

CHEM 1423
Chapters 21
Homework Solutions

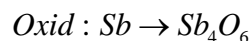
TEXTBOOK HOMEWORK

Note: In various homework questions, the author is assuming that you're looking up the Reduction Potential in Appendix D. On a test, you will be given the required Reduction Potentials. In addition, the table will be displayed on the web site.

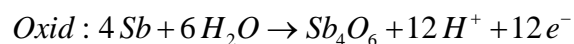
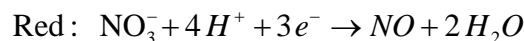
- 21.5** (a) Cl^- is oxidized
(b) MnO_4^- is reduced
(c) MnO_4^- is the oxidizing agent
(d) Cl^- is the reducing agent
(e) Electrons flow from Cl^- which is losing electrons,
to MnO_4^- which is gaining electrons
(f) $8 \text{H}_2\text{SO}_4(\text{aq}) + 2 \text{KMnO}_4(\text{aq}) + 10 \text{KCl}(\text{aq}) \rightarrow$
 $2 \text{MnSO}_4 + 5 \text{Cl}_2(\text{g}) + 8 \text{H}_2\text{O}(\text{l}) + 6 \text{K}_2\text{SO}_4(\text{aq})$

- 21.9** (a) $\text{Sb} + \text{NO}_3^- \rightarrow \text{Sb}_4\text{O}_6 + \text{NO}$ (*acid*)

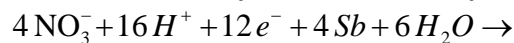
Initial Half Reactions



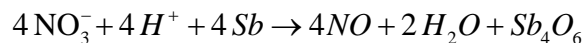
Balanced Half Reactions

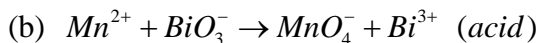


Mult Red Rxn. by 4, Oxid. Rxn. by 1 and add

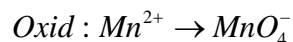
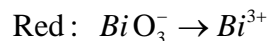


Cancel to get final balanced reaction

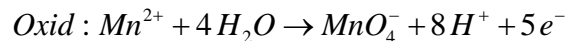
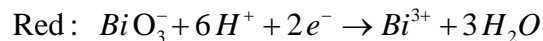




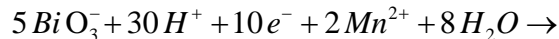
Initial Half Reactions



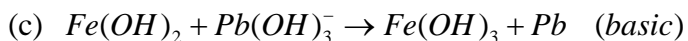
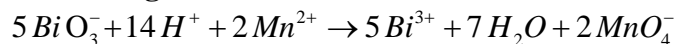
Balanced Half Reactions



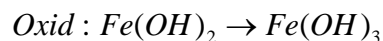
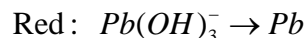
Mult Red Rxn. by 5, Oxid. Rxn. by 2 and add



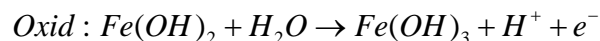
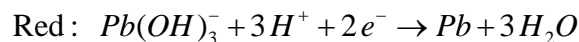
Cancel to get final balanced reaction



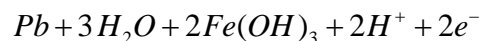
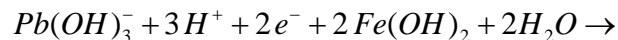
Initial Half Reactions



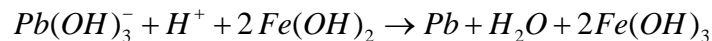
Balanced Half Reactions



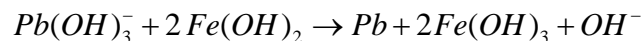
Mult Red Rxn. by 1, Oxid. Rxn. by 2 and add

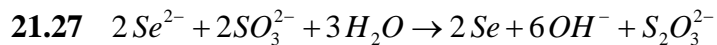


Cancel to get final balanced reaction IN ACID SOLUTION



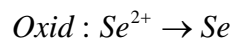
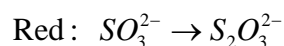
Add OH⁻ to each side and cancel waters to get final balanced reaction in BASIC SOLUTION



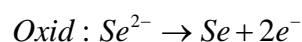
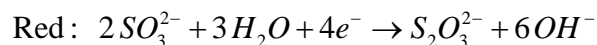


(a) Balanced Half Reactions

Initial Half Reactions



Half Reactions balanced in basic solution



(b) Given $E_{cell}^{\circ} = +0.35\text{ V}$ and $E_{red}^{\circ}(SO_3^{2-}) = -0.57\text{ V}$, what is $E_{red}^{\circ}(Se)$?

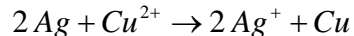
$$E_{cell}^{\circ} = +0.35\text{ V} = E_{red}^{\circ}[SO_3^{2-}] + E_{ox}^{\circ}[Se^{2-}] = -0.57\text{ V} + E_{ox}^{\circ}[Se^{2-}]$$

$$E_{ox}^{\circ}[Se^{2-}] = +0.35 + 0.57 = +0.92\text{ V}$$

$$E_{red}^{\circ}[Se] = -E_{ox}^{\circ}[Se^{2-}] = -0.92\text{ V}$$

21.33 Reduction potentials are taken from Appendix D.

(a)



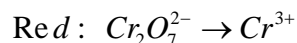
$$E_{cell}^{\circ} = E_{red}^{\circ}(Cu^{2+}) + E_{ox}^{\circ}(Ag) = E_{red}^{\circ}(Cu^{2+}) - E_{red}^{\circ}(Ag^+)$$

$$= +0.34 - 0.80 = -0.46\text{ V}$$

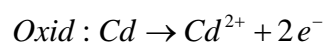
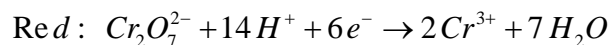
This reaction is NOT spontaneous.

(b) Unlike (a) [and c)], this reaction cannot be readily balanced by inspection.

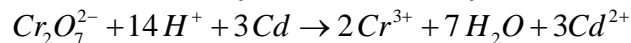
Initial Half Reactions



Balanced Half Reactions



Mult Red Rxn. by 1, Oxid. Rxn. by 3 and add

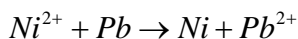


$$E_{cell}^{\circ} = E_{red}^{\circ}(Cr_2O_7^{2-}) + E_{ox}^{\circ}(Cd) = E_{red}^{\circ}(Cr_2O_7^{2-}) - E_{red}^{\circ}(Cd^{2+})$$

$$= +1.33 - (-0.40) = +1.73\text{ V}$$

This reaction IS Spontaneous

(c)

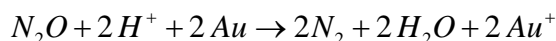


$$\begin{aligned} E_{cell}^{\circ} &= E_{red}^{\circ}(Ni^{2+}) + E_{oxid}^{\circ}(Pb) = E_{red}^{\circ}(Ni^{2+}) - E_{red}^{\circ}(Pb^{2+}) \\ &= -0.25 - (-0.13) = -0.12V \end{aligned}$$

This reaction is NOT spontaneous.

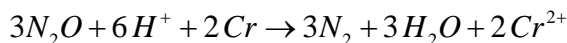
21.36 For a reaction to be spontaneous, the species with the higher reduction potential must be reduced, while the species with the lower reduction potential must be oxidized.

a. N_2O is reduced, Au is oxidized.



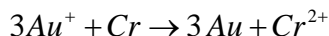
$$\begin{aligned} E_{cell}^{\circ} &= E_{red}^{\circ}(N_2O) + E_{oxid}^{\circ}(Au) = E_{red}^{\circ}(N_2O) - E_{red}^{\circ}(Au^+) \\ &= +1.77 - (+1.69) = +0.08V \end{aligned}$$

b. N_2O is reduced, Cr is oxidized



$$\begin{aligned} E_{cell}^{\circ} &= E_{red}^{\circ}(N_2O) + E_{oxid}^{\circ}(Cr) = E_{red}^{\circ}(N_2O) - E_{red}^{\circ}(Cr^{2+}) \\ &= +1.77 - (-0.74) = +2.51V \end{aligned}$$

c. Au^+ is reduced, Cr is oxidized



$$\begin{aligned} E_{cell}^{\circ} &= E_{red}^{\circ}(Au^+) + E_{oxid}^{\circ}(Cr) = E_{red}^{\circ}(Au^+) - E_{red}^{\circ}(Cr^{2+}) \\ &= +1.69 - (-0.74) = +2.43V \end{aligned}$$

Ranking Oxidizing Agents

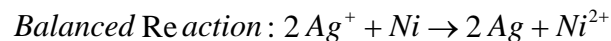
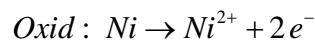
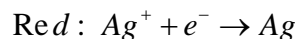
Because an oxidizing agent is reduced, the strongest oxidizing agent will have the highest Reduction Potential

Therefore: $N_2O > Au^+ > Cr^{3+}$

Ranking Reducing Agents

Because the reducing agent is oxidized, the strongest reducing agent will have the highest Oxidation Potential, which corresponds to the lowest Reduction Potential; i.e. the order is exactly the opposite from the order of oxidizing agents

Therefore: $Cr > Au > N_2$

20.45 Reduction Potentials taken from Appendix D**(a) Ni and Ag⁺**

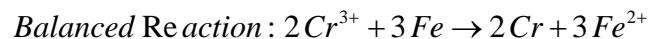
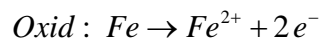
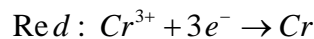
$$n = 2$$

$$\begin{aligned} E_{\text{cell}}^{\circ} &= E_{\text{red}}^{\circ}(\text{Ag}^+) + E_{\text{oxid}}^{\circ}(\text{Ni}) = E_{\text{red}}^{\circ}(\text{Ag}^+) - E_{\text{red}}^{\circ}(\text{Ni}^{2+}) \\ &= +0.80 - (-0.25) = 1.05\text{V} \end{aligned}$$

$$E_{\text{cell}}^{\circ} = \frac{0.0592}{n} \log(K)$$

$$\log(K) = \frac{n \cdot E_{\text{cell}}^{\circ}}{0.0592} = \frac{2(1.05)}{0.0592} = 35.47$$

$$K = 10^{35.47} = 3.0 \times 10^{35}$$

(b) Fe and Cr³⁺

$$n = 6$$

$$\begin{aligned} E_{\text{cell}}^{\circ} &= E_{\text{red}}^{\circ}(\text{Cr}^{3+}) + E_{\text{oxid}}^{\circ}(\text{Fe}) = E_{\text{red}}^{\circ}(\text{Cr}^{3+}) - E_{\text{red}}^{\circ}(\text{Fe}^{2+}) \\ &= -0.74 - (-0.44) = -0.30\text{V} \end{aligned}$$

$$E_{\text{cell}}^{\circ} = \frac{0.0592}{n} \log(K)$$

$$\log(K) = \frac{n \cdot E_{\text{cell}}^{\circ}}{0.0592} = \frac{6(-0.30)}{0.0592} = -30.41$$

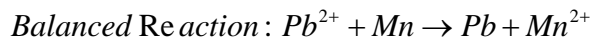
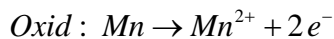
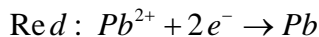
$$K = 10^{30.41} = 3.9 \times 10^{-31} \approx 4 \times 10^{-31}$$

21.50 $n = 2$, $K = 0.065$

$$E_{\text{cell}}^{\circ} = \frac{0.0592}{2} \log(0.065) = -0.035\text{V}$$

$$\begin{aligned} \Delta G^{\circ} &= -nFE_{\text{cell}}^{\circ} = -(2\text{mol})(96,500\text{C/mol})(-0.035\text{V}) \\ &= +6780\text{C} \cdot \text{V} = +6780\text{J} \approx +6.8\text{kJ} \end{aligned}$$

21.52 Note: The problem as written doesn't tell you which species is being oxidized and which is being reduced. As written, you are supposed to write the reaction so that it is spontaneous (i.e. positive E_{cell}°). However, on a test, I would tell you the reaction; e.g. this reaction is $\text{Mn}|\text{Mn}^{2+}||\text{Pb}^{2+}|\text{Pb}$



$$\begin{aligned} E_{\text{cell}}^{\circ} &= E_{\text{red}}^{\circ}(\text{Pb}^{2+}) + E_{\text{oxid}}^{\circ}(\text{Mn}) = E_{\text{red}}^{\circ}(\text{Pb}^{2+}) - E_{\text{red}}^{\circ}(\text{Mn}^{2+}) \\ &= -0.13 - (-1.18) = +1.05\text{V} \end{aligned}$$

$$n = 2$$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.592}{n} \log(Q) = E_{\text{cell}}^{\circ} - \frac{0.592}{n} \log\left(\frac{[\text{Mn}^{2+}]}{[\text{Pb}^{2+}]}\right)$$

$$0.44\text{V} = 1.05\text{V} - \frac{0.592}{2} \log\left(\frac{1.4\text{M}}{[\text{Pb}^{2+}]}\right)$$

$$\frac{0.592}{2} \log\left(\frac{1.4\text{M}}{[\text{Pb}^{2+}]}\right) = 1.05 - 0.44 = +0.61\text{V}$$

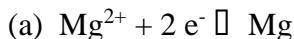
$$\log\left(\frac{1.4\text{M}}{[\text{Pb}^{2+}]}\right) = (0.61) \cdot \frac{2}{0.592} = 20.61$$

$$\frac{1.4\text{M}}{[\text{Pb}^{2+}]} = 10^{20.61} = 4.06 \times 10^{20}$$

$$[\text{Pb}^{2+}] = \frac{1.4\text{M}}{4.06 \times 10^{20}} = 3.5 \times 10^{-21}\text{M}$$

Note: The above answer is correct. However, I don't think you would ever really have a 21 order of magnitude difference between half-cell reaction concentrations.

21.76 $M(\text{Mg}) = 24.3\text{ g/mol}$



$$n(\text{Mg}) = 45.6\text{ g Mg} \cdot \frac{1\text{ mol Mg}}{24.3\text{ g Mg}} = 1.865\text{ mol Mg}$$

$$n(e^{-}) = 1.865\text{ mol Mg} \cdot \frac{1\text{ mol } e^{-}}{1\text{ mol Mg}} = 3.75\text{ mol } e^{-}$$

$$(b) \quad q = 3.75 \text{ mol } e^{-} \cdot \frac{96,500 \text{ C}}{1 \text{ mol } e^{-}} = 3.62 \times 10^5 \text{ C}$$

$$(c) \quad t = 3.5 \text{ hr} \times 3600 \text{ s/hr} = 12,600 \text{ s}$$
$$q = i \cdot t$$

$$i = \frac{q}{t} = \frac{3.62 \times 10^5 \text{ C}}{12,600 \text{ s}} = 28.7 \text{ C/s} = 28.7 \text{ A}$$

21.80 $\text{Zn}^{2+} + 2 e^{-} \rightarrow \text{Zn}$, $M(\text{Zn}) = 65.4 \text{ g/mol}$, $i = 21.0 \text{ A} = 21.0 \text{ C/s}$

$$n(\text{Zn}) = 65.5 \text{ g Zn} \cdot \frac{1 \text{ mol Zn}}{65.4 \text{ g Zn}} = 1.0015 \text{ mol Zn}$$

$$n(e^{-}) = 1.0015 \text{ mol Zn} \cdot \frac{2 \text{ mol } e^{-}}{1 \text{ mol Zn}} = 2.003 \text{ mol } e^{-}$$

$$q = 2.003 \text{ mol } e^{-} \cdot \frac{96,500 \text{ C}}{1 \text{ mol } e^{-}} = 1.93 \times 10^5 \text{ C}$$

$$q = i \cdot t$$

$$t = \frac{q}{i} = \frac{1.93 \times 10^5 \text{ C}}{21.0 \text{ C/s}} = 9.20 \times 10^3 \text{ s}$$

21.84 $\text{Zn}^{2+} + 2 e^{-} \rightarrow \text{Zn}$, $M(\text{Zn}) = 65.4 \text{ g/mol}$

$$i = 0.855 \text{ A} = 0.855 \text{ C/s}, \quad t = 2.5 \text{ days} \times 24 \text{ hr/day} \times 3600 \text{ s/hr} = 2.16 \times 10^5 \text{ s}$$

$$q = i \cdot t = (0.855 \text{ C/s})(2.16 \times 10^5 \text{ s}) = 1.85 \times 10^5 \text{ C}$$

$$n(e^{-}) = 1.85 \times 10^5 \text{ C} \cdot \frac{1 \text{ mol } e^{-}}{96,500 \text{ C}} = 1.914 \text{ mol } e^{-}$$

$$n(\text{Zn}) = 1.91 \text{ mol } e^{-} \cdot \frac{1 \text{ mol Zn}}{2 \text{ mol } e^{-}} = 0.957 \text{ mol Zn}$$

$$\text{mass}(\text{Zn}) = 0.957 \text{ mol Zn} \cdot \frac{65.4 \text{ g Zn}}{1 \text{ mol Zn}} = 62.5 \text{ g Zn}$$