

1. Silver is electroplated onto a spoon by suspending the spoon in a 1.00 M solution of  $\text{AgNO}_3$  and passing a 2.00 amp current through it for 15.0 min. What mass of silver is deposited on the spoon?

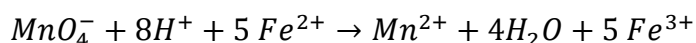
The half-cell reaction for the reduction of silver is given by



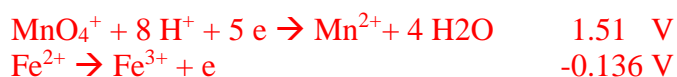
The mass of silver deposited is given by

$$2.0 \text{ amp} \cdot 15.0 \text{ min} \cdot \frac{60 \text{ sec}}{\text{min}} \cdot \frac{1 \text{ mol } e}{96484 \text{ amp} \cdot \text{sec}} \cdot \frac{1 \text{ mol Ag}}{\text{mol } e} \cdot \frac{107.9 \text{ g}}{\text{mol Ag}} = 2.01 \text{ g}$$

2. Calculate the standard cell potential for the reaction



Given the standard reduction potentials,



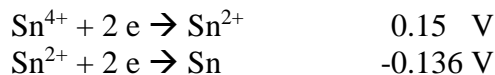
The standard cell potential is given by

$$E^\circ = E_{\text{red}}^\circ - E_{\text{ox}}^\circ$$

$$E^\circ = 1.51 \text{ V} - (-0.136 \text{ V})$$

$$E^\circ = 1.646 \text{ V}$$

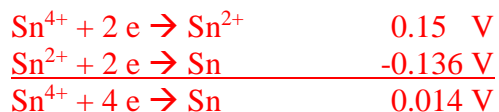
3. The following data can be found in a table of standard reduction potentials at 25 °C:



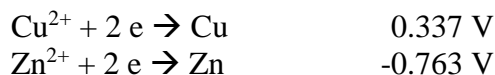
From these data, Calculate the standard reduction potential for the half-cell



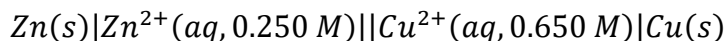
The target reaction can be generated by simply adding the two data reactions



4. From a table of standard reduction potentials at 25 °C, the following is found:



From these data, calculate the cell potential for the cell constructed as



The standard cell potential is given by

$$E^{\circ} = E_{\text{red}}^{\circ} - E_{\text{ox}}^{\circ} = 0.337 \text{ V} - (-0.763 \text{ V}) = 1.100 \text{ V}$$

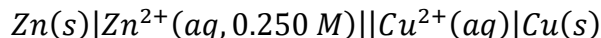
The cell potential can then be calculated using the Nernst equation:

$$E = E^{\circ} - \frac{0.0592 \text{ V}}{n} \log Q$$

So

$$\begin{aligned} E &= 1.100 \text{ V} - \frac{0.0592 \text{ V}}{2} \log \left( \frac{0.250 \text{ M}}{0.650 \text{ M}} \right) \\ &= 1.112 \text{ V} \end{aligned}$$

5. A Daniel cell is constructed



and the cell potential is measured to be 1.05 V. Calculate the concentration of  $\text{Cu}^{2+}$  ions in the cathode half-cell.

As in the previous problem, the cell potential is given by the Nernst equation.

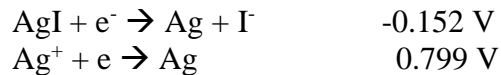
$$E = E^{\circ} - \frac{0.0592 \text{ V}}{n} \log Q$$

So

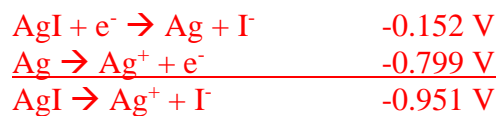
$$1.05 \text{ V} = 1.100 \text{ V} - \frac{0.0592 \text{ V}}{2} \log \left( \frac{0.250 \text{ M}}{[\text{Cu}^{2+}]} \right)$$

$$[\text{Cu}^{2+}] = 5.11 \cdot 10^{-3} \text{ M}$$

6. Given the following standard reduction potentials, calculate the value of  $K_{\text{sp}}$  for AgI.



The dissociation reaction can be generated by flipping the second half-cell and adding the half reactions.



The equilibrium constant is then obtained from

$$E^\circ = \frac{0.0592 \text{ V}}{n} \log K_{sp}$$

So

$$-0.951 \text{ V} = \frac{0.0592 \text{ V}}{1} \log K_{sp}$$

$$K_{sp} = 8.63 \cdot 10^{-17} \text{ M}^2$$

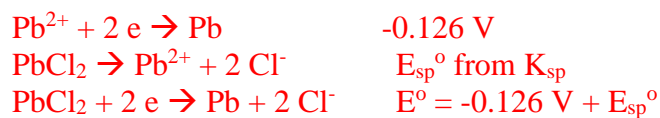
7.  $K_{sp}$  for  $\text{PbCl}_2(\text{s})$  is  $1.8 \times 10^{-4} \text{ M}^3$ . Based on this, and the standard reduction potential



calculate the standard reduction potential for



The target reaction can be generated for the data reactions indicated in the problem from



Using the equilibrium constant, the standard cell potential for the dissociation ( $E_{sp}^\circ$ ) is found from

$$E_{sp}^\circ = \frac{0.0592 \text{ V}}{n} \log K_{sp}$$

So

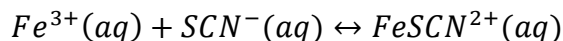
$$E_{sp}^o = \frac{0.0592 \text{ V}}{2} \log(1.8 \cdot 10^{-4})$$

$$E_{sp}^o = -0.111 \text{ V}$$

So,  $E^o$  for the target half-reaction is given by

$$\begin{aligned} E^o &= (-0.126 \text{ V}) + (-0.111 \text{ V}) \\ &= -0.237 \text{ V} \end{aligned}$$

8. At 25 °C,  $K_f = 8.9 \times 10^2 \text{ M}^{-1}$  for the complexation reaction



Given that the standard reduction potential at 25 °C



determine the standard reduction potential for the half-reaction



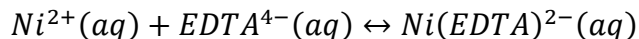
The target reaction can be generated from the data reactions by



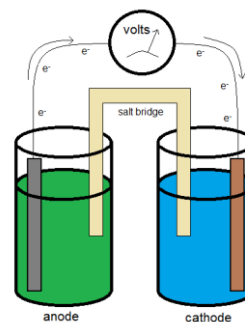
So

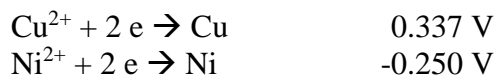
$$E^o = 0.771 \text{ V} - \frac{0.0592 \text{ V}}{3} \log(890) = 0.712 \text{ V}$$

9.  $Ni^{2+}$  Ions complex with EDTA by the reaction



$K_f$  for this complex formation equilibrium is  $3.6 \times 10^{18} \text{ M}^{-1}$ . A half-cell is prepared to be 0.100 M in  $Ni^{2+}$  and 1.00 M in EDTA. Its standard reduction potential is measured relative to a copper half-cell, in which  $[Cu^{2+}] = 1.00 \text{ M}$ . The standard reduction potentials for the bare-ion reductions are





From these data, calculate the cell potential once the complexation reaction of  $\text{Ni}^{2+}$  with EDTA has reached equilibrium.

First, find the concentration of  $\text{Ni}^{2+}$ .



	$\text{Ni}^{2+}$	$\text{EDTA}^{4-}$	$\text{NiEDTA}^{2-}$
<b>Initial</b>	0.100 M	1.00 M	0
<b>Change</b>	-0.100 M	-0.100 M	+0.100 M
<b>End</b>	y	0.90 M	0.100 M

$$K_f = \frac{[\text{NiEDTA}^{2-}]}{[\text{Ni}^{2+}][\text{EDTA}^{4-}]}$$

$$3.6 \cdot 10^{18} \text{ M}^{-1} = \frac{0.100 \text{ M}}{y(0.90 \text{ M})}$$

$$y = 3.1 \cdot 10^{-20} \text{ M}$$

Now, use the concentration in the Nernst equation to find the cell potential. The reaction is



For this reaction,  $E^\circ$  is given by

$$E^\circ = 0.337 \text{ V} - (-0.250 \text{ V}) = +0.587 \text{ V}$$

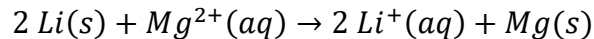
Also,  $n = 2$  for the reaction as two electrons are transferred per reaction equivalent. So, the Nernst equation is given by

$$E = E^\circ - \frac{0.0592 \text{ V}}{n} \log Q$$

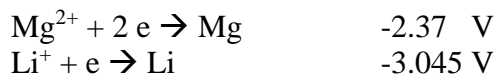
Using values from the problem,

$$\begin{aligned} E &= 0.587 \text{ V} - \frac{0.0592 \text{ V}}{2} \log \left( \frac{3.1 \cdot 10^{-20} \text{ M}}{1.00 \text{ M}} \right) \\ &= 1.164 \text{ V} \end{aligned}$$

10. Consider the redox reaction



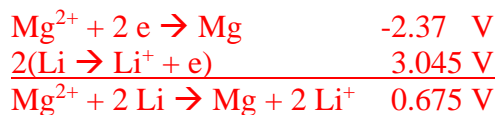
Given the following data



Species	$S_f^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )
Mg <sup>2+</sup> (aq)	-138.1
Mg(s)	32.68
Li <sup>+</sup> (aq)	13.4
Li(s)	29.12

a) Calculate the standard cell potential ( $E^\circ$ ) at 25 °C,

The target reaction can be generated by adding the data reactions (with the lithium half-reaction flipped and doubled):



b) the standard reaction entropy ( $\Delta S_{\text{rxn}}^\circ$ ) at 25 °C,

The reaction entropy is found in the usual way of adding up the total entropy for the products and subtracting that for the reactants:

$$\begin{aligned} \Delta S_{\text{rxn}}^\circ &= \sum_{\text{products}} \nu_i S_{f,i}^\circ - \sum_{\text{reactants}} \nu_i S_{f,i}^\circ \\ \Delta S_{\text{rxn}}^\circ &= (1 \text{ mol}) \left( 32.68 \frac{\text{J}}{\text{mol K}} \right) + (2 \text{ mol}) \left( 13.4 \frac{\text{J}}{\text{mol K}} \right) \\ &\quad - (1 \text{ mol}) \left( -138.1 \frac{\text{J}}{\text{mol K}} \right) - (2 \text{ mol}) \left( 29.12 \frac{\text{J}}{\text{mol K}} \right) \\ \Delta S_{\text{rxn}}^\circ &= 139.34 \frac{\text{J}}{\text{K}} \end{aligned}$$

c) and the standard cell potential at 37 °C.

The temperature dependence of the standard cell potential is given by

$$\left(\frac{\partial E^o}{\partial T}\right)_p = \frac{\Delta S_{rxn}^o}{nF}$$

and

$$\Delta E^o = \int_{T_1}^{T_2} \left(\frac{\partial E^o}{\partial T}\right)_p dT = \int_{T_1}^{T_2} \left(\frac{\Delta S_{rxn}^o}{nF}\right) dT$$

So, so long as the reaction entropy change is constant across the temperature range:

$$E^o(T_2) = E^o(T_1) + \left(\frac{\Delta S_{rxn}^o}{nF}\right) \Delta T$$

$$\begin{aligned} E^o(310\text{ K}) &= 0.675\text{ V} + \left[ \frac{139.34 \frac{\text{J}}{\text{K}}}{2 \cdot 96484\text{ C}} \left( \frac{\text{V} \cdot \text{C}}{\text{J}} \right) \right] (12\text{ K}) \\ &= 0.684\text{ V} \end{aligned}$$