

$$1 F = 96,500 \text{ C/mol}$$

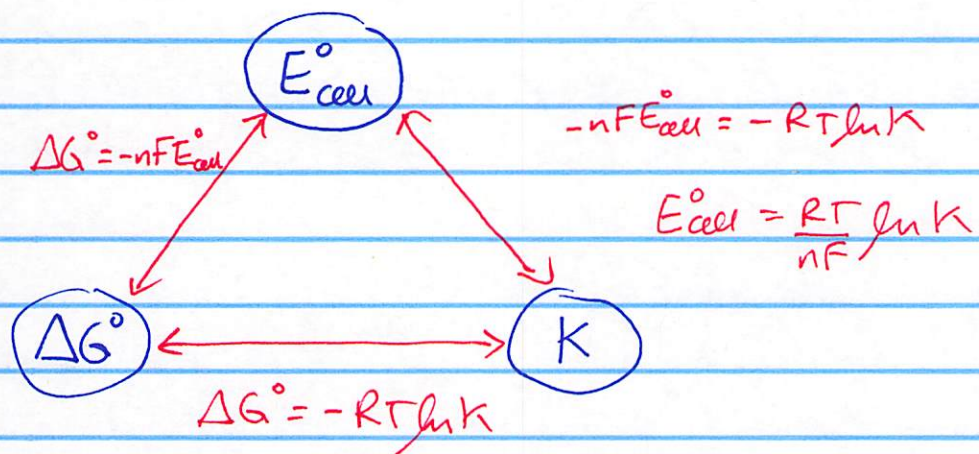
(Faraday) (1 charge on a mol of e⁻s)

$$\Delta G = \text{charge} \times \text{voltage} \quad (\text{physics})$$

$$\Delta G = -nF \times E_{\text{cell}} \quad (\text{non-sta.})$$

-ve charge # mol e⁻ cell voltage.

$$\Delta G^\circ = -nFE_{\text{cell}}^\circ$$



ΔG°	-ve	0	+ve
K	> 1	1	< 1
E_{cell}°	+ve	0	-ve

Rosetta stone

Example 19.6 Relating ΔG° and E°_{cell}

Use the tabulated electrode potentials to calculate ΔG° for the reaction:



Is the reaction spontaneous?

Sort

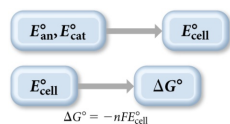
You are given a redox reaction and asked to find ΔG° .

Given: $\text{I}_2(\text{s}) + 2 \text{Br}^-(\text{aq}) \longrightarrow 2 \text{I}^-(\text{aq}) + \text{Br}_2(\text{l})$

Find: ΔG°

Strategize

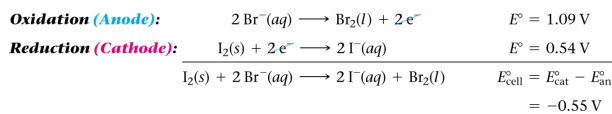
Refer to the values of electrode potentials in Table 19.1 to calculate E°_{cell} . Then use Equation 19.3 to calculate ΔG° from E°_{cell} .

Conceptual Plan**Solve**

Separate the reaction into oxidation and reduction half-reactions and find the standard electrode potentials for each. Determine E°_{cell} by subtracting E_{an} from E_{cat} .

Example 19.6 Relating ΔG° and E°_{cell}

Continued

Solution

Calculate ΔG° from E°_{cell} . The value of n (the number of moles of electrons) corresponds to the number of electrons that are canceled in the half-reactions. Remember that $1 \text{ V} = 1 \text{ J/C}$.

$$\begin{aligned} \Delta G^\circ &= -nFE^\circ_{\text{cell}} \\ &= -2 \text{ mol e}^- \left(\frac{96,485 \text{ C}}{\text{mol e}^-} \right) (-0.55 \frac{\text{J}}{\text{C}}) \\ &= +1.1 \times 10^5 \text{ J} \end{aligned}$$

Since ΔG° is positive, the reaction is not spontaneous under standard conditions.

Example 19.6 Relating ΔG° and E°_{cell}

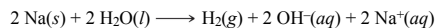
Continued

Check

The answer is in the correct units (joules) and seems reasonable in magnitude (≈ 110 kJ). You have seen (in Chapter 18) that values of ΔG° typically range from plus or minus tens to hundreds of kilojoules. The sign is positive, as expected for a reaction in which E°_{cell} is negative.

For Practice 19.6

Use tabulated electrode potentials to calculate ΔG° for the reaction.



Is the reaction spontaneous?

Example 19.7 Relating E°_{cell} and K

Use the tabulated electrode potentials to calculate K for the oxidation of copper by H^+ (at 25°C):

**Sort**

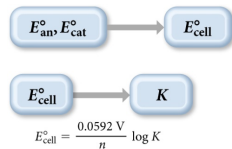
You are given a redox reaction and asked to find K .

Given: $\text{Cu}(s) + 2 \text{H}^+(aq) \longrightarrow \text{Cu}^{2+}(aq) + \text{H}_2(g)$

Find: K

Strategize

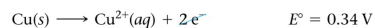
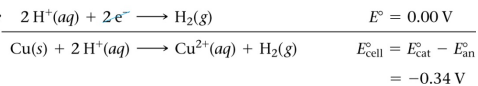
Refer to the values of electrode potentials in Table 19.1 to calculate E°_{cell} . Then use Equation 19.6 to calculate K from E°_{cell} .

Conceptual Plan**Solve**

Separate the reaction into oxidation and reduction half-reactions and find the standard electrode potentials for each. Find E°_{cell} by subtracting E°_{an} from E°_{cat} .

Example 19.7 Relating E°_{cell} and K

Continued

Solution**Oxidation****(Anode):****Reduction****(Cathode):**

Calculate K from E°_{cell} . The value of n (the number of moles of electrons) corresponds to the number of electrons that are canceled in the half-reactions.

$$E^\circ_{\text{cell}} = \frac{0.0592 \text{ V}}{n} \log K$$

$$\log K = E^\circ_{\text{cell}} \frac{n}{0.0592 \text{ V}}$$

$$\log K = -0.34 \text{ V} \frac{2}{0.0592 \text{ V}} = -11.486$$

$$K = 10^{-11.486} = 3.3 \times 10^{-12}$$

Example 19.7 Relating E°_{cell} and K

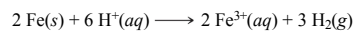
Continued

Check

The answer has no units, as expected for an equilibrium constant. The magnitude of the answer is small, indicating that the reaction lies far to the left at equilibrium, as expected for a reaction in which E°_{cell} is negative.

For Practice 19.7

Use the tabulated electrode potentials to calculate K for the oxidation of iron by H^+ (at 25 °C):



E_{cell} vs E_{cell}°

$$\Delta G = -nFE$$

$$\Delta G^{\circ} = -nFE^{\circ}$$

$$\Delta G = \Delta G^{\circ} + RT \ln Q$$

$$\Rightarrow -nFE = -nFE^{\circ} + RT \ln Q \quad \left. \begin{array}{l} \text{ } \\ \text{ } \end{array} \right\} \div -nF$$

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

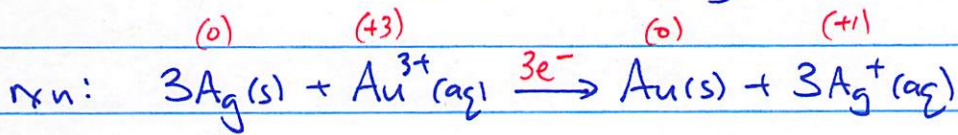
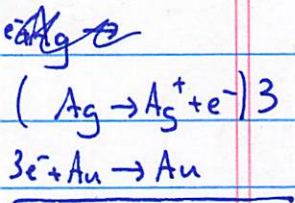
NERNST EQ.

ex: What's E_{cell} for: $Ag(s) | Ag^+(aq, 0.010M) || Au^{3+}(aq, 2M) | Au(s)$
@25°C

on monday: $E_{cell} = +0.70V$

$$= E^{\circ}_{cathode} - E^{\circ}_{anode}$$

$$= E^{\circ}_{Au^{3+}/Au} - E^{\circ}_{Ag^+/Ag}$$



$$E = +0.70V - \frac{8.3145 \frac{J}{mol \cdot K} \times 298.15K}{3 \times 96,500 \frac{C}{mol}} \ln Q$$

$1V = 1 \frac{J}{C}$

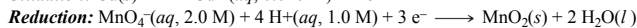
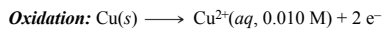
$$\frac{[Ag^+]^3}{[Au^{3+}]} = \frac{0.010^3}{2.0} = 5.0 \times 10^{-7}$$

$$E = +0.70V - 8.56 \times 10^{-3} \frac{J}{C} \times \ln(5.0 \times 10^{-7})$$

$$= +0.70V - -0.12V = +0.82V$$

Example 19.8 Calculating E_{cell} under Nonstandard Conditions

Determine the cell potential for an electrochemical cell based on the following two half-reactions:



Sort

You are given the half-reactions for a redox reaction and the concentrations of the aqueous reactants and products. You are asked to find the cell potential.

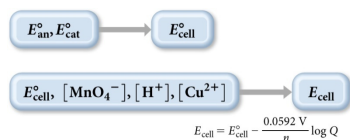
Given: $[\text{MnO}_4^{-}] = 2.0 \text{ M}$; $[\text{H}^{+}] = 1.0 \text{ M}$; $[\text{Cu}^{2+}] = 0.010 \text{ M}$

Find: E_{cell}

Strategize

Use the tabulated values of electrode potentials to calculate E°_{cell} . Then use Equation 19.9 to calculate E_{cell} .

Conceptual Plan



Solve

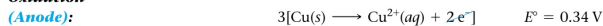
Write the oxidation and reduction half-reactions, multiplying by the appropriate coefficients to cancel the electrons. Find the standard electrode potentials for each half-reaction. Find E°_{cell} .

Example 19.8 Calculating E_{cell} under Nonstandard Conditions

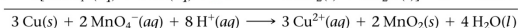
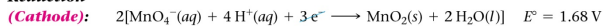
Continued

Solution

Oxidation



Reduction



$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cat}} - E^{\circ}_{\text{an}} = 1.34 \text{ V}$$

Calculate E_{cell} from E°_{cell} . The value of n (the number of moles of electrons) corresponds to the number of electrons (six in this case) canceled in the half-reactions. Determine Q based on the overall balanced equation and the given concentrations of the reactants and products. (Note that pure liquid water, solid MnO_2 , and solid copper are omitted from the expression for Q .)

$$\begin{aligned} E_{\text{cell}} &= E^{\circ}_{\text{cell}} - \frac{0.0592 \text{ V}}{n} \log Q \\ &= E^{\circ}_{\text{cell}} - \frac{0.0592 \text{ V}}{n} \log \frac{[\text{Cu}^{2+}]^3}{[\text{MnO}_4^{-}]^2 [\text{H}^{+}]^8} \\ &= 1.34 \text{ V} - \frac{0.0592 \text{ V}}{6} \log \frac{(0.010)^3}{(2.0)^2 (1.0)^8} \\ &= 1.34 \text{ V} - (-0.065 \text{ V}) \\ &= 1.41 \text{ V} \end{aligned}$$

Example 19.8 Calculating E_{cell} under Nonstandard Conditions

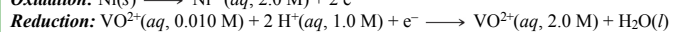
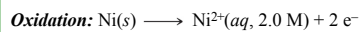
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Check

The answer has the correct units (V). The value of E_{cell} is larger than E°_{cell} , as expected based on Le Châtelier's principle because one of the aqueous reactants has a concentration greater than standard conditions and the one aqueous product has a concentration less than standard conditions. Therefore, the reaction has a greater tendency to proceed toward products and a greater cell potential.

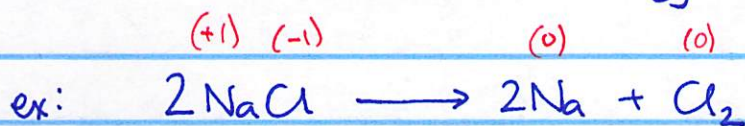
For Practice 19.8

Determine the cell potential of an electrochemical cell based on the following two half-reactions:

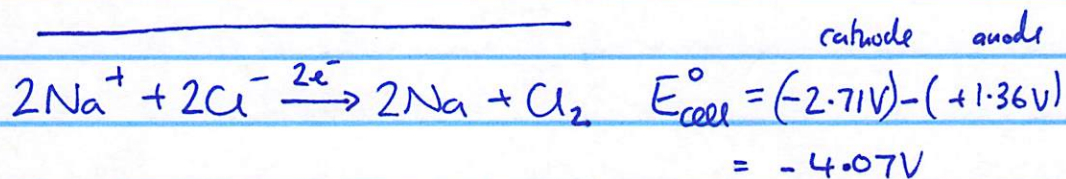
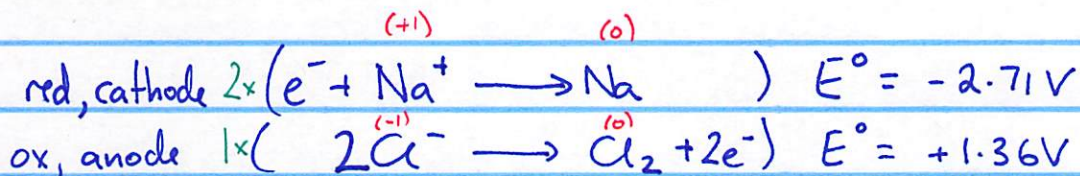


Electrolysis

$E_{\text{cell}}^{\circ} = -ve$ ~ non-spont
but we can drive w/ input
of elec. energy



elec. pot.
red pot
↓



(non-spontaneous).

We must provide voltage $> 4.07\text{V}$ to drive rxn.

Stoichiometry of electrolysis

We can predict mass of products formed during electrolysis.
How? Need to know: (1) Electrical current (A)
(2) time (s)

$$\text{Current (A)} = \frac{\overset{Q}{\text{Charge (C)}}}{\underset{t}{\text{time (s)}}} \quad I = \frac{Q}{t}$$

$$1\text{A} = 1\text{C/s}$$

ex: What's total charge if 30.0A flows for 51.0min ?

$$I = \frac{Q}{t} \quad \Rightarrow \quad Q = I \cdot t$$

$$= 30.0 \cancel{\%} \times 51.0 \cancel{\text{min}} \times \frac{60 \cancel{\text{s}}}{1 \cancel{\text{min}}}$$

$$= \cancel{37,800 \text{ C}} \quad 91,800 \text{ C}$$

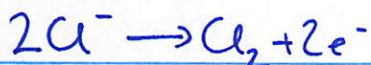
Ex: how many mol e^- is this?

$$1F = 96,500 \text{ C/mol}$$

$$\# \text{ mol } e^- = \frac{91,800}{96,500} \times \frac{1 \text{ mol } e^-}{1} = 0.9513 \text{ mol } e^-$$

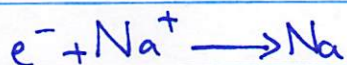
Ex: What mass of Cl_2 can we make?

$$0.9513 \text{ mol } e^- \times \frac{1 \text{ mol } \text{Cl}_2}{2 \text{ mol } e^-} \times \frac{70.9 \text{ g } \text{Cl}_2}{1 \text{ mol } \text{Cl}_2} = 33.7 \text{ g } \text{Cl}_2$$



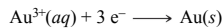
ex: What mass of Na can we make?

$$0.9513 \text{ mol } e^- \times \frac{1 \text{ mol } \text{Na}}{1 \text{ mol } e^-} \times \frac{22.99 \text{ g } \text{Na}}{1 \text{ mol } \text{Na}} = \underline{21.9 \text{ g } \text{Na}}$$



Example 19.10 Stoichiometry of Electrolysis

Gold can be plated out of a solution containing Au^{3+} according to the half-reaction:



What mass of gold (in grams) is plated by a 25-minute flow of 5.5 A current?

Sort

You are given the half-reaction for the plating of gold, which shows the stoichiometric relationship between moles of electrons and moles of gold. You are also given the current and duration. You must find the mass of gold that will be deposited in that time.

Given: 3 mol e^{-} : 1 mol Au
5.5 amps
25 min

Find: g Au

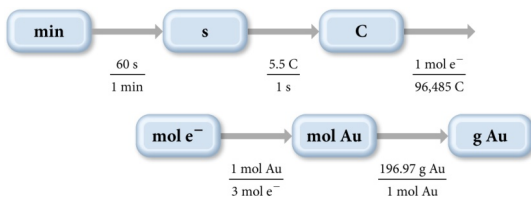
Strategize

You need to find the amount of gold, which is related stoichiometrically to the number of electrons that have flowed through the cell. Begin with time in minutes and convert to seconds. Then, because current is a measure of charge per unit time, use the given current and the time to find the number of coulombs. Use Faraday's constant to calculate the number of moles of electrons and the stoichiometry of the reaction to find the number of moles of gold. Finally, use the molar mass of gold to convert to mass of gold.

Example 19.10 Stoichiometry of Electrolysis

Continued

Conceptual Plan



Solve

Follow the conceptual plan to solve the problem, canceling units to arrive at the mass of gold.

Solution

$$25 \text{ min} \times \frac{60 \text{ s}}{1 \text{ min}} \times \frac{5.5 \text{ C}}{1 \text{ s}} \times \frac{1 \text{ mol e}^{-}}{96,485 \text{ C}} \times \frac{1 \text{ mol Au}}{3 \text{ mol e}^{-}} \times \frac{196.97 \text{ g Au}}{1 \text{ mol Au}} = 5.6 \text{ g Au}$$

Example 19.10 Stoichiometry of Electrolysis

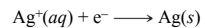
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Check

The answer has the correct units (g Au). The magnitude of the answer is reasonable if you consider that 10 amps of current for 1 hour is the equivalent of about 1/3 mol of electrons (check for yourself), which would produce 1/9 mol (or about 20 g) of gold.

For Practice 19.10

Silver can be plated out of a solution containing Ag^+ according to the half-reaction:



How much time (in minutes) does it take to plate 12 g of silver using a current of 3.0 A?