

Ch. 11: Answers to Selected Problems

18. Calculate E° values for the following cells. Which reactions are spontaneous as written, under standard conditions? Balance the reactions that are not already balanced.

- a. $2 \text{Ag}^+ + \text{Cu} \leftrightarrow \text{Cu}^{2+} + 2 \text{Ag}$ $E^\circ = 0.46 \text{ V}$ Spontaneous
b. $\text{Zn}^{2+} + \text{Ni} \leftrightarrow \text{Ni}^{2+} + \text{Zn}$ $E^\circ = -0.53 \text{ V}$ Not Spontaneous
c. $16 \text{H}^+ + 2 \text{MnO}_4^- + 10 \text{I}^- \leftrightarrow 5 \text{I}_2 + 2 \text{Mn}^{2+} + 8 \text{H}_2\text{O}$ $E^\circ = 0.97 \text{ V}$ Spont
d. $16 \text{H}^+ + 2 \text{MnO}_4^- + 10 \text{F}^- \leftrightarrow 5 \text{F}_2 + 2 \text{Mn}^{2+} + 8 \text{H}_2\text{O}$ $E^\circ = -1.36 \text{ V}$ Nonspont

22. The saturated calomel electrode, abbreviated SCE, is often used as a reference electrode in making electrochemical measurements. The SCE is composed of mercury in contact with a saturated solution of calomel (Hg_2Cl_2). The electrolyte solution of calomel is saturated KCl. E_{SCE} is +0.242 V relative to the standard hydrogen electrode. Calculate the potential for each of the following galvanic cells containing a saturated calomel electrode and the given half-cell components as standard conditions. In each case, indicate whether the SCE is the cathode or the anode.

- a. $\text{Cu}^{2+} + 2 \text{e}^- \rightarrow \text{Cu}$ $E_{\text{cell}} = 0.10 \text{ V}$, SCE is the anode.
b. $\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$ $E_{\text{cell}} = 0.53 \text{ V}$, SCE is the anode.
c. $\text{AgCl} + \text{e}^- \rightarrow \text{Ag} + \text{Cl}^-$ $E_{\text{cell}} = 0.02 \text{ V}$, SCE is the cathode.
d. $\text{Al}^{3+} + 3 \text{e}^- \rightarrow \text{Al}$ $E_{\text{cell}} = 1.90 \text{ V}$, SCE is the cathode.
e. $\text{Ni}^{2+} + 2 \text{e}^- \rightarrow \text{Ni}$ $E_{\text{cell}} = 0.47 \text{ V}$, SCE is the cathode.

24. Answer the following questions.

- a. Is H_2 capable of reducing Ag^+ ?
Yes, because Ag^+ has a more positive reduction potential than does H_2 .
b. Is H_2 capable of reducing Ni^{2+} ?
No, Ni^{2+} has a more negative reduction potential than does H_2 .
c. Is Fe^{2+} capable of reducing VO_2^+ ?
Yes, VO_2^+ has the more positive reduction potential.
d. Is Fe^{2+} capable of reducing Cr^{3+} to Cr^{2+} ?
No, in this case, Fe^{2+} has the more positive reduction potential.

28. Consider only the species Ce^{4+} , Ce^{3+} , Fe^{2+} , Fe^{3+} , Fe , Mg^{2+} , Mg , Ni^{2+} , and Sn in answering the following questions. Give reasons for your answers.
- Which is the strongest oxidizing agent?
 Ce^{4+} has the most positive reduction potential so it is the strongest oxidizing agent.
 - Which is the strongest reducing agent?
 Mg has the most negative reduction potential, so it is the strongest reducing agent.
 - Will iron dissolve in a 1.0 M solution of Ce^{4+} ?
Yes, Ce^{4+} is a strong enough oxidizing agent that it will convert solid Fe into Fe^{3+} .
 - Which of the species can be oxidized by H^+ ?
 Fe , Sn , and Mg can all be oxidized by H^+ because they have negative reduction potentials.
 - Which of the species can be reduced by H_2 ?
 Ce^{4+} and Fe^{3+} can be reduced by H_2 because they have positive reduction potentials.
34. For reactions that occur in Exercise 33, write a balanced equation and calculate E° , ΔG° , and K at 25°C .
- Crystals of I_2 are added to a solution of NaCl .
No reaction will occur here because I_2 cannot oxidize Cl^- .
 - Cl_2 gas is bubbled into a solution of NaI .

$$\text{Cl}_2 + 2\text{I}^- \rightarrow 2\text{Cl}^- + \text{I}_2 \quad E^\circ = 0.82\text{ V (2 electron change) [1 V = 1 J/C]}$$

$$\Delta G^\circ = -nFE^\circ = -(2)(96485\text{ C/mol e})(0.82\text{ J/C}) = -160\text{ kJ}$$

$$\log(K) = nE^\circ/0.0591 = 2(0.82\text{ V})/0.0591 = 27.75$$

$$K = 10^{27.75} = 5.6 \times 10^{27}$$
 - A silver wire is placed in a solution of CuCl_2 .
No reaction will occur here because Cu^{2+} cannot oxidize Ag .
 - A lead wire is placed in a solution containing Cu^{2+} .

$$\text{Pb} + \text{Cu}^{2+} \rightarrow \text{Pb}^{2+} + \text{Cu} \quad E^\circ = 0.47\text{ V}$$

$$\Delta G^\circ = -91\text{ kJ}$$

$$K = 8.1 \times 10^{15}$$
38. The overall reaction and equilibrium constant value for a hydrogen-oxygen fuel cell at 298 K is
- $$2\text{H}_{2(\text{g})} + \text{O}_{2(\text{g})} \rightarrow 2\text{H}_2\text{O}_{(\text{l})} \quad K = 1.28 \times 10^{83}$$
- Calculate E° and ΔG° at 298 for the fuel cell reactions.

$$E_{\text{cell}} = 0.0591/n (\log K) = 1.23\text{ V}$$

$$\Delta G^\circ = -nFE = -(4\text{ mol e})(96485\text{ C/mol e})(1.23\text{ J/C}) = -475\text{ kJ}$$
 - Predict the signs of ΔH° and ΔS° for the fuel cell reaction.
 ΔS° is negative since the moles of gas decreases as the reaction proceeds. ΔH° must be negative as well in order for ΔG° to have a negative value.
 - As temperature increases, does the maximum amount of work obtained from the fuel cell reaction increase, decrease, or remain the same? Explain.
Since entropy is negative as the temperature increases the contribution from entropy becomes a more positive value ($-T\Delta S^\circ$) making the value for ΔG° more positive as well and decreasing the amount of work that can be generated by the cell.

44. A disproportionation reaction involves a substance that acts as both an oxidizing and a reducing agent, producing both higher and lower oxidation states of the same elements in the products.

Which of the following disproportionation reactions are spontaneous under standard conditions?

- a. $2 \text{Cu}^+ \rightarrow \text{Cu}^{2+} + \text{Cu}$ $E^\circ = 0.36 \text{ V}$, the reaction is spontaneous.
 b. $3 \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{Fe}$ $E^\circ = -1.21 \text{ V}$, the reaction is NOT spontaneous.
 c. $\text{HClO}_2 \rightarrow \text{ClO}_3^- + \text{HClO}$ $E^\circ = 0.44 \text{ V}$, the reaction is spontaneous.

52. The Nernst equation can be applied to half-reactions. Calculate the reduction potential at 25°C of each of the following half-cells.

- a. Cu/Cu^{2+} (0.10 M) $E^\circ = 0.31 \text{ V}$
 b. Cu/Cu^{2+} (2.0 M) $E^\circ = 0.35 \text{ V}$
 c. Cu/Cu^{2+} (1×10^{-4} M) $E^\circ = 0.22 \text{ V}$
 d. MnO_4^- (0.10 M) / Mn^{2+} (0.010 M) $E^\circ = 1.24 \text{ V}$
 e. MnO_4^- (0.10 M) / Mn^{2+} (0.010 M) at pH = 1.0 $E^\circ = 1.43 \text{ V}$

54. A chemist wishes to determine the concentration of CrO_4^{2-} electrochemically. A cell is constructed consisting of a SCE and a silver wire coated with Ag_2CrO_4 . The E° value for the following half reaction is +0.446 V relative to the SHE: $\text{Ag}_2\text{CrO}_4 + 2 e \rightarrow 2 \text{Ag} + \text{CrO}_4^{2-}$.

a. Calculate E_{cell} and ΔG at 25°C for the cell reaction when $[\text{CrO}_4^{2-}] = 1.00 \text{ M}$.

$$E^\circ = 0.204 \text{ V} \text{ and } \Delta G^\circ = -39.4 \text{ kJ}$$

b. Write the Nernst equation for the cell. Assume that the SCE concentrations are constant.

$$E_{\text{cell}} = 0.204 \text{ V} - \frac{0.0591 \text{ V}}{2} \log[\text{CrO}_4^{2-}]$$

c. If the coated silver wire is placed in a solution in which $[\text{CrO}_4^{2-}] = 1.00 \times 10^{-5}$, what is the expected cell potential?

$$E_{\text{cell}} = 0.204 \text{ V} - \frac{0.0591 \text{ V}}{2} \log[1.00 \times 10^{-5}] = 0.204 \text{ V} - (-0.148 \text{ V}) = 0.352 \text{ V}$$

d. The measured cell potential at 25°C is 0.504 V when the coated wire is dipped into a solution of unknown chromate concentration. What is the chromate concentration for the solution?

$$0.504 \text{ V} = 0.204 \text{ V} - \frac{0.0591 \text{ V}}{2} \log[\text{CrO}_4^{2-}]$$

$$[\text{CrO}_4^{2-}] = 7.05 \times 10^{-11} \text{ M}$$

e. Using data from this problem and from Table 1.11, calculate the K_{sp} for Ag_2CrO_4 .

You don't have to worry about this part.

62. It took 2.30 min with a current of 2.00 A to plate out all the silver from 0.250 L of a solution containing Ag^+ . What was the original concentration of Ag^+ in the solution?

$$2.30 \text{ min} \left(\frac{60 \text{ s}}{\text{min}} \right) \left(\frac{2.00 \text{ C}}{\text{s}} \right) \left(\frac{1 \text{ mol e}}{96485 \text{ C}} \right) \left(\frac{1 \text{ mol Ag}}{1 \text{ mol e}} \right) = 2.86 \times 10^{-3} \text{ mol Ag}$$

$$[\text{Ag}^+] = \frac{2.86 \times 10^{-3} \text{ mol Ag}}{0.250 \text{ L}} = 1.14 \times 10^{-2} \text{ M}$$