neutral or basic solution.

(c) $H_2O_2 \rightarrow O_2$? The balanced half-reaction is:

$$H_2O_2(aq) \rightarrow O_2(g) + 2H^+(aq) + 2e^-$$

Since hydrogen ions are produced by this oxidation half-reaction, raising the pH will favor the reaction. Thus, the reaction is favored in basic solution. This means that hydrogen peroxide is a better reducing agent in base than in acid.

(d) $I_2 \rightarrow 2\Gamma$? Since protons are neither consumed nor produced in this reduction half-reaction, and since Γ is not protonated in aqueous solution (because HI is a very strong acid), this reaction has the same potential in acidic or basic solution, 0.535 V (this can be confirmed by consulting Resource Section 3).

Determine the standard potential for the reduction of ClO₄⁻ to Cl₂? The Latimer diagram for chlorine in acidic solution is given in Resource Section 3 and the relevant portion of it is reproduced below:



To determine the potential for any couple, you must calculate the *weighted average* of the potentials of intervening couples. In general terms it is:

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$$(n_1 E^{\circ}_1 + n_2 E^{\circ}_2 + \dots + n_n E^{\circ}_n) / (n_1 + n_2 + \dots + n_n)$$

and in this specific case it is:

$$[(2)(1.201 \text{ V}) + (2)(1.181 \text{ V}) + (2)(1.674) + (1)(1.630 \text{ V})]/(2 + 2 + 2 + 1) = 1.392 \text{ V}$$

Thus, the standard potential for the ClO_4 -/ Cl_2 couple is 1.392 V. The half-reaction for this reduction is:

$$2ClO_4^{-}(aq) + 16H^{+}(aq) + 14e^{-} \rightarrow Cl_2(g) + 8H_2O(l)$$

Note that the point for ClO_4^- at pH 0 in the Frost diagram shown in Figure 5.18 has a y value of ~9.7, which is equal to NE^o/V or 7(1.392).

5.10 Calculate the equilibrium constant for $Au^+(aq) + 2CN^-(aq) \rightarrow [Au(CN)_2]^-(aq)$? To calculate an equilibrium constant using thermodynamic data, you can make use of the expressions $\Delta G = -RT \ln K$ and $\Delta G = -nFE$. You can use the given potential data to calculate ΔG for each of the two half-reactions, then you can use Hess's Law to calculate ΔG for the overall process, and finally calculate K from the net ΔG .

The net reaction $Au^+(aq) + 2 CN^-(aq) \rightarrow [Au(CN)_2]^-(aq)$ is the following sum:

$$Au^{+}(aq) + e^{-} \rightarrow Au(s)$$
$$Au(s) + 2CN^{-}(aq) \rightarrow [Au(CN)_{2}]^{-}(aq)$$

 $Au^+(aq) + 2 CN^-(aq) \rightarrow [Au(CN)_2]^-(aq)$

 ΔG for the first reaction is $-nFE = -(1)(96.5 \text{ kJ mol}^{-1} \text{ V}^{-1})(1.69 \text{ V}) = -163 \text{ kJ mol}^{-1}$. ΔG for the second reaction is $-(1)(96.5 \text{ kJ mol}^{-1} \text{ V}^{-1})(0.6 \text{ V}) = -58 \text{ kJ mol}^{-1}$. The net ΔG is the sum of these two values, $-221 \text{ kJ} \text{ mol}^{-1}$. Therefore, assuming that T = 298 K:

 $K = \exp[(221 \text{ kJ mol}^{-1}) / (8.31 \text{ J } \text{K}^{-1} \text{mol}^{-1})(298)] = \exp(89.2) = 5.7 \times 10^{38}$

5.11 Find the approximate potential of an aerated lake at pH = 6, and predict the predominant species? (a) Fe? According to Figure 5.12, the potential range for surface water at pH 6 is 0.5 - 0.6 V, so a value of 0.55 V can be used as the approximate potential of an aerated lake at this pH. Inspection of the Pourbaix diagram for iron (Figure 5.11) shows that at pH 6 and E = 0.55 V, the stable species of iron is Fe(OH)₃. Therefore, this compound of iron would predominate.

(b) Mn? Inspection of the Pourbaix diagram for manganese (Figure 5.13) shows that at pH 6 and E = 0.55 V, the stable species of manganese is Mn₂O₃. Therefore, this compound of manganese would predominate.

(c) S? At pH 0, the potential for the HSO_4^-/S couple is 0.387 V (this value was calculated using the weighted average of the potentials given in the Latimer diagram for sulfur in Resource Section 3), so the lake will oxidize S₈ all the way to HSO_4^- . At pH 14, the potentials for intervening couples are all negative, so SO_4^{2-} would again predominate. Therefore, HSO_4^- is the predominant sulfur species at pH 6.

5.12 What is the maximum *E* for an anaerobic environment rich in Fe^{2+} and H_2S ? Any species capable of oxidizing either Fe^{2+} or H_2S at pH 6 cannot survive in this environment. According to the Pourbaix diagram for iron (Figure 5.11), the potential for the $Fe(OH)_3/Fe^{2+}$ couple at pH 6 is approximately 0.3 V. Using the Latimer diagrams for sulfur in acid and base (see Resource Section 3), the H_2S , S potential at pH 6 can be calculated as follows:

$$0.14 \text{ V} - (6/14)[0.14 - (-0.45)] = -0.11 \text{ V}$$

Any potential higher than this will oxidize hydrogen sulfide to elemental sulfur. Therefore, as long as H_2S is present, the maximum potential possible is approximately -0.1 V.

- 5.13 How will dta^{4-} complexation affect $M^{2+} \rightarrow M^{0}$ reductions? Since dta^{4-} forms very stable complexes with $M^{2+}(aq)$ ions of period 4 *d*-block elements but *not* with the zerovalent metal atoms, the reduction of a $M(edta)^{2-}$ complex will be more difficult than the reduction of the analogous M^{2+} aqua ion. Since the reductions are more difficult, the reduction potentials become less positive (or more negative, as the case may be). The reduction of the $M(edta)^{2-}$ complex includes a decomplexation step, with a positive free energy change. The reduction of $M^{2+}(aq)$ does not require this additional expenditure of free energy.
- 5.14 Which of the boundaries depend on the choice of $[Fe^{2+}]$? Any boundary between a soluble species and an insoluble species will change as the concentration of the soluble species changes. For example, consider the line separating $Fe^{2+}(aq)$ from $Fe(OH)_3(s)$ in Figure 5.11. As shown in the text, $E = E^0 (0.059)$