

11 Electrochemical Cells, Batteries, and Fuel Cells

Problem numbers in italics indicate that the solution is included in the *Student Solutions Manual*.

Conceptual Problems

Q11.1 To determine standard cell potentials, measurements are carried out in very dilute solutions rather than at unit activity. Why is this the case?

In order to determine the standard potential, the mean ionic activity must be known. It can be calculated in dilute solutions using the Debye-Hückel limiting law, but there is no reliable way to calculate or measure the activity coefficient near unit activity.

Q11.2 Show that if $\Delta G_f^\circ(\text{H}^+, aq) = 0$ for all T , the potential of the standard hydrogen electrode is zero.

$$\phi_{\text{H}^+/\text{H}_2}^\circ = \frac{\mu_{\text{H}^+}^\circ - \frac{1}{2}\mu_{\text{H}_2}^\circ}{F} = -\frac{\mu_{\text{H}^+}^\circ}{F} \text{ and by convention: } \mu_{\text{H}^+}^\circ = \Delta G_f^\circ(\text{H}^+, aq) = 0$$

Q11.3 How is it possible to deposit Cu on a Au electrode at a potential lower than that corresponding to the reaction $\text{Cu}^{2+}(aq) + 2e^- \rightarrow \text{Cu}(s)$?

Cu^{2+} is more tightly bound to the Au surface than to Cu. Thus a lower potential is needed to reduce Cu^{2+} on the Au surface.

Q11.4 Explain why the magnitude of the maximum work available from a battery can be greater than the magnitude of the reaction enthalpy of the overall cell reaction.

$$|w_{\text{electrical}}| = |-\Delta G| = \left| -\Delta H \left(1 - \frac{T\Delta S}{\Delta H} \right) \right| > |-\Delta H| \text{ if } \Delta S/\Delta H < 0$$

Q11.5 How can one conclude from Figure 11.23 that Cu atoms can diffuse rapidly over a well-ordered Au electrode in an electrochemical cell?

The copper atoms would be dispersed randomly over the Au surface if they could not diffuse laterally. Instead, they are seen only in islands and on edges, where they are tightly bound. They must have diffused there freely over the surface.

Q11.6 The temperature dependence of the potential of a cell is vanishingly small. What does this tell you about the thermodynamics of the cell reaction?

$$\text{Because } \Delta S_R^\circ = -\left(\frac{\partial \Delta G_R^\circ}{\partial T} \right)_p = nF \left(\frac{\partial E^\circ}{\partial T} \right)_p, \Delta S_R^\circ \approx 0$$

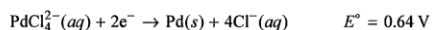
Q11.7 Why is the capacitance of an electrolytic capacitor so high compared with conventional capacitors?

The positive and negative plates of an electrolytic capacitor are separated by an extremely small distance (the thickness of the electrical double layer, essentially). And so, the electric field is very strong and the capacitance large. $\left(\frac{\epsilon A}{d}, d \sim 30 \text{ \AA} \right)$

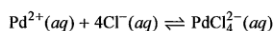
- Q11.8** What is the difference in the chemical potential and the electrochemical potential for an ion and for a neutral species in solution? Under what conditions is the electrochemical potential equal to the chemical potential for an ion?
 $\bar{\mu} = \mu + z\phi$. For a neutral species, the chemical potential and electrochemical potential have the same value. They differ by $z\phi$ for an ion. The electrochemical potential is equal to the chemical potential for an ion if $\phi = 0$.
- Q11.9** Why is it possible to achieve high-resolution electrochemical machining by applying a voltage pulse rather than a dc voltage to the electrode being machined?
For a tool that is very close to a surface, the RC time constant for charging the double layer depends strongly on location. Thus, pulsed voltage charges will charge the layer in those locations where the tool is closest to the surface—allowing subsequent electrochemical reactions—but not in other locations. Therefore, the reactions are localized. This gives the high spatial selectivity needed for nanomachining.
- Q11.10** Can specifically adsorbed ions in the electrochemical double layer influence electrode reactions?
Yes, specifically adsorbed ions can play a central role in the atomic-scale processes occurring on an electrode surface (e.g. Cl^- , on Cu electrode).
- Q11.11** Why is it not necessary to know absolute half-cell potentials to determine the emf of an electrochemical cell?
The emf of a cell depends on the difference between the half-cell emfs. Therefore the common reference level of the half-cells cancels out.
- Q11.12** What is the voltage between the terminals of a battery in which the contents are in chemical equilibrium?
It is zero because only for this value is there no driving force for change.
- Q11.13** By convention, the anode of a battery is where oxidation takes place. Is this true when the battery is charged, discharged, or both?
Both, but the relative location of the anode and cathode change in going from the discharge to the charge mode because the direction of the current flow in the external circuit changes.
- Q11.14** You wish to maximize the emf of an electrochemical cell. To do so, should the concentrations of the products in the overall reaction be high or low relative to those of the reactants? Explain your answer.
To maximize the emf, the concentration dependent term in the Nernst equation should be positive. This is the case if $Q < 1$ or if the concentration of products is low compared to that of the reactants.
- Q11.15** If you double all the coefficients in the overall chemical reaction in an electrochemical cell, the equilibrium constant changes. Does the emf change? Explain your answer.
No, the emf will not change because it is an intensive quantity.
- Q11.16** Why can batteries only be recharged a limited number of times?
As a battery is discharged, reactants are converted into products which in the case of solids leads to a change in structure at the microscopic level. Cycling between two different solid structures with different crystalline structures and densities induces mechanical stress in the electrodes which over time causes them to disintegrate.
- Q11.17** Why can more work be extracted from a fuel cell than a combustion engine for the same overall reaction?
In a fuel cell, electrical work is converted to mechanical work. In principle, this conversion can approach 100% efficiency. By contrast, the efficiency of the conversion of heat into work in a heat engine is limited by the second law.
- Q11.18** What is the function of a salt bridge in an electrochemical cell?
The salt bridge allows current flow in the internal circuit while preventing the mixing of reactants and products of the two half-cells.
- Q11.19** How does the emf of an electrochemical cell change if you increase the temperature?
It is positive (negative) if the reaction entropy is positive (negative).
- Q11.20** What thermodynamic quantity that cannot be measured directly can be calculated from absolute half-cell potentials?
The solvation Gibbs energies of individual ions can only be determined from absolute half-cell emfs.

Numerical Problems

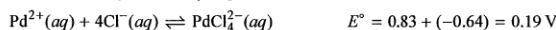
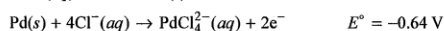
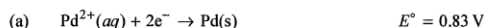
P11.1 You are given the following half-cell reactions:



a. Calculate the equilibrium constant for the reaction



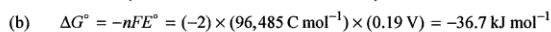
b. Calculate ΔG° for this reaction.



$$E^{\circ} = \frac{RT}{nF} \ln K$$

$$K = e^{nFE^{\circ}/RT}$$

$$K = \exp\left(\frac{2(96,485 \text{ C mol}^{-1}) \times (0.19 \text{ V})}{(8.3145 \text{ J mol}^{-1} \text{ K}^{-1}) \times (298.15 \text{ K})}\right) = 2.65 \times 10^6$$



P11.2 For the half-cell reaction $\text{AgBr}(s) + e^{-} \rightarrow \text{Ag}(s) + \text{Br}^{-}(aq)$, $E^{\circ} = +0.0713 \text{ V}$.

Using this result and $\Delta G_f^{\circ}(\text{AgBr}, s) = -96.9 \text{ kJ mol}^{-1}$, determine $\Delta G_f^{\circ}(\text{Br}^{-}, aq)$.

$$\Delta G_R^{\circ} = -nFE^{\circ} = \Delta G_f^{\circ}(\text{Br}^{-}, aq) - \Delta G_f^{\circ}(\text{AgBr}, s)$$

$$\Delta G_f^{\circ}(\text{Br}^{-}, aq) = \Delta G_f^{\circ}(\text{AgBr}, s) - nFE^{\circ}$$

$$\Delta G_f^{\circ}(\text{Br}^{-}, aq) = -96.9 \text{ kJ mol}^{-1} - 1 \text{ mol} \times 96485 \text{ C mol}^{-1} \times 0.0713 \text{ V} = -103.8 \text{ kJ mol}^{-1}$$

P11.3 For the half-cell reaction $\text{Hg}_2\text{Cl}_2(s) + 2e^{-} \rightarrow 2\text{Hg}(l) + 2\text{Cl}^{-}(aq)$, $E^{\circ} = +0.26808 \text{ V}$.

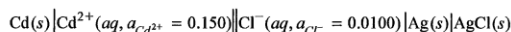
Using this result and $\Delta G_f^{\circ}(\text{Hg}_2\text{Cl}_2, s) = -210.7 \text{ kJ mol}^{-1}$, determine $\Delta G_f^{\circ}(\text{Cl}^{-}, aq)$.

$$\Delta G_R^{\circ} = -nFE^{\circ} = 2\Delta G_f^{\circ}(\text{Cl}^{-}, aq) - \Delta G_f^{\circ}(\text{Hg}_2\text{Cl}_2, s)$$

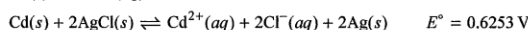
$$\Delta G_f^{\circ}(\text{Cl}^{-}, aq) = \frac{-\Delta G_f^{\circ}(\text{Hg}_2\text{Cl}_2, s) - nFE^{\circ}}{2}$$

$$\Delta G_f^{\circ}(\text{Cl}^{-}, aq) = \frac{-210.7 \text{ kJ mol}^{-1} - 2 \text{ mol} \times 96485 \text{ C mol}^{-1} \times 0.26808 \text{ V}}{2} = -131.2 \text{ kJ mol}^{-1}$$

P11.4 Determine the half-cell reactions and the overall cell reaction, calculate the cell potential, and determine the equilibrium constant at 298.15 K for the cell



Is the cell reaction spontaneous as written?



$$E = E^{\circ} - \frac{RT}{2F} \ln a_{\text{Cd}^{2+}} a_{\text{Cl}^{-}}^2 = 0.6253 \text{ V} - \frac{0.05916}{2} \log_{10} 0.150 \times (0.0100)^2 \text{ V}$$

$$= 0.7680 \text{ V}$$

$$\begin{aligned}\ln K &= \frac{nF}{RT} E^\circ = \frac{2 \times 96485 \text{ C mol}^{-1} \times (0.6253 \text{ V})}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}} \\ &= 48.6781 \\ K &= 1.38 \times 10^{21}\end{aligned}$$

The reaction is spontaneous as written because $Q = 0.150 \times (0.0100)^2 = 1.5 \times 10^{-5} < K$. Another criterion is that $E > 0$.

- P11.5** The standard half-cell potential for the reaction $\text{O}_2(g) + 4\text{H}^+(aq) + 4e^- \rightarrow 2\text{H}_2\text{O}(l)$ is +1.229 V and 298.15 K. Calculate E for a 0.300-molal solution of H_2SO_4 for $a_{\text{O}_2} = 1.00$ (a) assuming that the a_{H^+} is equal to the molality and (b) using the measured mean ionic activity coefficient for this concentration from the Data Tables. How large is the relative error if the concentrations, rather than the activities, are used?

Because K_a for HSO_4^- is 0.012, we assume that only one H^+ is produced upon dissociation.

$$E^\circ = 1.229 \text{ V}; \quad a_{\text{O}_2} = 1; \quad E = E^\circ - \frac{RT}{nF} \ln \frac{1}{(a_{\text{H}^+})^4}$$

a. $a_{\text{H}^+} = 0.300$

$$E = 1.229 \text{ V} - \frac{(8.314 \text{ J mol}^{-1} \text{ K}^{-1}) \times (298.15 \text{ K})}{(4) \times (96,485 \text{ C mol}^{-1})} \ln \frac{1}{0.300^4} = 1.216 \text{ V}$$

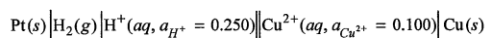
b. $a_{\text{H}^+} = (0.300) \times (0.1826)$

$$E = 1.229 - \frac{(8.3145 \text{ J mol}^{-1} \text{ K}^{-1}) \times (298.15 \text{ K})}{(4) \times (96,485 \text{ C mol}^{-1})} \ln [(0.311) \times (0.1826)]^4 = 1.172 \text{ V}$$

The relative error is given by

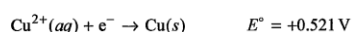
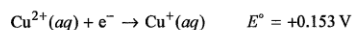
$$\frac{1.172 \text{ V} - 1.216 \text{ V}}{1.172 \text{ V}} 100\% = -3.73\%$$

- P11.6** Determine the half-cell reactions and the overall cell reaction, calculate the cell potential, and determine the equilibrium constant at 298.15 K for the cell



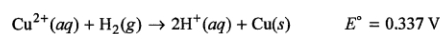
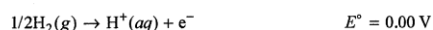
Is the cell reaction spontaneous as written?

We first calculate the E° for the reaction $\text{Cu}^{2+}(aq) + 2e^- \rightarrow \text{Cu}(s)$ from the tabulated values for the reactions $\text{Cu}^{2+}(aq) + e^- \rightarrow \text{Cu}^+(aq)$ and $\text{Cu}^+(aq) + e^- \rightarrow \text{Cu}(s)$ in the Data Tables.



As in Example Problem 11.3, n_1 electrons are transferred in the reaction with the potential $E_{A/B}^\circ$, and n_2 electrons are transferred in the reaction with the potential $E_{B/C}^\circ$. If n_3 electrons are transferred in the reaction with the potential $E_{A/C}^\circ$, then $n_3 E_{A/C}^\circ = n_1 E_{A/B}^\circ + n_2 E_{B/C}^\circ$. Therefore

$$\text{Cu}^{2+}(aq) + 2e^- \rightarrow \text{Cu}(s) \quad E^\circ = \frac{0.153 \text{ V} + 0.521 \text{ V}}{2} = 0.337 \text{ V}$$



$$E = E^\circ - \frac{RT}{2F} \ln \frac{a_{H^+}^2}{a_{Cu^{2+}}} = 0.337 \text{ V} - \frac{0.05916 \text{ V}}{2} \log_{10} \frac{(0.250)^2}{0.100} = 0.3430 \text{ V}$$

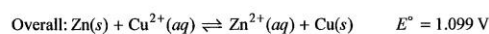
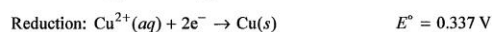
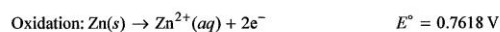
$$\ln K = \frac{nF}{RT} E^\circ = \frac{2 \times 96485 \text{ C mol}^{-1} \times (0.337 \text{ V})}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}}$$

$$= 26.235$$

$$K = 2.47 \times 10^{11}$$

The reaction is spontaneous as written because $Q \ll K$ and $E > 0$.

- P11.7** Consider the Daniell cell for the indicated molalities: $\text{Zn}(s) | \text{ZnSO}_4(aq, 0.200 \text{ m}) || \text{CuSO}_4(aq, 0.400 \text{ m}) | \text{Cu}(s)$. The activity coefficient γ_{\pm} for the indicated concentrations can be found in the Data Tables. Calculate E a) by setting the activity equal to the molality and b) by using the correct values of the γ_{\pm} . How large is the relative error if the concentrations, rather than the activities, are used?



$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{RT}{nF} \ln \left(\frac{a_{\text{Zn}^{2+}}}{a_{\text{Cu}^{2+}}} \right)$$

- a. Activities equal to molality divided by standard molality:

$$E_{\text{cell}}^\circ = 1.099 - \frac{8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K}}{2 \times 96,485 \text{ C mol}^{-1}} \ln \left(\frac{0.200 \text{ mol kg}^{-1}/m^\circ}{0.400 \text{ mol kg}^{-1}/m^\circ} \right) = 1.108 \text{ V}$$

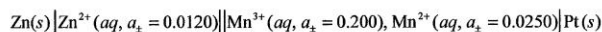
- b. Using γ_{\pm} :

$$E_{\text{cell}}^\circ = 1.099 - \frac{8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K}}{2 \times 96,485 \text{ C mol}^{-1}} \ln \left(\frac{0.14 \times 0.200 \text{ mol kg}^{-1}/m^\circ}{0.0704 \times 0.400 \text{ mol kg}^{-1}/m^\circ} \right) = 1.099 \text{ V}$$

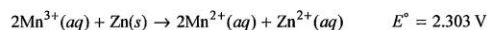
Relative error:

$$\frac{1.099 \text{ V} - 1.108 \text{ V}}{1.099 \text{ V}} \times 100\% = -0.8\%$$

- P11.8** Determine the half-cell reactions and the overall cell reaction, calculate the cell potential, and determine the equilibrium constant at 298.15 K for the cell



Is the cell reaction spontaneous as written?



$$E = E^\circ - \frac{0.05916 \text{ V}}{2} \log_{10} \frac{(0.0250)^2 \cdot 0.0120}{(0.200)^2} = 2.413 \text{ V}$$

$$\ln K = \frac{nF}{RT} E^\circ = \frac{2 \times 96485 \text{ C mol}^{-1} \times (2.413 \text{ V})}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}}$$

$$= 179.3$$

$$K = 7.44 \times 10^{77}$$

The reaction is spontaneous as written because $E > 0$.

- P11.9** Consider the half-cell reaction $\text{AgCl}(s) + e^- \rightarrow \text{Ag}(s) + \text{Cl}^-(aq)$. If $\mu(\text{AgCl}, s) = -109.71 \text{ kJ mol}^{-1}$, and if $E^\circ = +0.222 \text{ V}$ for this half-cell, calculate the standard Gibbs energy of formation of $\text{Cl}^-(aq)$.

$$\Delta G_f^\circ(\text{AgCl}, s) = -109.71 \text{ kJ mol}^{-1}$$

$$\Delta G_R^\circ = -1 \times 96,485 \text{ C mol}^{-1} \times 0.222 \text{ V} = 21.4 \text{ kJ mol}^{-1}$$

$$\Delta G_f^\circ(\text{Cl}^-(aq)) = \Delta G_f^\circ + \Delta G_R^\circ(\text{AgCl}, s) = -131.1 \text{ kJ mol}^{-1}$$

- P11.10** For a given overall cell reaction, $\Delta S_R^\circ = 16.5 \text{ J mol}^{-1} \text{ K}^{-1}$ and $\Delta H_R^\circ = -270.0 \text{ kJ mol}^{-1}$. Calculate E° and $(\partial E^\circ / \partial T)_P$. Assume that $n = 2$.

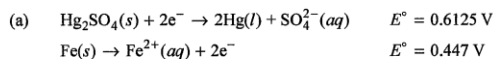
$$E^\circ = \frac{\Delta G_R^\circ}{nF} = -\frac{\Delta H_R^\circ - T\Delta S_R^\circ}{nF} = -\frac{-270.0 \text{ kJ mol}^{-1} - 298.15 \text{ K} \times 16.5 \text{ J K}^{-1} \text{ mol}^{-1}}{2 \times 96485 \text{ C mol}^{-1}}$$

$$= 1.42 \text{ V}$$

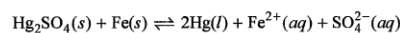
$$\left(\frac{\partial E^\circ}{\partial T}\right)_P = \frac{\Delta S_R^\circ}{nF} = \frac{16.5 \text{ J K}^{-1} \text{ mol}^{-1}}{2 \times 96485 \text{ C mol}^{-1}} = 8.55 \times 10^{-5} \text{ V K}^{-1}$$

- P11.11** Consider the cell $\text{Fe}(s) | \text{FeSO}_4(aq, a = 0.0250) | \text{Hg}_2\text{SO}_4(s) | \text{Hg}(l)$.

- Write the cell reaction.
- Calculate the cell potential, the equilibrium constant for the cell reaction, and ΔG_R° at 25°C .



Cell reaction:



$$E_{\text{cell}}^\circ = 0.6125 + 0.447 = 1.0595 \text{ V}$$

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{RT}{nF} \ln a_{\text{Fe}^{2+}} a_{\text{SO}_4^{2-}}$$

$$= 1.0595 - \frac{8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K}}{2 \times 96,485 \text{ C mol}^{-1}} \ln ((0.0250)^2)$$

$$= 1.154 \text{ V}$$

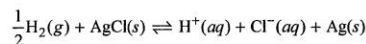
$$\Delta G_{\text{reaction}}^\circ = -nFE^\circ = -2 \times 96,485 \text{ C mol}^{-1} \times (1.0595 \text{ V})$$

$$= -204.5 \text{ kJ mol}^{-1}$$

$$K = e^{-\Delta G_R^\circ / RT} = 6.61 \times 10^{35}$$

- P11.12** Between 0° and 90°C , the potential of the cell $\text{Pt}(s) | \text{H}_2(g, f = 1 \text{ atm}) | \text{HCl}(aq, m = 0.100) | \text{AgCl}(s) | \text{Ag}(s)$ is described by the equation $E(V) = 0.35510 - 0.3422 \times 10^{-4} t - 3.2347 \times 10^{-6} t^2 + 6.314 \times 10^{-9} t^3$, where t is the temperature on the Celsius scale. Write the cell reaction and calculate ΔG_R° , ΔH_R° , and ΔS_R° for the cell reaction at 50°C .

Cell reaction:



At 50.°C

$$E = 0.35510 \text{ V} - (0.3422 \times 10^{-4} \text{ V}^\circ\text{C}^{-1}) \times 50.^\circ\text{C} \\ - (3.2347 \times 10^{-6} \text{ V}^\circ\text{C}^{-2})(50.)^2\text{C}^2 + (6.314 \times 10^{-9} \text{ V}^\circ\text{C}^{-3})(50.)^3\text{C}^3 = 0.3461 \text{ V}$$

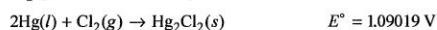
$$\Delta G_R = -nFE = (-1)(96,485 \text{ C mol}^{-1})(0.3461 \text{ V}) = -33.4 \text{ kJ mol}^{-1}$$

$$\left(\frac{\partial E}{\partial T}\right)_P = -0.3422 \times 10^{-4} - 2(3.2347 \times 10^{-6})(50.) + 3(6.314 \times 10^{-9})(50.)^2 \\ = -3.10 \times 10^{-4} \text{ V K}^{-1}$$

$$\Delta S = nF\left(\frac{\partial E}{\partial T}\right)_P = -29.9 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Delta H = \Delta G + T\Delta S = -33.4 \text{ kJ mol}^{-1} + (348.15 \text{ K})(-29.9 \text{ J mol}^{-1} \text{ K}^{-1}) = -43.1 \text{ kJ mol}^{-1}$$

P11.13 a. Calculate ΔG_R° and the equilibrium constant, K , at 298.15K for the reaction $2\text{Hg}(\text{l}) + \text{Cl}_2(\text{g}) \rightleftharpoons \text{Hg}_2\text{Cl}_2(\text{s})$.
b. Calculate K using Table 4.1. What value of ΔG_R° would make the value of K the same as calculated from the half-cell potentials?



$$\Delta G_R^\circ = -nFE^\circ = -2 \times 96485 \text{ C mol}^{-1} \times 1.09019 \text{ V} = -210.4 \text{ kJ mol}^{-1}$$

$$\ln K = \frac{nF}{RT} E^\circ = \frac{2 \times 96485 \text{ C mol}^{-1} \times 1.09019 \text{ V}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}} \\ = 84.8686$$

$$K = 7.21 \times 10^{36}$$

(b) $\ln K = \frac{\Delta G_R^\circ}{RT} = \frac{210700 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}} \\ = 85.0002 \\ K = 8.22 \times 10^{36}$

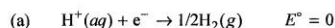
The results would agree exactly if $\Delta G_R^\circ = -210374 \text{ J mol}^{-1}$.

P11.14 Consider the couple $\text{Ox} + \text{e}^- \rightarrow \text{Red}$ with the oxidized and reduced species at unit activity. What must be the value of E° for this half-cell if the reductant Red is to liberate hydrogen at 1 atm from

a. an acid solution with $a_{\text{H}^+} = 2.50$?

b. a basic solution with $\text{pH} = 9.00$?

c. Is hydrogen a better reducing agent in acid or basic solution? Explain your answer.



Overall: $\text{H}^+(aq) + \text{Red} \rightarrow 1/2\text{H}_2(g) + \text{Ox}$

$$E = E^\circ - \frac{RT}{nF} \ln \frac{\sqrt{a_{\text{H}_2}}}{a_{\text{H}^+}} = E^\circ - 0.05916 \log_{10} \frac{1}{2.50} = E^\circ + 0.02354 \text{ V} > 0 \text{ V}$$

To liberate H_2 , E for the reaction must be $> 0 \text{ V}$.

Therefore, E° for $\text{Ox} + e^- \rightarrow \text{Red}$ must be $> -0.02354 \text{ V}$.

- (b) For a pH of 9, $a_{\text{H}^+} = 10^{-9}$

$$E = E^\circ - \frac{RT}{nF} \ln \frac{\sqrt{a_{\text{H}_2}}}{a_{\text{H}^+}} = E^\circ - 0.05916 \log_{10}(10^9) = E^\circ - 0.5324 \text{ V} > 0 \text{ V}$$

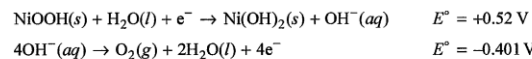
For the overall reaction to be spontaneous, E° for $\text{Red} \rightarrow \text{Ox} + e^-$ must be $> 0.5324 \text{ V}$.

- (c) It is a better reducing agent in basic solution, because the oxidation potential for the reaction $1/2\text{H}_2(g) \rightarrow \text{H}^+(g) + e^-$ becomes more positive as the pH decreases.

P11.15 By finding appropriate half-cell reactions, calculate the equilibrium constant at 298.15 K for the following reactions:

- a. $4\text{NiOOH}(s) + 2\text{H}_2\text{O}(l) \rightleftharpoons 4\text{Ni}(\text{OH})_2(s) + \text{O}_2(g)$
 b. $4\text{NO}_3^-(aq) + 4\text{H}^+(aq) \rightleftharpoons 4\text{NO}(g) + 2\text{H}_2\text{O}(l) + 3\text{O}_2(g)$

- (a) The half-cell reactions are



The overall reaction is

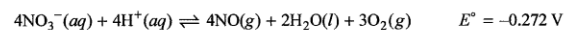


$$\begin{aligned} \ln K &= \frac{nF}{RT} E^\circ = \frac{4 \times 96485 \text{ C mol}^{-1} \times 0.119 \text{ V}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}} \\ &= 18.527 \end{aligned}$$

$$K = 1.11 \times 10^8$$

- (b) $\text{NO}_3^-(aq) + 4\text{H}^+(aq) + 3e^- \rightarrow \text{NO}(g) + 2\text{H}_2\text{O}(l) \quad E^\circ = +0.957 \text{ V}$
 $2\text{H}_2\text{O}(l) \rightarrow \text{O}_2(g) + 4\text{H}^+(aq) + 4e^- \quad E^\circ = -1.229 \text{ V}$

The overall reaction is



$$\begin{aligned} \ln K &= \frac{nF}{RT} E^\circ = \frac{12 \times 96485 \text{ C mol}^{-1} \times 0.272 \text{ V}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}} \\ &= -127.047 \end{aligned}$$

$$K = 6.67 \times 10^{-56}$$

P11.16 The cell potential E for the cell $\text{Pt}(s) | \text{H}_2(g, a_{\text{H}_2} = 1) | \text{H}^+(aq, a_{\text{H}^+} = 1) || \text{NaCl}(aq, m = 0.300) | \text{AgCl}(s) | \text{Ag}(s)$ is $+0.260 \text{ V}$. Determine γ_{Cl^-} assuming that $\gamma_{\pm} = \gamma_{\text{Na}^+} = \gamma_{\text{Cl}^-}$.

Overall: $\text{H}^+(aq) + \text{Red} \rightarrow 1/2\text{H}_2(g) + \text{Ox}$

$$E = E^\circ - \frac{RT}{nF} \ln \frac{\sqrt{a_{\text{H}_2}}}{a_{\text{H}^+}} = E^\circ - 0.05916 \log_{10} \frac{1}{2.50} = E^\circ + 0.02354 \text{ V} > 0 \text{ V}$$

To liberate H_2 , E for the reaction must be $> 0 \text{ V}$.

Therefore, E° for $\text{Ox} + e^- \rightarrow \text{Red}$ must be $> -0.02354 \text{ V}$.

- (b) For a pH of 9, $a_{\text{H}^+} = 10^{-9}$

$$E = E^\circ - \frac{RT}{nF} \ln \frac{\sqrt{a_{\text{H}_2}}}{a_{\text{H}^+}} = E^\circ - 0.05916 \log_{10}(10^9) = E^\circ - 0.5324 \text{ V} > 0 \text{ V}$$

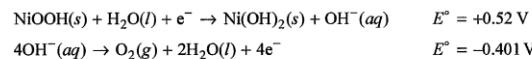
For the overall reaction to be spontaneous, E° for $\text{Red} \rightarrow \text{Ox} + e^-$ must be $> 0.5324 \text{ V}$.

- (c) It is a better reducing agent in basic solution, because the oxidation potential for the reaction $1/2\text{H}_2(g) \rightarrow \text{H}^+(g) + e^-$ becomes more positive as the pH decreases.

P11.15 By finding appropriate half-cell reactions, calculate the equilibrium constant at 298.15 K for the following reactions:

- a. $4\text{NiOOH}(s) + 2\text{H}_2\text{O}(l) \rightleftharpoons 4\text{Ni}(\text{OH})_2(s) + \text{O}_2(g)$
 b. $4\text{NO}_3^-(aq) + 4\text{H}^+(aq) \rightleftharpoons 4\text{NO}(g) + 2\text{H}_2\text{O}(l) + 3\text{O}_2(g)$

- (a) The half-cell reactions are



The overall reaction is

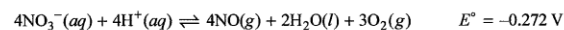


$$\begin{aligned} \ln K &= \frac{nF}{RT} E^\circ = \frac{4 \times 96485 \text{ C mol}^{-1} \times 0.119 \text{ V}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}} \\ &= 18.527 \end{aligned}$$

$$K = 1.11 \times 10^8$$

- (b) $\text{NO}_3^-(aq) + 4\text{H}^+(aq) + 3e^- \rightarrow \text{NO}(g) + 2\text{H}_2\text{O}(l) \quad E^\circ = +0.957 \text{ V}$
 $2\text{H}_2\text{O}(l) \rightarrow \text{O}_2(g) + 4\text{H}^+(aq) + 4e^- \quad E^\circ = -1.229 \text{ V}$

The overall reaction is



$$\begin{aligned} \ln K &= \frac{nF}{RT} E^\circ = \frac{12 \times 96485 \text{ C mol}^{-1} \times 0.272 \text{ V}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}} \\ &= -127.047 \end{aligned}$$

$$K = 6.67 \times 10^{-56}$$

P11.16 The cell potential E for the cell $\text{Pt}(s) | \text{H}_2(g, a_{\text{H}_2} = 1) | \text{H}^+(aq, a_{\text{H}^+} = 1) || \text{NaCl}(aq, m = 0.300) | \text{AgCl}(s) | \text{Ag}(s)$ is $+0.260 \text{ V}$. Determine γ_{Cl^-} assuming that $\gamma_{\pm} = \gamma_{\text{Na}^+} = \gamma_{\text{Cl}^-}$.

We next calculate the mean ionic activity coefficients.

$$I_{\text{ZnSO}_4} = \frac{m}{2}(v_+z_+^2 + v_-z_-^2) = \frac{1}{2}(m_+z_+^2 + m_-z_-^2)$$

$$I = \frac{1}{2}(4 \times 0.00110 \text{ mol kg}^{-1} + 4 \times 0.00110 \text{ mol kg}^{-1}) = 0.00440 \text{ mol kg}^{-1}$$

$$\ln \gamma_{\pm} = -1.173 |z_+z_-| \sqrt{\frac{I}{\text{mol kg}^{-1}}} = -1.173 \times 4 \times \sqrt{0.00440} = -0.3112$$

$$\gamma_{\pm} = 0.733$$

$$I_{\text{CuSO}_4} = \frac{m}{2}(v_+z_+^2 + v_-z_-^2) = \frac{1}{2}(m_+z_+^2 + m_-z_-^2)$$

$$I = \frac{1}{2}(4 \times 0.00250 \text{ mol kg}^{-1} + 4 \times 0.00250 \text{ mol kg}^{-1}) = 0.0100 \text{ mol kg}^{-1}$$

$$\ln \gamma_{\pm} = -1.173 |z_+z_-| \sqrt{\frac{I}{\text{mol kg}^{-1}}} = -1.173 \times 4 \times \sqrt{0.0100} = -0.4692$$

$$\gamma_{\pm} = 0.626$$

We next calculate E using the activities.

$$E = E^\circ - \frac{RT}{nF} \ln \frac{a_{\text{Zn}^{2+}}}{a_{\text{Cu}^{2+}}} = E^\circ - \frac{RT}{nF} \ln \frac{m_+ \gamma_{\pm} (\text{Zn}^{2+})}{m_- \gamma_{\pm} (\text{Cu}^{2+})}$$

$$= 1.099 \text{ V} - \frac{0.05916 \text{ V}}{2} \log_{10} \frac{(1.10 \times 10^{-3} \text{ m}) \times (0.733)}{(2.50 \times 10^{-3} \text{ m}) \times (0.626)}$$

$$E = 1.108 \text{ V}$$

The relative error is -0.2% .

P11.19 The standard potential E° for a given cell is 1.135 V at 298.15 K and $(\partial E^\circ / \partial T)_P = -4.10 \times 10^{-5} \text{ V K}^{-1}$. Calculate ΔG_R° , ΔS_R° , and ΔH_R° . Assume that $n = 2$.

$$\Delta G_R^\circ = -nFE^\circ = -2 \times 96485 \text{ C mol}^{-1} \times 1.135 \text{ V} = -219.0 \text{ kJ mol}^{-1}$$

$$\Delta S_R^\circ = - \left(\frac{\partial \Delta G_R^\circ}{\partial T} \right)_P = nF \left(\frac{\partial E^\circ}{\partial T} \right)_P$$

$$= -2 \times 96485 \text{ C mol}^{-1} \times 4.10 \times 10^{-5} \text{ V K}^{-1} = -7.91 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Delta H_R^\circ = \Delta G_R^\circ + T \Delta S_R^\circ$$

$$= -219.0 \text{ kJ mol}^{-1} - 298.15 \text{ K} \times (-7.91 \text{ J mol}^{-1} \text{ K}^{-1}) = -221.4 \text{ kJ mol}^{-1}$$

P11.20 Determine E° for the reaction $\text{Cr}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cr}(\text{s})$ from the one-electron reduction potential for $\text{Cr}^{3+}(\text{aq})$ and the three-electron reduction potential for $\text{Cr}^{3+}(\text{aq})$ given in Table 11.1 (see Appendix B).

$$\text{Cr}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{Cr}(\text{s}) \quad \Delta G^\circ = -nFE^\circ = -3 \times 96485 \text{ C mol}^{-1} \times (-0.744 \text{ V}) = 215.4 \text{ kJ mol}^{-1}$$

$$\text{Cr}^{2+}(\text{aq}) \rightarrow \text{Cr}^{3+}(\text{aq}) + \text{e}^- \quad \Delta G^\circ = -nFE^\circ = -1 \times 96485 \text{ C mol}^{-1} \times 0.407 \text{ V} = -39.27 \text{ kJ mol}^{-1}$$

$$\text{Cr}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cr}(\text{s}) \quad \Delta G^\circ = 215.4 \text{ kJ mol}^{-1} - 39.27 \text{ kJ mol}^{-1} = 176.1 \text{ kJ mol}^{-1}$$

$$E_{\text{Cr}^{2+}/\text{Cr}}^\circ = -\frac{\Delta G^\circ}{nF} = -\frac{176.1 \times 10^3 \text{ J mol}^{-1}}{2 \times 96485 \text{ C mol}^{-1}} = -0.913 \text{ V}$$

- P11.21** Harnet and Hamer [*J. American Chemical Society* 57 (1935): 33] report values for the potential of the cell $\text{Pt}(s)|\text{PbSO}_4(s)|\text{H}_2\text{SO}_4(aq, a)|\text{PbSO}_4(s)|\text{PbO}_2(s)|\text{Pt}(s)$ over a wide range of temperature and H_2SO_4 concentrations. In 1 *m* H_2SO_4 , their results were described by $E(\text{V}) = 1.91737 + 56.1 \times 10^{-6}t + 108 \times 10^{-8}t^2$, where t is the temperature on the Celsius scale. Calculate ΔG_R , ΔH_R , and ΔS_R for the cell reaction at 11° and 35°C.

$$E(\text{V}) = 1.91737 + 56.1 \times 10^{-6}t + 108 \times 10^{-8}t^2$$

$$\left(\frac{\partial E}{\partial T}\right)_P = 56.1 \times 10^{-6} + 2 \times 108 \times 10^{-8}t$$

$$\Delta G = -nFE; \quad \Delta S = nF\left(\frac{\partial E}{\partial T}\right)_P; \quad \Delta H = \Delta G + T\Delta S$$

a. 11°C

$$E = [1.91737 + (56.1 \times 10^{-6}) \times (11) + (108 \times 10^{-8}) \times (11)^2] \text{V} = 1.91812 \text{V}$$

$$\Delta G = -2 \times 96,485 \text{ C mol}^{-1} \times 1.91812 \text{V} = -370.1 \text{ kJ mol}^{-1}$$

$$\left(\frac{\partial E}{\partial T}\right)_P = 7.99 \times 10^{-5} \text{ V K}^{-1}$$

$$\Delta S = 2 \times 96,485 \text{ C mol}^{-1} \times 7.99 \times 10^{-5} \text{ V K}^{-1} = 15.4 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Delta H = -370.1 \text{ kJ mol}^{-1} + \frac{284.15 \text{ K} \times 15.4 \text{ J mol}^{-1} \text{ K}^{-1}}{1000 \text{ J kJ}^{-1}} = -365.8 \text{ kJ mol}^{-1}$$

b. 35°C

$$E = [1.91737 + (56.1 \times 10^{-6}) \times (35) + (108 \times 10^{-8}) \times (35)^2] \text{V} = 1.92066 \text{V}$$

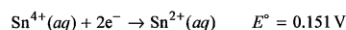
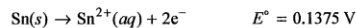
$$\Delta G = -370.6 \text{ kJ mol}^{-1}$$

$$\left(\frac{\partial E}{\partial T}\right)_P = 1.317 \times 10^{-4} \text{ V K}^{-1}$$

$$\Delta S = 25.4 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Delta H = -370.6 \text{ kJ mol}^{-1} + \frac{308.15 \text{ K} \times 25.4 \text{ J mol}^{-1} \text{ K}^{-1}}{1000 \text{ J kJ}^{-1}} = -362.8 \text{ kJ mol}^{-1}$$

- P11.22** Consider the reaction $\text{Sn}(s) + \text{Sn}^{4+}(aq) \rightleftharpoons 2\text{Sn}^{2+}(aq)$. If metallic tin is in equilibrium with a solution of $\text{Sn}^{2+}(aq)$ in which $a_{\text{Sn}^{2+}} = 0.250$, what is the activity of $\text{Sn}^{4+}(aq)$ at equilibrium at 298.15 K?



For $\text{Sn}(s) + \text{Sn}^{4+}(aq) \rightleftharpoons 2\text{Sn}^{2+}(aq)$

$$E^\circ = 0.1375 + 0.151 = 0.2885 \text{V}$$

$$\Delta G^\circ = -nFE^\circ = -2 \times 96,485 \text{ C mol}^{-1} \times 0.2885 \text{V} = -55.7 \text{ kJ mol}^{-1}$$

$$K = e^{-\Delta G^\circ/RT} = 5.67 \times 10^9$$

$$K = \frac{(a_{\text{Sn}^{2+}})^2}{a_{\text{Sn}^{4+}}}$$

$$a_{\text{Sn}^{4+}} = \frac{(a_{\text{Sn}^{2+}})^2}{K} = \frac{(0.250)^2}{5.67 \times 10^9} = 1.10 \times 10^{-11}$$

P11.23 Consider the half-cell reaction $\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}(\text{l})$. By what factor are n , Q , E , and E° changed if all the stoichiometric coefficients are multiplied by the factor two? Justify your answers.

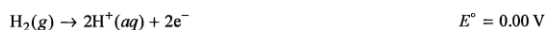
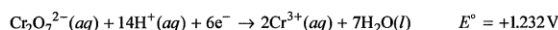
n is proportional to the number of electrons transferred, and increases by the factor two.

Q is squared if all stoichiometric factors are doubled. The factor by which it is increased depends on the activities of O_2 and H^+ .

$E^\circ = \frac{\Delta G^\circ}{nF}$ is unchanged because both ΔG° and n are doubled.

$E = E^\circ - \frac{RT}{nF} \ln Q$ is unchanged because the squaring of Q is offset exactly by the doubling of n .

P11.24 Calculate ΔG_R° and the equilibrium constant at 298.15 K for the reaction $\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 3\text{H}_2(\text{g}) + 8\text{H}^+(\text{aq}) \rightarrow 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$.



$$\Delta G_R^\circ = -nFE^\circ = -6 \times 96485 \text{ C mol}^{-1} \times 1.232 \text{ V} = -713.2 \text{ kJ mol}^{-1}$$

$$\ln K = \frac{nF}{RT} E^\circ = \frac{6 \times 96485 \text{ C mol}^{-1} \times 1.232 \text{ V}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}}$$

$$= 287.7$$

$$K = 9.06 \times 10^{124}$$

P11.25 The half-cell potential for the reaction $\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}(\text{l})$ is +1.03 V at 298.15 K when $a_{\text{O}_2} = 1$. Determine a_{H^+} .

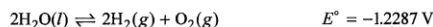
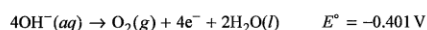
$$E = E^\circ - \frac{RT}{nF} \ln \frac{1}{a_{\text{O}_2} a_{\text{H}^+}^4}$$

$$1.03 \text{ V} = 1.23 \text{ V} - \frac{0.05916 \text{ V}}{4} \log_{10} \frac{1}{a_{\text{H}^+}^4}$$

$$\log_{10} a_{\text{H}^+} = \frac{1.03 \text{ V} - 1.23 \text{ V}}{0.05916 \text{ V}} = -3.381$$

$$a_{\text{H}^+} = 4.16 \times 10^{-4}$$

P11.26 Using half-cell potentials, calculate the equilibrium constant at 298.15 K for the reaction $2\text{H}_2\text{O}(\text{l}) \rightleftharpoons 2\text{H}_2(\text{g}) + \text{O}_2(\text{g})$. Compare your answer with that calculated using ΔG_f° values from Table 4.1 (see Appendix B). What is the value of E° for the overall reaction that makes the two methods agree exactly?



$$\ln K = \frac{nF}{RT} E^\circ = -\frac{4 \times 96485 \text{ C mol}^{-1} \times 1.2287 \text{ V}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}}$$

$$= -191.303$$

$$K = 8.28 \times 10^{-84}$$

$$\ln K = -\frac{2\Delta G_f^\circ(\text{H}_2\text{O}, l)}{RT} = -\frac{2 \text{ mol} \times 237.1 \times 10^3 \text{ J mol}^{-1}}{8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K}} = -191.301$$

$$K = 8.30 \times 10^{-84}$$

For the two results to agree, E° must be given by

$$E^\circ = -\frac{191.325 \times 8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K}}{4 \times 96485 \text{ C mol}^{-1}} = -1.22869 \text{ V}$$

This value lies within the error limits of the determination of E° .

P11.27 The data in the following table have been obtained for the potential of the cell $\text{Pt}(s)|\text{H}_2(g, f = 1 \text{ atm})|\text{HCl}(aq, m)|\text{AgCl}(s)|\text{Ag}(s)$ as a function of m at 25°C.

m (mol kg ⁻¹)	E (V)	m (mol kg ⁻¹)	E (V)	m (mol kg ⁻¹)	E (V)
0.00100	0.57915	0.0200	0.43024	0.500	0.27231
0.00200	0.54425	0.0500	0.38588	1.000	0.23328
0.00500	0.49846	0.100	0.35241	1.500	0.20719
0.0100	0.46417	0.200	0.31874	2.000	0.18631

- Determine E° using a graphical method.
- Calculate γ_{\pm} for HCl at $m = 0.00100$, 0.0100 , and $0.100 \text{ mol kg}^{-1}$.

Cell reaction: $2\text{AgCl}(s) + \text{H}_2(g) \rightleftharpoons 2\text{Ag}(s) + 2\text{H}^+(aq) + 2\text{Cl}^-(aq)$

$$E = E^\circ - \frac{RT}{2F} \ln(a_{\text{H}^+} a_{\text{Cl}^-})^2 = E^\circ - \frac{RT}{F} \ln(a_{\text{H}^+} a_{\text{Cl}^-})$$

$$a_{\text{H}^+} a_{\text{Cl}^-} = a_{\pm}^2 = \gamma_{\pm}^2 m_{\pm}^2$$

$$E = E^\circ - \frac{2RT}{F} \ln\left(\frac{m_{\pm}}{m^\circ}\right) - \frac{2RT}{F} (\ln \gamma_{\pm})$$

In the low concentration limit we can use the Debye–Hückel result.

$$\ln \gamma_{\pm} = -1.172614 \sqrt{\frac{m}{m^\circ}}$$

Therefore, for dilute solutions

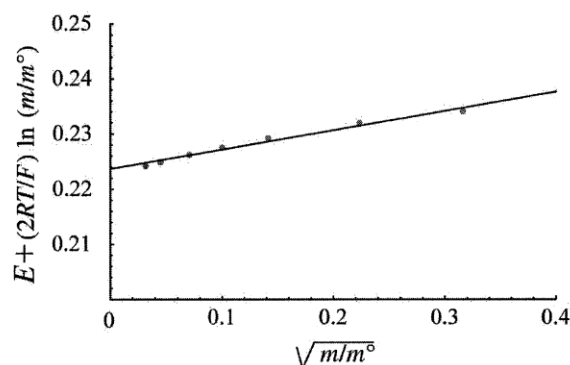
$$E + \frac{2RT}{F} \ln\left(\frac{m}{m^\circ}\right) = E^\circ + \frac{2RT}{F} \times 1.172614 \times \sqrt{\frac{m}{m^\circ}}$$

Using this result, a plot of $E + \frac{2RT}{F} \ln\left(\frac{m}{m^\circ}\right)$ (y axis) vs. $\sqrt{\frac{m}{m^\circ}}$ (x axis) will have an intercept of E° .

We use the data up to $m = 0.100$, as the Debye–Hückel model is not valid for more concentrated solutions.

$\frac{m}{m^\circ}$	$\sqrt{\frac{m}{m^\circ}}$	E (V)	$E + \frac{2RT}{F} \ln\left(\frac{m}{m^\circ}\right)$ (V)
0.001	0.031623	0.57915	0.224212
0.002	0.044721	0.54425	0.224909
0.005	0.070711	0.49846	0.226203
0.010	0.1	0.46417	0.227531
0.020	0.141421	0.43024	0.229218
0.050	0.223607	0.38588	0.231943
0.100	0.316228	0.35241	0.234090

The data in the table is graphed below. The best fit line gives a value for E° of 0.224 V.



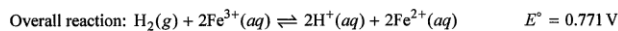
Given E° we can now find γ_{\pm} from

$$\ln \gamma_{\pm} = \frac{F}{RT}(E^\circ - E) - \ln\left(\frac{m}{m^\circ}\right)$$

m/m°	$E^\circ = 0.224$ V	
	$\ln \gamma_{\pm}$	γ_{\pm}
0.001	-0.010654	0.989
0.010	-0.0755112	0.927
0.100	-0.203036	0.816

P11.28 Consider the cell $\text{Pt}(s)|\text{H}_2(g, 1\text{atm})|\text{H}^+(aq, a=1)|\text{Fe}^{3+}(aq), \text{Fe}^{2+}(aq)|\text{Pt}(s)$ given that $\text{Fe}^{3+}(aq) + e^- \rightleftharpoons \text{Fe}^{2+}(aq)$ and $E^\circ = 0.771$ V.

- If the cell potential is 0.712 V, what is the ratio of $\text{Fe}^{2+}(aq)$ to $\text{Fe}^{3+}(aq)$?
- What is the ratio of these concentrations if the cell potential is 0.830 V?
- Calculate the fraction of the total iron present as $\text{Fe}^{3+}(aq)$ at cell potentials of 0.650, 0.700, 0.750, 0.771, 0.800, and 0.900 V. Graph the result as a function of the cell potential.



$$\begin{aligned} \text{(a)} \quad E &= E^\circ - \frac{RT}{2F} \ln(a_{\text{Fe}^{2+}}/a_{\text{Fe}^{3+}})^2 \\ &= E^\circ - \frac{RT}{F} \ln(a_{\text{Fe}^{2+}}/a_{\text{Fe}^{3+}}) \end{aligned}$$

$$\frac{a_{\text{Fe}^{2+}}}{a_{\text{Fe}^{3+}}} = \exp\left(\frac{(E^\circ - E)F}{RT}\right)$$

If $E = 0.712 \text{ V}$

$$\frac{a_{\text{Fe}^{2+}}}{a_{\text{Fe}^{3+}}} = \exp\left(\frac{(0.771 \text{ V} - 0.712 \text{ V}) \times 96,485 \text{ C mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K}}\right) = 9.95$$

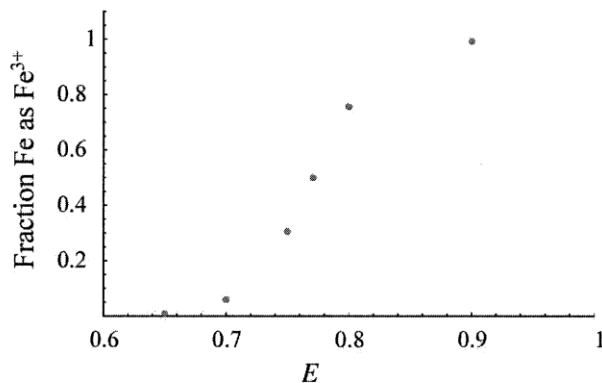
(b) If $E = 0.830 \text{ V}$

$$\frac{a_{\text{Fe}^{2+}}}{a_{\text{Fe}^{3+}}} = \exp\left(\frac{(0.771 \text{ V} - 0.830 \text{ V}) \times 96,485 \text{ C mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K}}\right) = 0.100$$

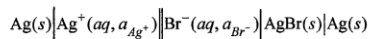
$$\text{(c) Fraction of Fe}^{3+}: \frac{a_{\text{Fe}^{3+}}}{a_{\text{Fe}^{3+}} + a_{\text{Fe}^{2+}}} = \frac{1}{1 + (a_{\text{Fe}^{2+}}/a_{\text{Fe}^{3+}})}$$

We use the method described above to find $a_{\text{Fe}^{2+}}/a_{\text{Fe}^{3+}}$. We find the following results:

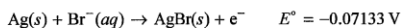
$E \text{ (V)}$	$a_{\text{Fe}^{2+}}/a_{\text{Fe}^{3+}}$	Fraction of Fe^{3+}
0.650	111	8.93×10^{-3}
0.700	15.9	0.0593
0.750	2.26	0.306
0.771	1.0	0.5
0.800	0.323	0.756
0.900	6.60×10^{-3}	0.993



P11.29 Determine K_{sp} for AgBr at 298.15 K using the electrochemical cell described by



The half-cell and overall reactions are

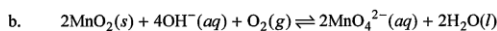
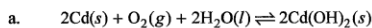


$$\log_{10} K_{sp} = \frac{nE^\circ}{0.05916 \text{ V}} = \frac{0.72827 \text{ V}}{0.05916 \text{ V}} = 12.31$$

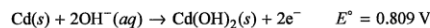
$$K = 2.04 \times 10^{12}$$

$$K_{sp} = 1/K = 4.89 \times 10^{-13}$$

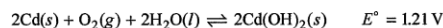
P11.30 By finding appropriate half-cell reactions, calculate the equilibrium constant at 298.15 K for the following reactions:



(a) The half-cell reactions are



The overall reaction is

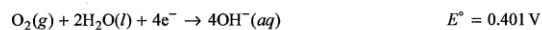
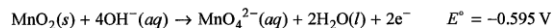


$$\ln K = \frac{nF}{RT} E^\circ = \frac{4 \times 96485 \text{ C mol}^{-1} \times 1.21 \text{ V}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}}$$

$$= 188.391$$

$$K = 6.56 \times 10^{81}$$

(b) The half-cell reactions are



The overall reaction is



$$\ln K = \frac{nF}{RT} E^\circ = \frac{4 \times 96485 \text{ C mol}^{-1} \times 0.194 \text{ V}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}}$$

$$= -30.2049$$

$$K = 7.62 \times 10^{-14}$$