Chapter 11

Electrochemistry & Electron Transfer

1. **Define the oxidation and reduction processes.**

   Oxidation is the loss of electrons and reduction is the gain of electrons. Oxidation results in an increase in an atom's oxidation state and reduction results in a lowering (reduction) of the oxidation state.

3. **Distinguish between donor and acceptor orbitals. Which orbital is on the oxidizing agent?**

   Transferred electrons move from the donor to the acceptor orbital in a redox reaction. The donor orbital is on the reducing agent and the acceptor orbital is on the oxidizing agent.

5. **What change in potential does an electron experience when it moves from a potential of +0.5 V to one at -0.3 V? Is this a spontaneous process?**
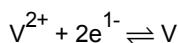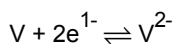
   Change in potential = final potential – initial potential = -0.3 – 0.5 = -0.8 V. An electron's free energy is greater at the more positive potential, so moving from high potential to low potential is moving from low free energy to high. $\Delta G > 0$, so the process is not spontaneous.

7. **The A/A^{1+} couple is 0.5 V above the B/B^{2+} couple. Which of the four species is the best oxidizing agent? Which is the best reducing agent. Write the balanced chemical equation for the spontaneous process that occurs when the two couples are connected in a galvanic cell.**

   The A/A^{1+} couple is at the higher potential, so it is at lower free energy. The direction of spontaneous electron flow is "downhill" in free energy, i.e., $A \rightarrow B^{2+}$. Consequently, A is the best reducing agent and B^{2+} is the best oxidizing agent. The spontaneous reaction occurring when the couples are connected is $2A + B^{2+} \rightarrow 2A^{1+} + B$.

9. **The energy level diagrams for elements V and W are shown in the text. Assume that the redox orbital energies are the dominant term in ΔG.**

   a) **Write the standard reduction half-reactions for V, W, V^{2+} and W^{2+} and order them from most negative at top to most positive at the bottom.**
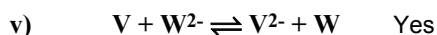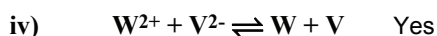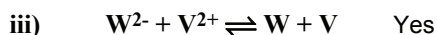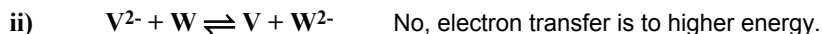
   $W + 2e^{1-} \rightleftharpoons W^{2-}$ highest energy redox orbital

   $V + 2e^{1-} \rightleftharpoons V^{2-}$

   $V^{2+} + 2e^{1-} \rightleftharpoons V$

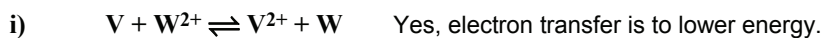 $W^{2+} + 2e^{1-} \rightleftharpoons W$ lowest energy redox orbital

   b) **Of the species, V^{2+}, W^{2+}, V, W, V^{2-}, W^{2-}, which is the best oxidizing agent? Which is the best reducing agent?**
   The best oxidizing agent is W^{2+}, lowest unfilled orbital.
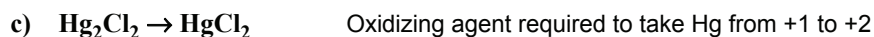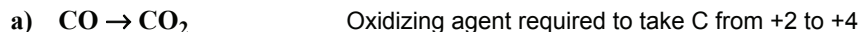   The best reducing agent is W^{2-}, highest occupied orbital.

   c) **Indicate whether each of the following electron transfer reactions would be extensive:**

   i) $V + W^{2+} \rightleftharpoons V^{2+} + W$ Yes, electron transfer is to lower energy.

   ii) $V^{2-} + W \rightleftharpoons V + W^{2-}$ No, electron transfer is to higher energy.

   iii) $W^{2-} + V^{2+} \rightleftharpoons W + V$ Yes

   iv) $W^{2+} + V^{2-} \rightleftharpoons W + V$ Yes

   v) $V + W^{2-} \rightleftharpoons V^{2-} + W$ Yes

11. **Determine the oxidation state of carbon in each of the following compounds:**

    a) CH_4 (-4)   b) CH_2O (0)   c) CO_2 (+4)   d) CH_3F (-2)   e) CH_3OH (-2)
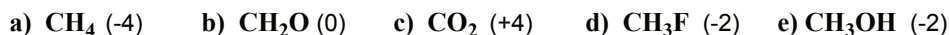
13. **Indicate whether each of the following chemical conversions requires an oxidant, a reductant, or neither:**

    a) $CO \rightarrow CO_2$ Oxidizing agent required to take C from +2 to +4

    b) $BaSO_4 \rightarrow Ba$ Reducing agent required to take Ba from +2 to 0

    c) $Hg_2Cl_2 \rightarrow HgCl_2$ Oxidizing agent required to take Hg from +1 to +2

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15. Determine the oxidant, the reductant, and the number of electrons transferred in each of the following reactions:
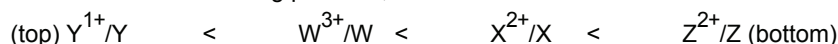
	Oxidizing Agent	Reducing Agent	Electrons Tansferred
a) $3C_2H_5OH + 2Cr_2O_7^{2-} + 16H^{1+} \rightarrow 3CH_3COOH + 4Cr^{3+} + 11H_2O$	$Cr_2O_7^{2-}$	C_2H_5OH	12
b) $4NH_3 + 6NO \rightarrow 5N_2 + 6H_2O$	NO	NH_3	12
c) $5Pb + 2MnO_4^{1-} + 16H^{1+} \rightarrow 5Pb^{2+} + 2Mn^{2+} + 8H_2O$	MnO_4^{1-}	Pb	10
d) $C_8H_{16} + 12O_2 \rightarrow 8CO_2 + 8H_2O$	O_2	C_8H_{16}	48

17. The following processes are all spontaneous:

a) $2Y+Z^{2+} \rightarrow 2Y^{1+}+Z$ b) $3Y+W^{3+} \rightarrow 3Y^{1+}+W$ c) $X+Z^{2+} \rightarrow X^{2+}+Z$ d) $2W+3X^{2+} \rightarrow 2W^{3+}+3X$

List the four redox couples that are involved in the above reactions in order of their standard reduction potentials in a manner similar to Table 11.1, *i.e.*, the most negative at the top.

The couple that is reduced is at the higher potential in each case, i.e., lower on the table. Reactions a and b indicate that Y^{1+}/Y is above both Z^{2+}/Z and W^{3+}/W. Reactions c and d show that X^{2+}/X is above Z^{2+}/Z but below W^{3+}/W. In order decreasing potential,

(top) Y^{1+}/Y < W^{3+}/W < X^{2+}/X < Z^{2+}/Z (bottom)

Y is the best reducing agent and Z^{2+} is the best oxidizing agent.

19. What is the difference between an anode and a cathode?

The anode is the electrode at which oxidation occurs, while the cathode is the electrode at which reduction occurs.

21. The standard reduction potentials for U^{3+} and In^{3+} are determined by measuring the voltage of the cell made by connecting a standard Ni^{2+}/Ni half-cell to the "Lo" terminal of a voltmeter and a standard U^{3+}/U half-cell or standard In^{3+}/In half-cell to the "hi" terminal.

a) **If the voltmeter reading was -1.43 V when the U^{3+}/U half-cell was attached, what is the standard reduction potential of uranium(III)? Write the *spontaneous* cell reaction between the U^{3+}/U and the Ni^{2+}/Ni half-cells.**

$\mathscr{E}_{Lo} = \mathscr{E}^{o}_{ANODE} = \mathscr{E}^{o}_{Ni} = $ -0.23 V (see Table 11.1)
$\mathscr{E}^{o}_{CELL} = \mathscr{E}_{Hi} - \mathscr{E}_{Lo} = \mathscr{E}^{o}_{CATHODE} - \mathscr{E}^{o}_{ANODE} = $ -1.43 V
Solving for $\mathscr{E}_{Hi}$, $\mathscr{E}_{Hi} = \mathscr{E}^{o}_{CATHODE} = \mathscr{E}^{o}_{CELL} + \mathscr{E}_{Lo} = $ -1.43 - 0.23 = -1.66 V $= \mathscr{E}^{o}_{U}$
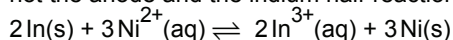The standard reduction potential of U(III) is -1.66 V
Since the cell potential is negative, the spontaneous half-reactions are the opposite of those used above. Consequently, the nickel half-reaction occurs at the cathode not the anode and the uranium half-reaction occurs at the anode not the cathode. $2U(s) + 3Ni^{2+}(aq) \rightleftharpoons 2U^{3+}(aq) + 3Ni(s)$

b) **If the voltmeter reading was -0.11 V when the In^{3+}/In half-cell was attached, what is the standard reduction potential of indium(III)? Write the *spontaneous* cell reaction between the In^{3+}/In and the Ni^{2+}/Ni half-cells.**

$\mathscr{E}^{o}_{CELL} = \mathscr{E}_{Hi} - \mathscr{E}_{Lo} = \mathscr{E}^{o}_{CATHODE} - \mathscr{E}^{o}_{ANODE} = $ -0.11 V
Solving for $\mathscr{E}_{Hi}$, $\mathscr{E}_{Hi} = \mathscr{E}^{o}_{CATHODE} = \mathscr{E}^{o}_{CELL} + \mathscr{E}_{Lo} = $ -0.11 - 0.23 = -0.34 V $= \mathscr{E}^{o}_{In}$
The standard reduction potential of In(III) is -0.34 V. The cell potential is negative, so the spontaneous half-reactions are the opposite of those used above. Consequently, the nickel half-reaction occurs at the cathode not the anode and the indium half-reaction occurs at the anode not the cathode:
$2In(s) + 3Ni^{2+}(aq) \rightleftharpoons 2In^{3+}(aq) + 3Ni(s)$

c) **An In^{3+}/In half-cell and a U^{3+}/U half-cell are connected as a galvanic cell. Which compartment is the anode, and what is the cell voltage?**

The cathode of a galvanic cell is always the half-reaction with the more positive standard reduction potential (less negative in this case). Thus, we may write

Cathode: $In^{3+}(aq) + 3e^{1-} \rightleftharpoons In(s)$ $\mathscr{E}^{o} = $ -0.34 V

Anode: $U(s) \rightleftharpoons U^{3+}(aq) + 3e^{1-}$ $\mathscr{E}^{o} = $ -1.66 V
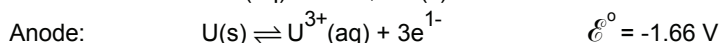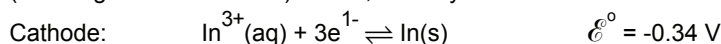
$\mathscr{E}^{o}_{CELL} = \mathscr{E}^{o}_{CATHODE} - \mathscr{E}^{o}_{ANODE} = $ -0.34 -(-1.66) = +1.32 V

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23. **In the following pairs of metals, one is used to protect the other by galvanization. Indicate which metal would be sacrificed.**

   a) Fe and <u>Mg</u>   b) <u>Ni</u> and Cu   c) <u>Fe</u> and Pb

   Note that the metal with the more negative standard reduction potential is sacrificed.

25. **Indicate whether each of the following cell reactions, run at standard conditions, would take place in a galvanic or an electrolytic cell.**
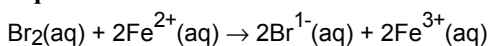
   a) $H_2O(l) \rightarrow H_2(g) + {}^1/_2\ O_2(g)$ $\quad\quad$ $\mathscr{E}^o$ = -0.44 - 0.88 < 0 $\quad$ ⇒ electrolytic
   b) $Zn^{2+}(aq) + 2\ I^{1-}(aq) \rightarrow Zn(s) + I_2(s)$ $\quad$ $\mathscr{E}^o$ = -0.76 - 0.54 < 0 $\quad$ ⇒ electrolytic
   c) $Cu^{2+}(aq) + Sn(s) \rightarrow Cu(s) + Sn^{2+}(aq)$ $\quad$ $\mathscr{E}^o$ = +0.34 + 0.14 > 0 $\quad$ ⇒ galvanic
   d) $2\ Fe^{3+}(aq) + Cu \rightarrow 2\ Fe^{2+}(aq) + Cu^{2+}(aq)$ $\quad$ $\mathscr{E}^o$ = +0.77 - 0.34 > 0 $\quad$ ⇒ galvanic

27. **Write net equations or "no appreciable reaction" for the following:**
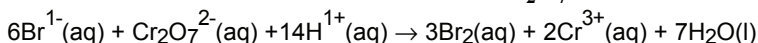
   a) **An aluminum bar is placed in 1 M HCl.**

   $2Al(s) + 6H^{1+}(aq) \rightarrow 2Al^{3+}(aq) + 3H_2(g)$
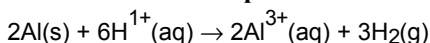
   b) **Aqueous bromine is added to a solution of Fe^{2+}.**

   $Br_2(aq) + 2Fe^{2+}(aq) \rightarrow 2Br^{1-}(aq) + 2Fe^{3+}(aq)$

   c) **A lead bar is placed in water.**

   $Pb(s) + H_2O(l) \rightarrow$ no appreciable reaction
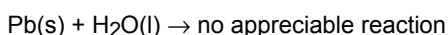
   d) **KBr is dissolved in an acidified solution of $Cr_2O_7^{2-}$.**

   $6Br^{1-}(aq) + Cr_2O_7^{2-}(aq) + 14H^{1+}(aq) \rightarrow 3Br_2(aq) + 2Cr^{3+}(aq) + 7H_2O(l)$

   e) **KF is dissolved in an aqueous bromine solution.**
   no appreciable reaction

   f) **Steel wool is placed into a solution of $NiSO_4$.**
   $Fe(s) + Ni^{2+}(aq) \rightarrow Fe^{2+}(aq) + Ni(s)$
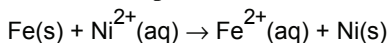
29. **Lead acid batteries indicate that there should be no smoking during recharge because of the possibility of dangerous gases being released. Suggest what gas might be generated in the recharge cycle of a lead acid battery. (Hint: the gas reacts explosively with oxygen.) Write the half-reaction for its production.**

   As the name suggests, lead acid batteries contain acid, H^{1+}, and under an applied voltage, the following reaction can be initiated, $2H^{1+} + 2e^{1-} \rightarrow H_2(g)$. Hydrogen can react explosively with oxygen in the presence of a fire.

31. **The following redox couples are combined to make galvanic cells; in each case, indicate which couple is the anode and which is the cathode:**
   The couple with the more negative standard reduction potential is the anode.

	Anode	Cathode
a) Br_2/Br^{1-} and Cl_2/Cl^{1-}	Br_2/Br^{1-}	Cl_2/Cl^{1-}
b) Sn^{2+}/Sn and Ag^{1+}/Ag	Sn^{2+}/Sn	Ag^{1+}/Ag
c) I_2/I^{1-} and Ni^{2+}/Ni	Ni^{2+}/Ni	I_2/I^{1-}
d) Zn^{2+}/Zn and Fe^{3+}/Fe^{2+}	Zn^{2+}/Zn	Fe^{3+}/Fe^{2+}

33. **Write the cell reaction and determine $\mathscr{E}^o$ for the galvanic cells constructed from the following redox couples:**

   a) **$Br_2(l)/Br^{1-}(aq)$ and $Cl_2(g)/Cl^{1-}(aq)$** $\quad$ $Cl_2(g) + 2Br^{1-}(aq) \rightarrow 2Cl^{1-}(aq) + Br_2(l)$ $\quad$ $\mathscr{E}^o$ = 0.27 V
   b) **$Sn^{2+}(aq)/Sn(s)$ and $Ag^{1+}(aq)/Ag(s)$** $\quad$ $Sn(s) + 2Ag^{1+}(aq) \rightarrow Sn^{2+}(aq) + 2Ag(s)$ $\quad$ $\mathscr{E}^o$ = 0.94 V
   c) **$I_2(s)/I^{1-}(aq)$ and $Ni^{2+}(aq)/Ni(s)$** $\quad$ $Ni(s) + I_2(s) \rightarrow Ni^{2+}(aq) + 2I^{1-}(aq)$ $\quad$ $\mathscr{E}^o$ = 0.77 V
   d) **$Zn^{2+}(aq)/Zn(s)$ and $Fe^{3+}(aq)/Fe^{2+}(aq)$** $\quad$ $Zn(s) + 2Fe^{3+}(aq) \rightarrow Zn^{2+}(aq) + 2Fe^{2+}(aq)$ $\quad$ $\mathscr{E}^o$ = 1.53 V

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35. **Determine how many moles of electrons and how many coulombs are must be transferred for each of the following processes:**

   a) **reduction of 1.3 mol Al^{3+} to Al**

   The half-reaction is $Al^{3+} + 3e^{1-} \rightarrow Al$, so 3 moles of electrons are required for each mole of Al.

   $$1.3 \text{ mol Al}^{3+} \times \frac{3 \text{ mol e}^{1-}}{1 \text{ mol Al}^{3+}} = 3.9 \text{ mol e}^{1-} ; \qquad 3.9 \text{ mol e}^{1-} \times 96,500 \text{ C/mol} = 3.8 \times 10^5 \text{ C}$$

   b) **oxidation of 3.4 mol Br^{1-} to Br_2**

   The half-reaction is $2Br^{1-} \rightarrow Br_2 + 2e^{1-}$, so 2 mol e^{1-} are transferred for each mole of Br^{1-} ions.

   $$3.4 \text{ mol Br}^{1-} \times \frac{2 \text{ mol e}^{1-}}{1 \text{ mol Br}^{1-}} = 6.8 \text{ mol e}^{1-} ; \qquad 6.8 \text{ mol e}^{1-} \times 96,500 \text{ C/mol} = 6.6 \times 10^5 \text{ C}$$

   c) **oxidize 2.8 g of copper to Cu^{2+}**

   The half-reaction is $Cu \rightarrow Cu^{2+} + 2e^{1-}$, so 2 mol e^{1-} are transferred for each mole of copper.

   $$2.8 \text{ g Cu}^{2+} \times \frac{1 \text{ mol Cu}}{63.5 \text{ g Cu}} \times \frac{2 \text{ mol e}^{1-}}{1 \text{ mol Cu}} = 0.088 \text{ mol e}^{1-}; \quad 0.088 \text{ mol e}^{1-} \times 96,500 \text{ C/mol} = 8.5 \times 10^3 \text{ C}$$

37. **A standard galvanic cell, constructed with Ag^{1+}/Ag and Zn^{2+}/Zn couples, is discharged until 3.3 g of Ag forms.**

   a) **What are the overall cell reaction and the standard cell potential?**

   $2Ag^{1+} + Zn \rightarrow 2Ag + Zn^{2+}$
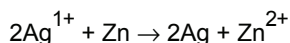
   $\mathscr{E}^{\circ} = \mathscr{E}^{\circ}_{\text{cathode}} - \mathscr{E}^{\circ}_{\text{anode}} = \mathscr{E}^{\circ}(Ag^{1+}/Ag) - \mathscr{E}^{\circ}(Zn^{2+}/Zn) = +0.80 - (-0.76) = 1.56 \text{ V}$

   b) **How many moles of electrons flow through the circuit during the discharge?**

   The Ag^{1+}/Ag half-reaction is $Ag^{1+} + 1e^{1-} \rightarrow Ag$, so 1 mol e^{1-} are transferred for each mole of silver(I) ions that are reduced.

   $$3.3 \text{ g Ag} \times \frac{1 \text{ mol Ag}}{108 \text{ g Ag}} \times \frac{1 \text{ mol e}^{1-}}{1 \text{ mol Ag}} = 0.031 \text{ mol e}^{1-}$$

   c) **How many coulombs of charge flow through the circuit?**

   $0.031 \text{ mol e}^{1-} \times 96,500 \text{ C/mol} = 2.9 \times 10^3 \text{ C}$
   (Note that the calculator answer to part a (0.03556) not 0.031 was used in the calculation.)

   d) **What is the maximum work that could be done by the electrons during the discharge?**

   The maximum work is $-\Delta G$, which can be determined with Equation 11.3:

   $$w = -\Delta G = n\mathscr{F}\mathscr{E}^{\circ} = 0.031 \text{ mol e}^{1-} \times \frac{96,500 \text{ C}}{\text{mol e}^{1-}} \times \frac{1.56 \text{ J}}{\text{C}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = 4.6 \text{ kJ}$$

   (See note to part c.)