

Chapter 20

Electrochemistry

Concept Check 20.1

If you were to construct a wet cell and decided to replace the salt bridge with a piece of copper wire, would the cell produce sustainable current? Be sure to explain your answer.

Solution

No sustainable current would flow. The wire does not contain mobile positively and negatively charged species that are necessary to balance the accumulation of charges in each of the half-cells.

Concept Check 20.2

Let's say that we define the reduction of I_2 to I^- ions, $I_2(s) + 2e^- \rightarrow 2I^-(aq)$, as the standard reduction reaction with $E^\circ = 0.00$ V. We then construct a new standard reduction table based on this definition.

- What would be the new standard reduction potential of H^+ ?
- Would using a new standard reduction table change the measured value of a freshly prepared voltaic cell made from Cu and Zn (assume you have the appropriate solutions and equipment to construct the cell)?
- Would the calculated voltage for the cell in part b. be different than if you were using the values presented in Table 20.1? Do the calculations to justify your answer.

Solution

- Standard reduction potentials are measured against some arbitrarily chosen standard reference half-reaction. Only differences in potentials can be measured. A voltaic cell made from H_2 and I_2 , and corresponding solutions, will have the same voltage, regardless of the choice of the reference cell. If the I_2/I^- half-reaction is assigned a value of $E^\circ = 0.00$

V, then the H_2/H^+ half-reaction must have a voltage of $E^\circ = -0.54 \text{ V}$ to keep the overall voltage the same.

- The voltage of a voltaic cell made from Cu and Zn, and corresponding solutions, will have the same measured voltage, regardless of the choice of the reference half-reaction.
- The calculated voltage is 1.10 V and is the same either way.

Concept Check 20.3

Consider the voltaic cell: $\text{Fe}(s) | \text{Fe}^{2+}(aq) || \text{Cu}^{2+}(aq) | \text{Cu}(s)$ being run under standard conditions.

- Is ΔG° positive or negative for this process?
- Change the concentrations from their standard values in such a way that E_{cell} is reduced. Write your answer using the shorthand notation (Section 20.3).

Solution

- Using the standard reduction potentials in Table 20.1, you see that the voltage for this cell is positive, suggesting that ΔG° is negative.
- In order to reduce E_{cell} , you change the concentrations in a manner to increase the value of Q, where

$$Q = \frac{[\text{Fe}^{2+}]}{[\text{Cu}^{2+}]}$$

For example: $\text{Fe}(s) | \text{Fe}^{2+} (1.10 \text{ M}) || \text{Cu}^{2+} (0.50 \text{ M}) | \text{Cu}(s)$.

Concept Check 20.4

Keeping in mind that seawater contains a number of ions, explain why seawater corrodes iron much faster than fresh water.

Solution

Many of the ions contained in seawater have very high reduction potentials – higher than $\text{Fe}(s)$. This means that spontaneous electrochemical reactions will occur with the $\text{Fe}(s)$ causing the iron to form ions and go into solution, while at the same time, the ions in the sea are reduced and plate out on the surface of the iron.

Conceptual Problem 20.19

Keeping in mind the fact that aqueous Cu^{2+} is blue colored and aqueous Zn^{2+} is colorless, predict what you would observe over a several day period if you performed the following experiments.

- A strip of Zn is placed into a beaker containing aqueous Zn^{2+} .
- A strip of Cu is placed into a beaker containing aqueous Cu^{2+} .
- A strip of Zn is placed into a beaker containing aqueous Cu^{2+} .
- A strip of Cu is placed into a beaker containing aqueous Zn^{2+} .

Solution

- Since there is no species present to donate or accept electrons other than zinc, you would expect no change.
- Since there is no species present to donate or accept electrons other than copper, you would expect no change.
- According to the table of standard reduction potentials, the Cu^{2+} would undergo reduction and the Zn would undergo oxidation. You would expect the Zn strip to dissolve as it becomes Zn^{2+} , the blue color of the solution to fade as the Cu^{2+} becomes Cu, and the formation of the solid copper precipitate.
- According to the table of standard reduction potentials, since Zn^{2+} cannot oxidize Cu, you would expect no change.

Conceptual Problem 20.20

You are working at a plant that manufactures batteries. A client comes to you and asks for a 6.0-V battery that is made from silver and cadmium. Assuming that you are running the battery under standard conditions, how should it be constructed?

Solution

You could construct the battery by hooking together, in series, five individual cells, each with $E^\circ = 1.20 \text{ V}$.

Conceptual Problem 20.21

The composition of the hull of a submarine is mostly iron. Pieces of zinc, called “zincs”, are placed in contact with the hull throughout the inside of the submarine. Why is this done?

Solution

The Zn is a sacrificial electrode, keeping the hull from undergoing oxidation by the dissolved ions in sea water. Zn works because it is more easily oxidized than Fe.

Conceptual Problem 20.22

You place a battery in a flashlight in which all of the electrochemical reactions have reached equilibrium. What do you expect to observe when you turn the flashlight on? Explain your answer.

Solution

When an electrochemical reaction reaches equilibrium, $E_{\text{cell}} = 0$, which means no current will flow and nothing will happen when you turn on the flashlight. This is typically what has occurred when you have a dead battery.

Conceptual Problem 20.23

The difference between a “heavy-duty” and a regular zinc-carbon battery is that the zinc can in the heavy-duty battery is thicker walled. What makes this battery heavy-duty in terms of output?

Solution

Since there is more zinc present, the oxidation-reduction reactions in the battery will run for a longer period of time. This assumes that the zinc is the limiting reactant.

Conceptual Problem 20.24

From an electrochemical standpoint, what metal, other than zinc, would be a reasonable candidate to coat a piece of iron to prevent corrosion (oxidation)?

Solution

Any metal that has a more negative standard reduction potential (Mg, Al, etc.) could be used, keeping in mind that group IA metals that fall into this category are too reactive to be of practical use.

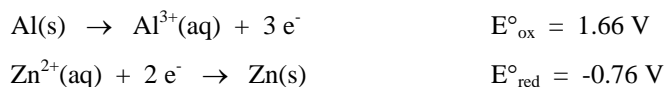
Conceptual Problem 20.25

Pick a combination of two metals from the Standard Reduction Potential table (Table 20.1 or Appendix I) that would result in a cell with a potential of about +0.90 V. For your answer,

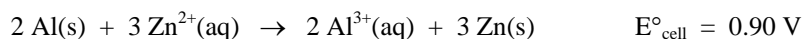
write both the half-reactions, write the overall balanced reaction, and calculate the cell potential for your choice.

Solution

One possible combination using two metals is a cell constructed from a $\text{Zn}^{2+}|\text{Zn}$ cathode with a voltage of -0.76 V , and an $\text{Al}|\text{Al}^{3+}$ anode with a voltage of 1.66 V . The appropriate half-reactions are



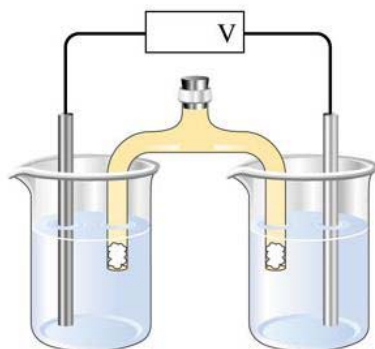
The overall balanced reaction and cell potential is



Conceptual Problem 20.26

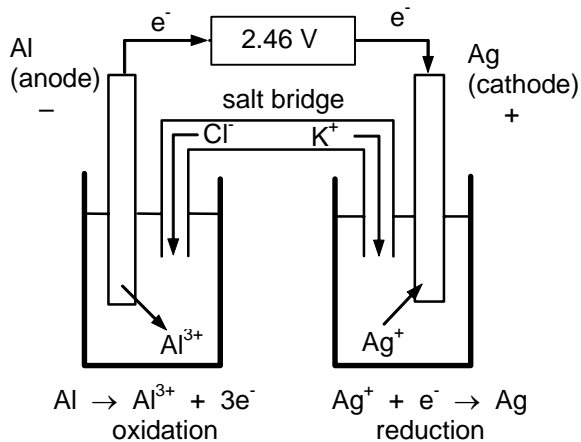
You have 1.0 M solutions of $\text{Al}(\text{NO}_3)_3$ and AgNO_3 along with Al and Ag electrodes to construct a voltaic cell. The salt bridge contains a saturated solution of KCl . Complete the picture below by

- writing the symbols of the elements and ions in the appropriate areas (both solution and electrodes).
- identifying the anode and cathode.
- indicating the direction of electron flow through the external circuit.
- indicating the cell emf (assume standard conditions).
- writing the appropriate half-reaction under each of the containers.
- indicating the direction of ion flow in the salt bridge.
- identifying the species undergoing oxidation and reduction.
- writing the balanced overall reaction for the cell.



Solution

(parts a to f) The completed diagram with all parts labeled is shown below.



d. The cell emf is determined as follows.



$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}} = 0.80 \text{ V} - (-1.66 \text{ V}) = 2.46 \text{ V}$$

g. The species undergoing oxidation is $\text{Al}(\text{s})$, and the species undergoing reduction is $\text{Ag}^{+}(\text{aq})$.

h. The balanced overall reaction is

