

Chapter 9: End-of-Chapter Solutions

1.

(a) Cl_2 will be reduced to Cl^- , Sn^{2+} will be oxidized to Sn^{4+}

(b) Cl_2 will be reduced to Cl^- , I^- will be oxidized to I_2

2.

$\text{Sn}(\text{s})$, $\text{Pb}(\text{s})$, etc. All of the metals that have an E value more negative than 0.0 V can be oxidized; thereby reducing $\text{H}^+(\text{aq})$ to $\text{H}_2(\text{g})$.

3.

(a) no reaction

(b) no reaction

(c) $\text{Ni}(\text{s}) + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Ni}^{2+}(\text{aq}) + \text{Cu}(\text{s})$

(d) no reaction

4.

(a) $3\text{ClO}_3^-(\text{aq}) + 5\text{NO}(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons 1.5\text{Cl}_2(\text{g}) + 5\text{NO}_3^-(\text{aq}) + 2\text{H}^+(\text{aq})$, 15 e^- transferred.

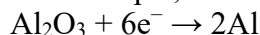
(b) $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightleftharpoons \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$, 8 e^- transferred.

(c) $\text{Zn}(\text{s}) + 2\text{MnO}_2(\text{s}) \rightleftharpoons \text{ZnO}(\text{s}) + \text{Mn}_2\text{O}_3(\text{s})$, 2 e^- transferred.

(d) $4\text{Zn}(\text{s}) + \text{NO}_3^-(\text{aq}) + 6\text{H}_2\text{O} + 7\text{OH}^-(\text{aq}) \rightleftharpoons 4\text{Zn}(\text{OH})_4^{2-}(\text{aq}) + \text{NH}_3(\text{aq})$, 8 e^- transferred.

5.

(a) Technologically important redox processes include smelting, corrosion, batteries, fuel cells, etc. As one example, aluminum is produced by reducing aluminum oxide:



in molten cryolite (sodium aluminum fluoride) in a giant steel furnace at 960 C. There is no chemical species directly oxidized in the furnace. An electric current passed through the cell causes the reduction. If the electric current is supplied by a fossil fuel burning generating plant, then a carbon species is oxidized to carbon dioxide.

(b) A significant environmental redox process is the oxidation of minerals, e.g.:



where the S is oxidized from -1 in disulfide, S_2^{2-} , to the $+7$ oxidation state in sulfate and Fe^{3+} is reduced to Fe^{2+} .

(c) Biological redox processes include cellular respiration (citric acid cycle), photosynthesis, and a whole bunch more. Almost all of these reactions are mediated by enzymes.

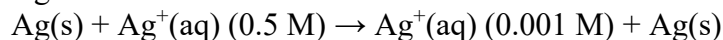
6.

(a) All species are at standard concentrations, so $E = -(-0.257) + 0.0 = 0.257\text{V}$

(b) All species are at standard concentrations, so $E = -(-0.763) + 0.0 = 0.763\text{V}$

(c) The contents of the two half-cells are identical, so there is no driving force for a reaction and $E = 0.0\text{V}$

(d) The same species are in each half cell (so $E = 0.0\text{ V}$), but there is a driving force to equalize Ag^+ concentrations. The reaction is:

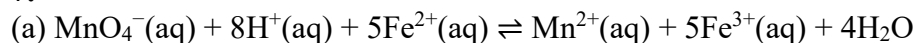


where the concentrations in parentheses are the starting concentrations. Using the Nernst equation to calculate E for the overall equation:

$$E = E^\circ - \frac{0.0592\text{ V}}{1} \log \frac{0.001\text{ M}}{0.5\text{ M}}$$

$$E = 0.0\text{V} - (-0.16\text{ V}) = 0.16\text{ V}$$

7.

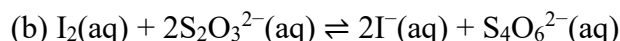
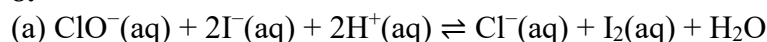


(b) From the balanced reaction, the stoichiometric factor is 1 mol MnO_4^- to 5 mol Fe^{2+} .

$$\text{(c) } (0.02240\text{ L})(0.150\text{ M}) = 3.36 \times 10^{-3}\text{ mol MnO}_4^-$$

$$(3.36 \times 10^{-3}\text{ mol MnO}_4^-) \frac{5\text{ mol Fe}^{2+}}{1\text{ mol MnO}_4^-} = 1.68 \times 10^{-2}\text{ mol Fe}^{2+}$$

8.



(c) From the combination of the two balanced reactions, the stoichiometric factor is 2 mol $\text{S}_2\text{O}_3^{2-}$ to 1 mol ClO^- .

9.

Since concentrations are 1.0 M, we can work with E° values:

$$E_{\text{cell}} = 0.340 + 0.7626 = 1.103 \text{ V.}$$

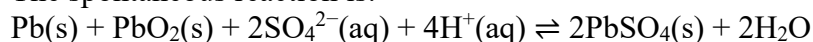
$$1.103 \text{ V} = \frac{RT}{nF} \ln(K)$$

$$K = 1.8 \times 10^{37}$$

As expected for the large cell potential, the equilibrium constant is very large.

10.

The spontaneous reaction is:



Recharging drives this reaction in reverse:



During charging solid lead sulfate is converted to solid lead metal and solid lead oxide on the plates of the battery and the concentration of sulfuric acid in solution increases.

11.

Unlike most biological molecules, Vitamin C easily undergoes a one-electron oxidation. It therefore serves as a sacrificial reagent to prevent strong oxidizing agents (known as reactive oxygen species, ROS) from damaging other molecules in biological cells. Because vitamin C can undergo a one-electron oxidation to a stable intermediate species, it reacts faster than other biochemical species that require an enzyme to mediate a two-electron reaction.

12.

Both are limited to measurement of analytes in solution and both can be specific for a given oxidation state. Voltammetry provides more parameters to vary and can be used to study physical processes or for analyte identification.

	potentiometry	voltammetry
measurement of:	voltage	current
experimental: set up:	passive measurement indicator and reference electrodes	variable voltage applied usually three electrodes
analytes:	ions only	ions and neutral species
general:	electrode is selective for a given ion	can be used to determine redox potentials and mechanistic information

13.

The advantages and disadvantages of potentiometric measurements versus wet chemical methods are similar to those of any instrumental method compared to a classical method:

	potentiometry	wet chemical
sensitivity:	can be very sensitive (μM or ppm)	less sensitive
selectivity:	usually very selective	depends on specific analytes/interferences
interferences:	levels of interferences are documented	interferences can require prior removal
calibration:	requires calibration standards	traceable to primary standards
general use:	rapid, can analyze many samples	rather slow due to solution manipulation
field use:	easily portable	mostly lab based, field kits can measure limited sample amounts

14.

- (a) Mg^{2+} in seawater: very high ionic strength, standards must match samples
- (b) NO_3^- in a freshwater stream: should be free of interferences and measurable directly with an ISE
- (c) NH_4^+ in a sample of solid fertilizer: sample must be dissolved and pH controlled
- (d) Cl^- in stainless steel: sample must be dissolved (not trivial for SS), interfering ions might require masking or removal.

15.

Per the convention in the chapter, I use concentration symbols rather than activity for clarity in these expressions. Doing so assumes that samples and standards have the same ionic strength.

- (a) $E_{\text{ISE}} = E_{\text{const}} + (0.0296 \text{ V})\log[\text{Mg}^{2+}]$
 (b) $E_{\text{ISE}} = E_{\text{const}} - (0.0592 \text{ V})\log[\text{NO}_3^-]$
 (c) $E_{\text{ISE}} = E_{\text{const}} + (0.0592 \text{ V})\log[\text{NH}_4^+]$
 (d) $E_{\text{ISE}} = E_{\text{const}} - (0.0592 \text{ V})\log[\text{Cl}^-]$

16.

- (a) For this data the lowest concentration point is not linear with the other points, so the linear range of the calibration data is from 10^{-4} to 10^{-1} M F^- .
- (b) The measured slope, -0.055 V , equals $(RT/nF) \times 2.303$. Inserting the constants and n (-1 for F^-):

$$-0.055 \text{ V} = \frac{8.3145 \text{ J mol}^{-1} \text{ K}^{-1}(T)}{(-1)(96485 \text{ C/mol})} 2.303$$

gives an absolute temperature of 277 K . Either the lab was quite chilly, or there is some deviation from the theoretical slope, which is quite common. Since standards and samples were

treated the same and measured on the same day, the deviation from the theoretical slope should not affect the accuracy of the unknown measurement.

(c) The calibration curve is $y = -55.0x - 149.0$. Inserting 48 mV for y gives an x of -3.58 . Taking the inverse log gives $[F^-] = 2.6 \times 10^{-4} \text{ M}$.

17.

In any potentiometric measurement there is a linear relationship between measured potential and $\log(a)$, where a is the activity of the analyte ion. The slope and intercept in this relationship are variable. The slope will change if the temperature of the experiment changes. The intercept will change if reference or junction potentials in the circuit change, which are also sensitive to temperature. By doing a two-point calibration, both the slope and intercept are corrected to establish an accurate linear relationship for the pH readout.

18.

An ion-selective electrode will be selective for only one specific analyte ion. Other ions will generally not interfere unless they are present at higher concentrations than the analyte. Cyclic voltammetry will detect all analytes present as the voltage is scanned. If voltages of different components in a mixture overlap, other components will interfere with measurement of the analyte. Voltammetry will detect neutral species in addition to ions.

19.

Based on Figure 9.13:

(a) The width of the transition for each analyte is approximately 60 mV. Two analytes with reduction potentials closer than 60 mV would overlap and be difficult to distinguish, so potentials $> 60 \text{ mV}$ are necessary to measure the waves separately.

(b) Taking the full range of the x scale, the scan range of 700 mV (-100 mV to -800 mV) takes 350 s. The scan rate is $(700 \text{ mV})/(350 \text{ s}) = 2.00 \text{ mV/s}$.

(c) The second analyte has a current signal of $\approx 7.0 \mu\text{A}$. The first analyte has a current signal of $\approx 9.0 \mu\text{A}$. Setting up a ratio for the second analyte being $1.0 \times 10^{-4} \text{ M}$ gives a concentration of $1.3 \times 10^{-4} \text{ M}$ for the first analyte.

(d) The direct ratio used in the previous answer assumes that the analytes are similar, i.e., they have equal diffusion constants.