

Chapter 8

OXIDATION AND REDUCTION

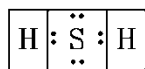
Exercises

- 8.1 (a) A substance that will oxidize another, itself being reduced.
 (b) A two-dimensional plot of free energy against temperature for series of reactions that involve elements and their oxides, sulfides, or chlorides, etc. An Ellingham diagram is used for the prediction of reaction feasibility.

- 8.3 (a) $4[\text{N}_{\text{ox}}(\text{P})] + 6(-2) = 0$
 $[\text{N}_{\text{ox}}(\text{P})] = +3$
 (b) $3(+1) + [\text{N}_{\text{ox}}(\text{P})] + 4(-2) = 0$
 $[\text{N}_{\text{ox}}(\text{P})] = +5$
 (c) $3(+1) + [\text{N}_{\text{ox}}(\text{P})] = 0$
 $[\text{N}_{\text{ox}}(\text{P})] = -3$
 (d) $[\text{N}_{\text{ox}}(\text{P})] + 4(+1) = +1$
 $[\text{N}_{\text{ox}}(\text{P})] = -3$
 (e) $[\text{N}_{\text{ox}}(\text{P})] + 1(-2) + 3(-1) = 0$
 $[\text{N}_{\text{ox}}(\text{P})] = +5$

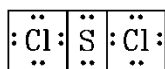
- 8.5 (a) -2; (b) +2; (c) -1; (d) +6; (e) -2.

The diagrams show how the answers for (a), (b), (c), and (e) were derived.



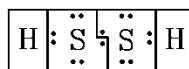
+1 -2 +1

(a)



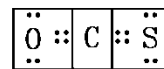
-1 +2 -1

(b)



+1 -1 -1 +1

(c)



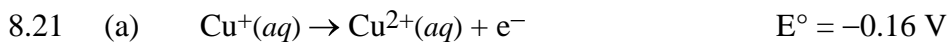
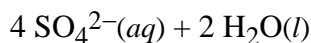
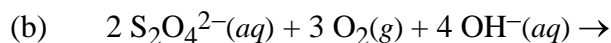
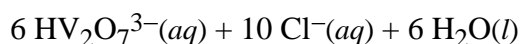
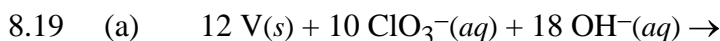
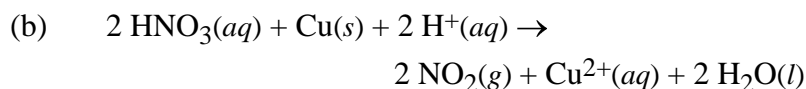
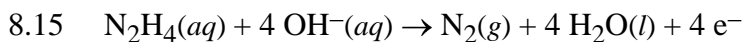
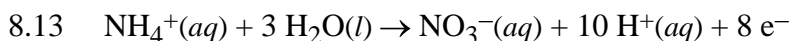
-2 +4 -2

(e)

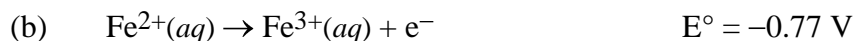
- 8.7 -1, +1, +3, +5, +7.

- 8.9 (a) +1; (b) +2; (c) +3; (d) +4; (e) +5. An increase by units of +1 from Group 13 to Group 17.

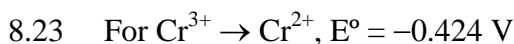
- 8.11 (a) Nickel from +2 to 0, carbon from 0 to +2.
 (b) Manganese from +7 to +2, sulfur from +4 to +6.



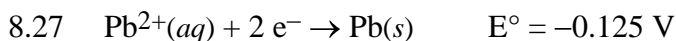
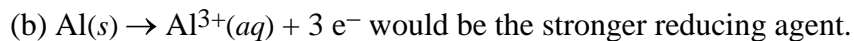
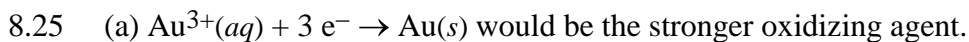
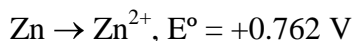
Net E° is positive, hence spontaneous.



Net E° is negative, hence nonspontaneous.



There are several possibilities for oxidizing agents, one being



$$E = E^\circ - \frac{RT}{nF} \ln \left(\frac{1}{[\text{Pb}^{2+}]} \right)$$

$$E = (-0.125 \text{ V}) - \frac{8.31 \text{ V} \cdot \text{C} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 298 \text{ K}}{2 \times (9.65 \times 10^4 \text{ C} \cdot \text{mol}^{-1})} \ln \left(\frac{1}{1.5 \times 10^{-5}} \right) = -0.267 \text{ V}$$

8.29 $\text{pH} = 7.00$, thus $[\text{H}^+] = 1.0 \times 10^{-7}$

$$E = E^\circ - \frac{RT}{nF} \ln \left(\frac{1}{[\text{H}^+]^4 (\text{pO}_2)} \right)$$

$$E = (+1.229 \text{ V}) - \frac{8.31 \text{ V} \cdot \text{C} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 298 \text{ K}}{4 \times (9.65 \times 10^4 \text{ C} \cdot \text{mol}^{-1})} \ln \left(\frac{1}{(1.0 \times 10^{-7})^4 \frac{20 \text{ kPa}}{100 \text{ kPa}}} \right)$$

$$= +0.805 \text{ V}$$

8.31 (a) Br_2

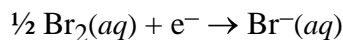
(b) $\text{BrO}_3^-(aq) \rightarrow \text{HBrO}(aq)$ is a four-electron reduction (+5 to +1 oxidation state), so $\Delta G^\circ = -4(F)(+0.54)$.

$\text{HBrO}(aq) \rightarrow \frac{1}{2} \text{Br}_2(aq)$ is a one-electron reduction, so $\Delta G^\circ = -1(F)(+0.45)$.

Total $\Delta G^\circ = (-2.16F) + (-0.45F) = -2.61F$

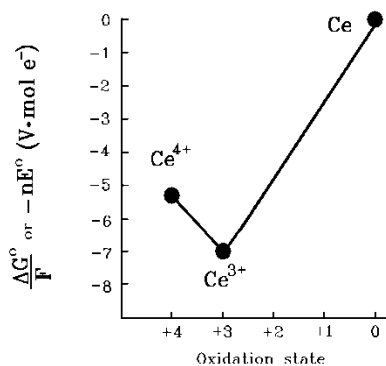
$E^\circ = -(-2.61F)/5F = +0.52 \text{ V}$

(c) The reduction half-reaction does not contain H^+ or OH^- :

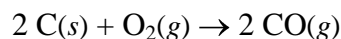
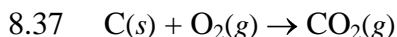


Hence the Nernst expression does not have a pH-dependent term.

8.33 The most thermodynamically stable oxidation state is +3. The metal is a very strong reducing agent while cerium(IV) is an oxidizing agent.



8.35 Perchlorate ion is a stronger oxidizing agent at pH 0.00 because the reduction potential is +1.201 V at pH 0.00 compared to +0.374 V at pH 14.00.

Beyond the Basics

The oxidation of carbon to carbon dioxide involves a near-zero entropy change; thus the slope of the ΔG versus temperature line will be close to zero. The oxidation to carbon monoxide, however, involves an increase of entropy (one mole of gas to two moles of gas); thus the $T\Delta S$ term will become increasingly negative with increase in temperature. The negative slope for this line will ultimately cross the carbon dioxide line, making the carbon monoxide production preferred at higher temperatures.

For oxidation to carbon dioxide:

$$\Delta H^\circ = -394 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta S^\circ = [(+214) - (+205) - (+6)] \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} = +3 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$$

$$\Delta G^\circ = (-394 \text{ kJ}\cdot\text{mol}^{-1}) - T(+0.003 \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$$

For oxidation to carbon monoxide:

$$\Delta H^\circ = 2(-111) \text{ kJ}\cdot\text{mol}^{-1} = -222 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta S^\circ = [2(+198) - (+205) - 2(+6)] \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} = +179 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$$

$$\Delta G^\circ = (-222 \text{ kJ}\cdot\text{mol}^{-1}) - T(-0.179 \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$$

At the crossover point, the values for ΔG° will be the same, thus

$$(-394 \text{ kJ}\cdot\text{mol}^{-1}) - T(+0.003 \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}) =$$

$$(-222 \text{ kJ}\cdot\text{mol}^{-1}) - T(+0.179 \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$$

$$T(0.182 \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}) = +172 \text{ kJ}\cdot\text{mol}^{-1}$$

$$T = 766 \text{ K} = 493^\circ\text{C}$$

- 8.39 In the well water at about pH 7 and E° about 0, the manganese will be present as the colorless $2+$ ion. On exposure to air (oxidizing conditions), E° will increase to the point where insoluble (brown) manganese(III) oxide will be formed, thus discoloring the toilet bowl.