

Chapter 8

OXIDATION AND REDUCTION

Exercises

8.2 (a) A two-dimensional plot of free energy against oxidation state. A Frost diagram is used to predict the comparative stability of oxidation states of an element.

(b) A two-dimensional plot of potential against pH. A Pourbaix diagram is used to identify the preferred species of an element under any given condition of potential and pH.

8.4 (a) With a less electronegative element, chlorine will have its “normal” oxidation state of -1 (rule 4).

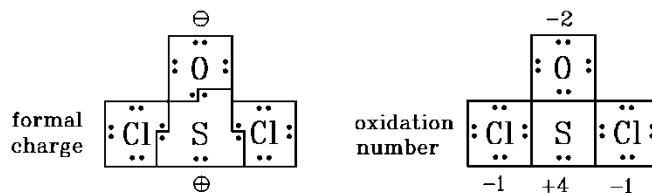
(b) $[N_{\text{ox}}(\text{Cl})] + 2(-2) = 0$
 $[N_{\text{ox}}(\text{Cl})] = +4$

(c) $2[N_{\text{ox}}(\text{Cl})] + 1(-2) = 0$
 $[N_{\text{ox}}(\text{Cl})] = +1$

(d) $2[N_{\text{ox}}(\text{Cl})] + 7(-2) = 0$
 $[N_{\text{ox}}(\text{Cl})] = +7$

(e) $1(+1) + [N_{\text{ox}}(\text{Cl})] = 0$
 $[N_{\text{ox}}(\text{Cl})] = -1$ (or from rule 4)

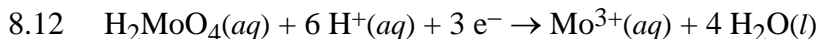
8.6

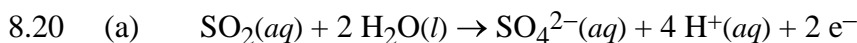
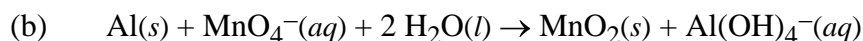
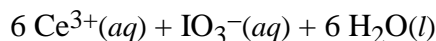
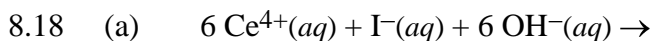
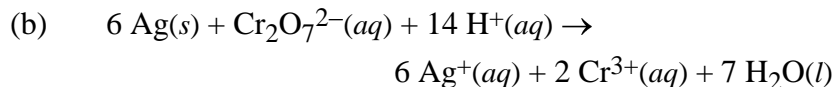
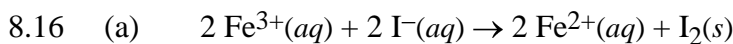
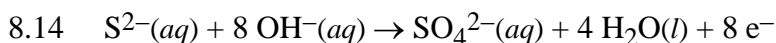


8.8 +8. Also +6, +4, and +2.

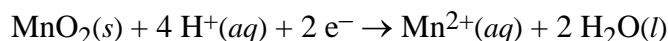
8.10 (a) Magnesium from 0 to +2, iron from +2 to 0.

(b) Nitrogen from +5 to +2, sulfur from -2 to 0.



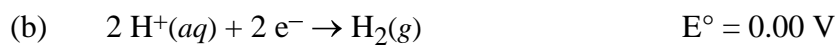


$$E^{\circ} = +0.16 \text{ V}$$

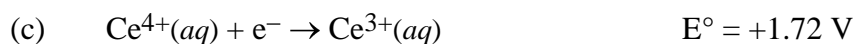


$$E^{\circ} = +1.23 \text{ V}$$

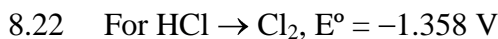
Net E° is positive, hence reaction will be spontaneous under standard conditions.



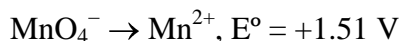
Net E° is negative, hence reaction will not be spontaneous under standard conditions.



Net E° is positive, hence reaction will be spontaneous under standard conditions.

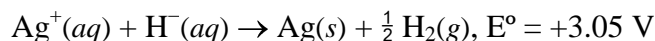


There are several possibilities for oxidizing agents, one being



(b) A potential of at least +1.98 V is needed. $\text{F}_2 \rightarrow \text{HF}$, thus $E^{\circ} = +3.053 \text{ V}$ is the only one of the four options that would be suitable.

(c) Combining the two half reactions



Thus decomposition, at least from the aqueous phase, would be very favorable thermodynamically.



Hence



$$\Delta G^{\circ} = -2.69F, \text{ hence } E^{\circ} = -(-2.69F)/2F = +1.34 \text{ V}$$

8.28 Because the $\text{pH} > 7$, it is more appropriate to use the standard reduction potential in basic solution:



$$\text{pOH} = 14.00 - 9.00 = 5.00, \text{ thus } [\text{OH}^{-}] = 1.0 \times 10^{-5}$$

$$E = E^{\circ} - \frac{RT}{nF} \ln \left(\frac{[\text{OH}^{-}]^4}{[\text{MnO}_4^{-}]} \right)$$

$$E = (+0.59 \text{ V}) - \frac{8.31 \text{ V} \cdot \text{C} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 298 \text{ K}}{3 \times 9.65 \times 10^4 \text{ C} \cdot \text{mol}^{-1}} \ln \left(\frac{(1.0 \times 10^{-5})^4}{1} \right) = +0.98 \text{ V}$$

8.30 (a) HBrO

(b) $\text{BrO}_3^{-}(aq) \rightarrow \text{HBrO}(aq)$ is a four-electron reduction (+5 to +1 oxidation state). Thus

$$\Delta G^{\circ} = -4(F)(+1.49)$$

$\text{HBrO}(aq) \rightarrow \frac{1}{2} \text{Br}_2(aq)$ is a one-electron reduction. Thus

$$\Delta G^{\circ} = -1(F)(+1.59)$$

$$\text{Total } \Delta G^{\circ} = (-5.96F) + (-1.59F) = -7.55F$$

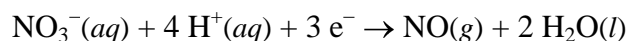
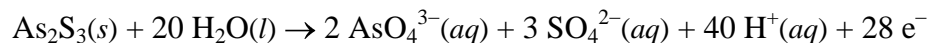
$$E^{\circ} = -(-7.55F)/5F = +1.51 \text{ V}$$

8.32 (a) PbO_2 ; (b) Pb^{2+} ; (c) SiO_2 ; (d) Si.

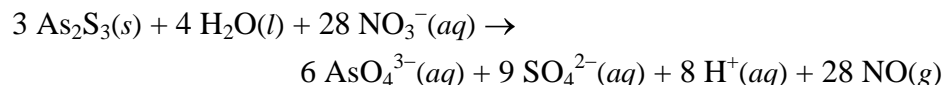
8.34 SO_4^{2-}

Beyond the Basics

8.36 Half reactions:



Balanced equation:



Arsenic is oxidized from +3 to +5, sulfur is oxidized from -2 to +6, nitrogen is reduced from +5 to +2.

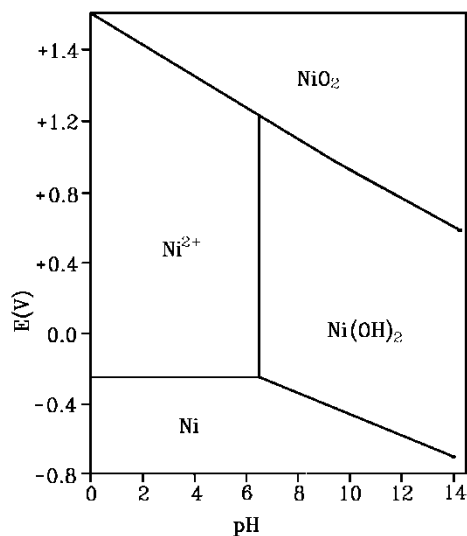
8.38 For $\text{Ni}^{2+}(aq) \rightarrow \text{Ni}(s)$, $E^\circ = -0.257 \text{ V}$ at pH 0.0; thus we can locate this point. Because the reaction is independent of pH, it will run as a horizontal line.

$\text{Ni}^{2+}(aq) + 2 \text{OH}^-(aq) \rightarrow \text{Ni}(\text{OH})_2(s)$ corresponds to a vertical line because it is E° independent. $K_{sp} = [\text{Ni}^{2+}][\text{OH}^-]^2 = 6 \times 10^{-16}$.

Because $[\text{Ni}^{2+}] = 1.0$ (standard conditions), $[\text{OH}^-]^2 = 6 \times 10^{-16}$; thus $\text{pOH} = 7.6$ and $\text{pH} = 6.4$.

We also know that $\text{Ni}(\text{OH})_2(aq) \rightarrow \text{Ni}(s)$, $E^\circ = -0.72 \text{ V}$ at pH 14.0.

The final line is that for $\text{NiO}_2(s)$. At pH 0.0, $E^\circ = +1.5$, while at pH 14.0, $E^\circ = +0.6$ (the average of 0.7 V and 0.52 V).



8.40 We need to calculate E for a pH of 14.00,

$$E = E^\circ - \frac{RT}{nF} \ln \left(\frac{1}{[\text{H}^+]^4} \right)$$
$$E = (+1.69 \text{ V}) - \frac{8.31 \text{ V} \cdot \text{C} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 298 \text{ K}}{3 \times (9.65 \times 10^4 \text{ C} \cdot \text{mol}^{-1})} \ln \left(\frac{1}{(1.0 \times 10^{-14})^4} \right)$$
$$= +1.69 \text{ V} - 1.10 \text{ V} = +0.59 \text{ V}$$

It would be meaningless to calculate the E° potential for $\text{MnO}_4^- \rightarrow \text{Mn}^{2+}$ at pH 14.00 because $\text{Mn}^{2+}(aq)$ does not exist at this high a pH. Instead, $\text{Mn}(\text{OH})_2(s)$ is formed.

