ALE 26. Equilibria for Cell Reactions

(Reference: 21.4 Silberberg 5th edition)

What happens to the cell potential as the reaction proceeds over time?

The Model: Basis for the Nernst Equation

Previously, we learned that the change in Gibbs free energy for a reaction occurring in a non-standard state is given by eqn **1**.

$$\Delta G_{rxn} = \Delta G^{o}_{rxn} + RT \ln Q \tag{1}$$

We have also learned that the change in Gibbs free energy for the reaction occurring in an electrochemical cell is related to the cell's potential by eqn **2**.

$$\Delta G_{rxn} = -n\mathcal{F}E_{cell} \tag{2}$$

Key Questions

1 a. Use eqn **2** as a guide to finish eqn **3** that relates the change in Gibbs free energy of a reaction at standard state with the standard-state cell potential.

$$\Delta G^{o}_{rxn} = \underline{\hspace{4cm}} \tag{3}$$

b. Substitute the expressions from eqns **2** and **3** involving the cell potentials (non-standard state and standard-state, respectively) into eqn **1** to complete eqn **4**.

$$\underline{\hspace{3cm}} = \underline{\hspace{3cm}} + RT \ln Q \tag{4}$$

$$\uparrow \qquad\qquad \uparrow$$

from eqn **2**   from eqn **3**

c. Divide both sides of eqn **4** by $-n\mathcal{F}$ to yield eqn **5**, the **Nernst equation**, and write it below.

2. Usually chemists are interested in reactions that are occurring at "room temperature", which is ~25 °C. (Thermodynamic data are tabulated at 25 °C.) If we are assured that the reaction occurring within a voltaic cell is doing so at 25 °C, then we can write the Nernst equation as eqn **6**.

$$E_{cell} = E^{o}_{cell} - \frac{0.0257\text{ V}}{n} \ln Q \tag{6}$$

Explain where the "0.0257 V" comes from. Also, explain why we were able to "get rid of" the R, the T, and the $\mathcal{F}$ in the Nernst equation but we weren't able to "get rid of" the n.

Exercises

3. As the cell reaction within the an automobile lead storage battery proceeds, the sulfuric acid is consumed:

$$Pb(s) \; + \; PbO_2(s) \; + \; 2\,H_2SO_4(aq) \; \rightarrow \; 2\,PbSO_4(s) \; + \; 2\,H_2O(l) \qquad E^o_{cell} = 2.043 \; V$$
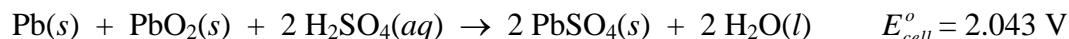
Thus the H_2SO_4 concentration of the solution within the battery goes down over time. Calculate ① the reaction quotient and ② the nonstandard cell potential of a lead storage battery at 25 °C when the molar concentration of sulfuric acid is 0.25 M. [Consider $H_2SO_4(aq)$ to be 100% dissociated into $H^+(aq)$ and $SO_4^{2-}(aq)$ when you calculate Q.] *Show your work and circle your answer*.

4. We have learned that the solvation of copper in hydrochloric acid

$$Cu(s) \; + \; 2\,H^+(aq) \; \rightarrow \; Cu^{2+}(aq) \; + \; H_2(g)$$
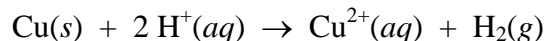
has a negative *standard* cell potential and is, therefore, nonspontaneous when [HCl] = 1 M and P_{H2} = 1 atm. However, let's consider what happens when we place a piece of solid copper in 12 M ("concentrated") hydrochloric acid at ambient conditions. (I say "ambient" because the air that we breathe typically has a partial pressure of hydrogen gas of 5×10^{-7} atm.) If we consider a spontaneous reaction to have a E_{cell} *just over* 0 V (say, +0.001 V), what is the molar solubility of copper (as Cu^{2+}) in 12 M HCl when $P_{H2} = 5 \times 10^{-7}$ atm and $T = 25$ °C? *Hints*: ① Calculate E^o_{cell} using standard reduction potentials found in Appendix D. ② Determine n for the cell reaction. ③ Use the Nernst equation to solve for Q. ④ Express Q in terms of $[Cu^{2+}]$, P_{H2}, and $[H^+]$, and solve for $[Cu^{2+}]$.)

Key Questions

5. a. In Key Question 1c you learned that the cell potential of a voltaic cell (battery) is described by the Nernst equation (eqn **4**). When a battery is dead, the cell potential is zero and the voltaic cell is in a state of equilibrium—i.e. the reaction quotient, $Q = K$, the equilibrium constant. Use this information and eqn **4** to complete eqn **7** to show how the standard cell potential, E^o_{cell}, is related to the equilibrium constant.

$$E_{cell} = E^o_{cell} - \frac{RT}{nF} \ln Q \qquad\qquad (4)$$

$$E^o_{cell} = \underline{\hspace{5cm}} \qquad\qquad (7)$$

   b. If the redox reaction within a voltaic cell occurs at 25 °C, then we can determine the standard cell potential from the known equilibrium constant with eqn **8** (unfinished). Finish eqn **9** by supplying the correct number (with units) in the numerator before the "ln K."
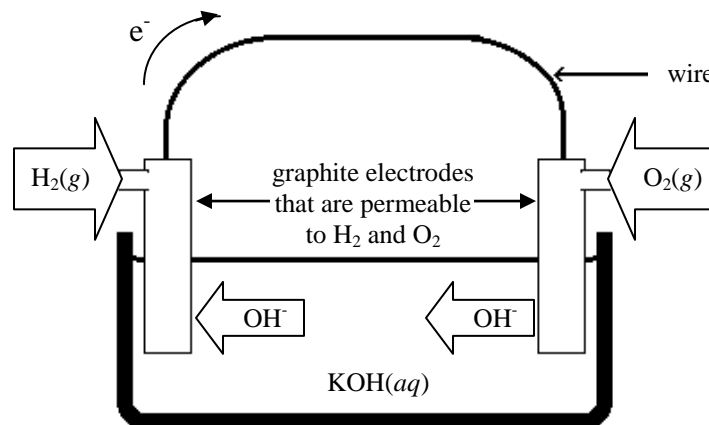
$$E^o_{cell} = \frac{}{n} \ln K \qquad\qquad (8)$$

Exercises

6. The hydrogen-oxygen fuel cell is very promising as a source of electrical power. The net cell reaction is

$$2\,H_2(g) \;+\; O_2(g) \;\rightarrow\; 2\,H_2O(l)$$
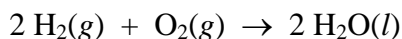
Therefore, one of its advantages is that the fuel cell produces no toxic by-products.

   a. Use the table of standard reduction potentials in your textbook to determine what the oxidation and reduction half-reactions are at the electrodes. (*Hint*: *Hydroxide ions*, not hydronium ions, are involved in each half-reaction.)

   Half reaction at anode: _____ E^o_{ox} = _____ v

   Half reaction at cathode: _____ E^o_{red} = _____ v

   b. Determine E^o_{cell} for the fuel cell at 25 °C: E^o_{cell} = _____ = _____ v

   c. Calculate K for the net reaction of the hydrogen fuel cell at 25 °C and comment on the magnitude of K.

Here's a summary of the various equations that you have derived. Be able to use/apply and understand these relationships

Relationships involving ΔG	$\Delta G = -n\,\mathscr{F}E_{cell}$	$\Delta G^o{}_{cell} = -n\,\mathscr{F}\,E^o_{cell}$	$\Delta G^o = -RT\ln K$
Calculating E_{cell} at non-standard conditions	$E_{cell} = E^o_{cell} - \dfrac{RT}{nF}\ln Q$ $E^o_{cell} = \dfrac{RT}{nF}\ln K$	<u>at 25 °C:</u> $E_{cell} = E^o_{cell} - \dfrac{0.0592V}{n}\log Q$ <u>at 25 °C:</u> $E^o_{cell} = \dfrac{0.0592V}{n}\log K$	

Exercises

7. a.   Write the balanced net ionic equation for a reaction between $Al_{(s)}$ and $Cd^{2+}{}_{(aq)}$.

    b. Calculate the standard cell potential, E^o_{cell}, for the reaction between $Al_{(s)}$ and $Cd^{2+}{}_{(aq)}$.

    c. Calculate the equilibrium constant at 25 °C for the reaction between $Al_{(s)}$ and $Cd^{2+}{}_{(aq)}$.

    d.   Use E^o_{cell} to calculate the ΔG^o_{cell}.

8. A voltaic cell consists of Mn/Mn^{2+} and Cd/Cd^{2+} half-cells with he following initial concentrations: [Mn^{2+}] = 0.090 M; [Cd^{2+}] = 0.060 M.

   a. Write the balanced net ionic equation for the redox reaction within the voltaic cell. *Hint*: Consult the table of reduction potential to see which ion is more easily reduced.

   b. What is the initial cell potential, E_{cell}? *Hint*: calculate E^{o}_{cell}, then E_{cell}.

   c. What happens to the concentration of Mn^{2+} as the voltaic cell is used to perform work? What about the Cd^{2+} concentration? *Explain*. (*Hint*: examine the net ionic equation!)

   d. What is the potential of the cell, E_{cell}, when half of the Cd^{2+} has been used—i.e. when [Cd^{2+}] = 0.030 M? (*Hint*: consider the initial concentrations of Cd^{2+} and Mn^{2+} and your response to part c, above.)