

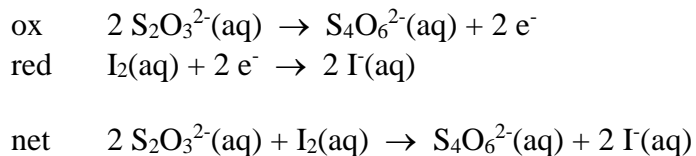
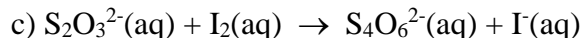
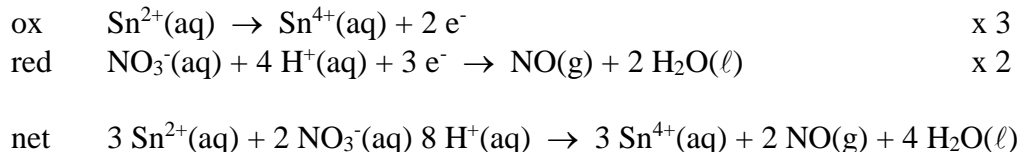
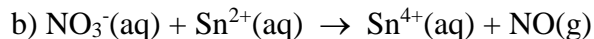
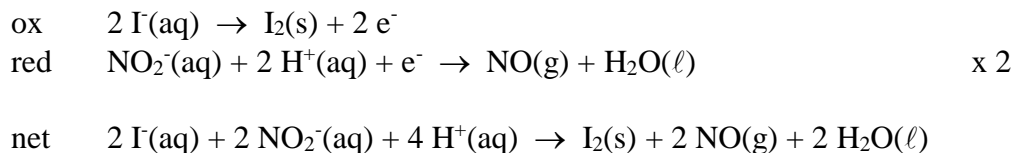
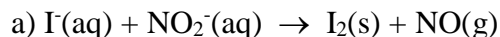
Chapter 18 problems (with solutions)

1) Assign oxidation numbers for all elements in the following species (for review see section 9.4)

| | |
|-------------------------------------|------------------------|
| a) H_2SO_3 | H = +1 S = +4 O = -2 |
| b) $\text{Ca}(\text{ClO}_3)_2$ | Ca = +2 Cl = +5 O = -2 |
| c) C_2H_4 | C = -2 H = +1 |
| d) H_3PO_4 | H = +1 P = +5 O = -2 |
| e) Cl_2 | Cl = 0 |
| f) BrO_4^- | Br = +7 O = -2 |
| g) KMnO_4 | K = +1 Mn = +7 O = -2 |
| h) NaOH | Na = +1 O = -2 H = +1 |
| i) H_2O_2 | H = +1 O = -1 |
| j) $\text{H}_4\text{P}_2\text{O}_7$ | H = +1 P = +5 O = -2 |

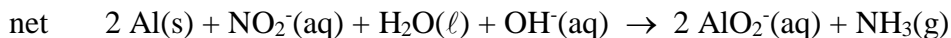
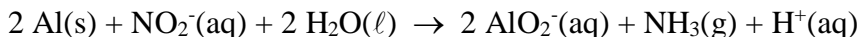
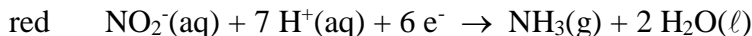
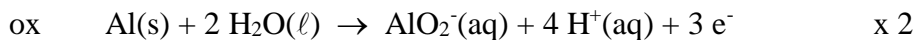
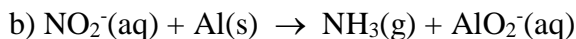
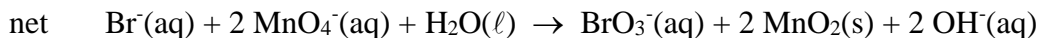
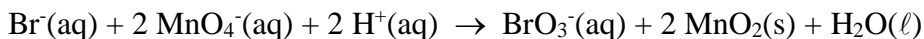
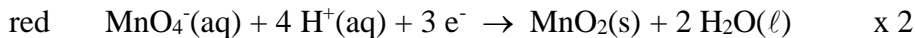
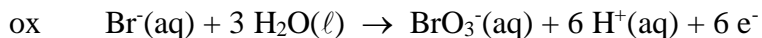
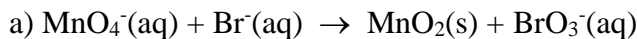
2) Balance each redox reaction occurring in acid aqueous solution.

In all cases we will use the procedure discussed in class. We will first find balanced half-cell oxidation and reduction half-reactions. We will multiply one or both reactions by an integer value so that the number of electrons transferred will cancel when the half-reactions are combined. Finally, we will combine the half-reactions and cancel any substances appearing as both reactants and products to obtain the final balanced net cell reaction.

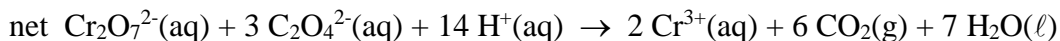
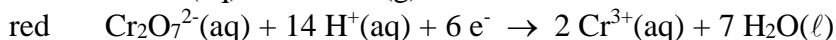
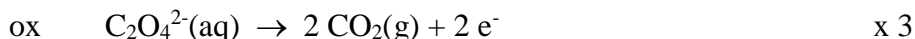
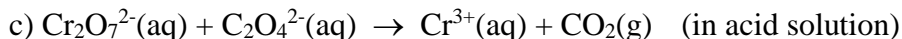
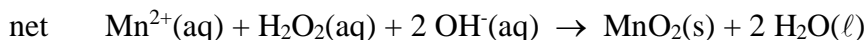
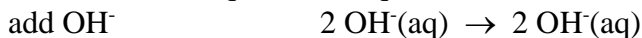
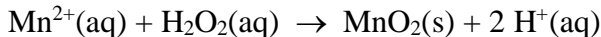
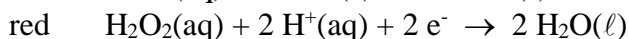
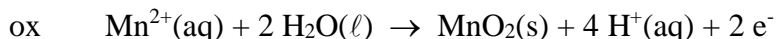
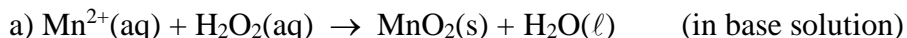


3) Balance each redox reaction occurring in base aqueous solution.

Balancing oxidation-reduction reactions for base conditions is exactly the same as balancing the reactions for acid conditions except that there is one additional step where OH⁻ ions are added, if necessary, to convert all H⁺ ions into water molecules.



4) (18.2 a,c) Balance the following redox reactions by the half-reaction method.



5) Explain the difference between a voltaic (or galvanic) electrochemical cell and an electrolytic cell.

In a voltaic cell (also called a galvanic cell or a battery) a chemical reaction is used to generate a voltage. In an electrolytic cell an external voltage is used to force a chemical reaction to occur in a particular direction.

6) Explain the purpose of a salt bridge in an electrochemical cell.

The salt bridge is used to complete the circuit. It provides a way in which charge can pass from one part of the cell to the other part without having the two parts of the cell directly react chemically.

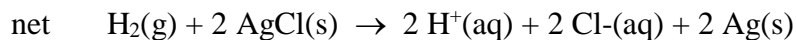
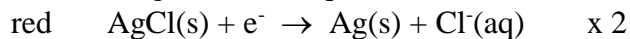
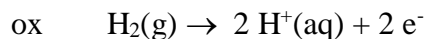
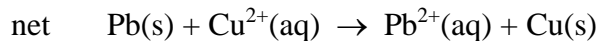
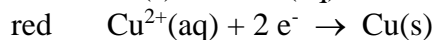
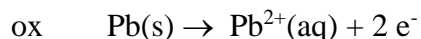
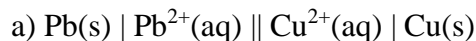
7) How can Table 18.1 be used to predict whether or not a metal will dissolve in HCl? In HNO₃?

Any metal below the H⁺/H₂ half-cell reduction potential, at 0.00 v, would be expected to dissolve in HCl (hydrochloric acid) for standard conditions. This is because when the half-cell oxidation potential for the metal (found by reversing the reaction and changing the sign of the potential) is combined with the half-cell reduction potential for H⁺/H₂, a positive voltage will result, indicating a spontaneous reaction.

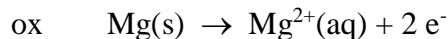
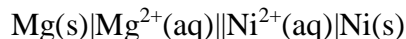
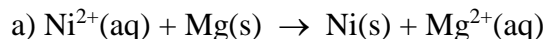
The same reasoning applies for HNO₃ (nitric acid) except that now there is a different reduction half-reaction to use, that for NO₃⁻/NO at 0.96 v. Metals lying below this half-cell reduction potential would be expected to dissolve in HNO₃.

So, for example, Ni (nickel) will dissolve in both HCl and HNO₃, Cu (copper) will dissolve in HNO₃ but not HCl, and Au (gold) will not dissolve in either acid.

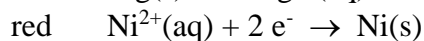
8) Give the half cell oxidation reaction, the half cell reduction reaction, and the net cell reaction for the following galvanic cells.



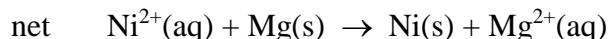
9) Calculate the standard cell potential for each of the following electrochemical cells. Also, represent each cell as a cell diagram using standard notation.



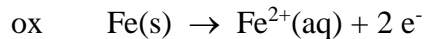
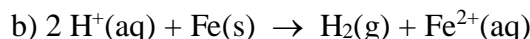
$E^\circ = + 2.37 \text{ v}$



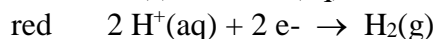
$E^\circ = - 0.23 \text{ v}$



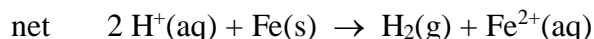
$E^\circ_{\text{net}} = + 2.14 \text{ v}$



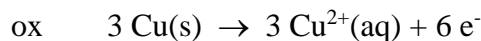
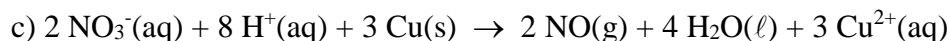
$E^\circ = + 0.45 \text{ v}$



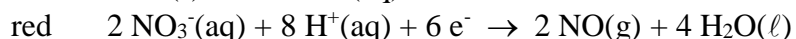
$E^\circ = 0.00 \text{ v}$



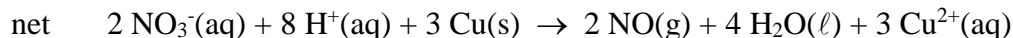
$E^\circ_{\text{net}} = + 0.45 \text{ v}$



$E^\circ = - 0.34 \text{ v}$

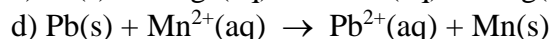
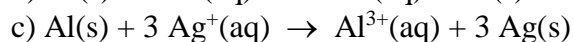
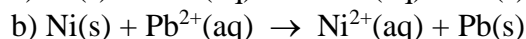
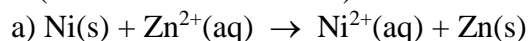


$E^\circ = + 0.96 \text{ v}$



$E^\circ_{\text{net}} = + 0.62 \text{ v}$

10) Which of the redox reactions do you expect to occur spontaneously in the forward direction (for standard conditions)?



There are two ways in which we can do this sort of problem. We could calculate the net cell potential, and then use the fact that for spontaneous processes the net cell potential will be positive. Alternatively, we can use the position of the half-cell reactions in Table 18.1. If the substance being reduced in the reaction is higher in Table 18.1 than the substance being oxidized then the reaction is spontaneous.

In this problem I will use the second method, but I will also give the net cell potential (although not the oxidation, reduction, and net cell reactions).

- a) Zn^{2+}/Zn is below Ni^{2+}/Ni , and so not spontaneous. $E^\circ = -0.53 \text{ v}$
- b) Pb^{2+}/Pb is above Ni^{2+}/Ni , and so spontaneous. $E^\circ = +0.10 \text{ v}$
- c) Ag^+/Ag is above Al^{3+}/Al , and so spontaneous. $E^\circ = +2.46 \text{ v}$
- d) Mn^{2+}/Mn is below Pb^{2+}/Pb , and so not spontaneous. $E^\circ = -1.05 \text{ v}$

11) Which metal cation below is the best oxidizing agent?

- a) Pb^{2+}
- b) Cr^{3+}
- c) Fe^{3+}
- d) Sn^{2+}

The best oxidizing agent will be the species that has the largest (most positive) reduction potential. Based on Table 18.1

| | | | |
|----------------------------|-----------------------------|----------------------------|-----------------------------|
| Pb^{2+}/Pb | $E^\circ = -0.13 \text{ v}$ | Cr^{3+}/Cr | $E^\circ = -0.73 \text{ v}$ |
| Fe^{2+}/Fe | $E^\circ = -0.45 \text{ v}$ | Sn^{2+}/Sn | $E^\circ = -0.14 \text{ v}$ |

So Pb^{2+} is the best oxidizing agent.

12) Which metal below is the best reducing agent?

- a) Mn
- b) Al
- c) Ni
- d) Cr

The best reducing agent will be the species that has the largest (most positive) oxidation potential. Note that to get the oxidation potential we have to reverse the reduction reaction, and so change the sign of the potential.

| | | | |
|----------------------------|-----------------------------|----------------------------|-----------------------------|
| Mn/Mn^{2+} | $E^\circ = +1.18 \text{ v}$ | Al/Al^{3+} | $E^\circ = +1.66 \text{ v}$ |
| Ni/Ni^{2+} | $E^\circ = +0.23 \text{ v}$ | Cr/Cr^{3+} | $E^\circ = +0.73 \text{ v}$ |

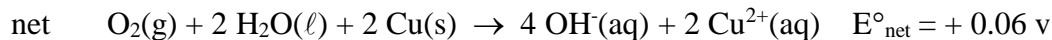
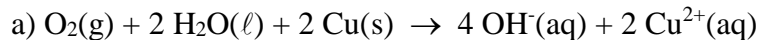
So Al is the best reducing agent.

13) Use tabulated electrode potentials to calculate $\Delta G^\circ_{\text{rxn}}$ for each reaction at 25. °C. Then calculate the equilibrium constant for each reaction.

To find $\Delta G^\circ_{\text{rxn}}$ and K (the thermodynamic equilibrium constant) we will use the expression

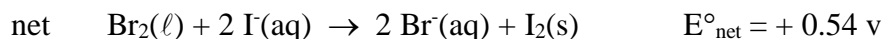
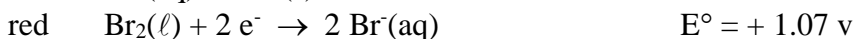
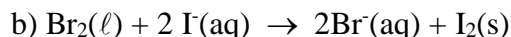
$$\Delta G^\circ_{\text{rxn}} = -nFE^\circ_{\text{cell}}$$
$$\ln K = nFE^\circ_{\text{cell}}/RT$$

Recall that (1 C) (1 v) = 1 J. Values for E° are given in the Table 18.1.



$$n = 4 \quad \Delta G^\circ_{\text{rxn}} = - (4) (96485 \text{ C/mol}) (+0.06 \text{ v}) = -23.2 \text{ kJ/mol}$$

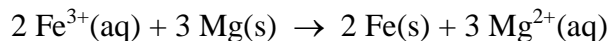
$$\ln K = \frac{(4) (96485 \text{ C/mol}) (+0.06 \text{ v})}{(8.314 \text{ J/mol}\cdot\text{K}) (298.2 \text{ K})} = 9.34 \quad K = e^{9.34} = 1.1 \times 10^4$$



$$n = 2 \quad \Delta G^\circ_{\text{rxn}} = - (2) (96485 \text{ C/mol}) (+0.54 \text{ v}) = -104.2 \text{ kJ/mol}$$

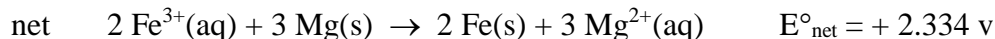
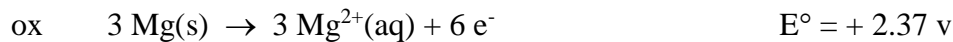
$$\ln K = \frac{(2) (96485 \text{ C/mol}) (+0.54 \text{ v})}{(8.314 \text{ J/mol}\cdot\text{K}) (298.2 \text{ K})} = 42.03 \quad K = e^{42.03} = 1.7 \times 10^{18}$$

14) A voltaic cell employs the redox reaction



Calculate the cell potential at 25. °C under each set of conditions

a) Standard conditions. We first need to find E°_{net} .



$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{nF} \ln Q \quad Q = \frac{[\text{Mg}^{2+}]^3}{[\text{Fe}^{3+}]^2} \quad n = 6$$

For standard conditions $E_{\text{cell}} = E^\circ_{\text{cell}} = +2.33 \text{ v}$

b) $[\text{Fe}^{3+}] = 1.0 \times 10^{-3} \text{ M}$; $[\text{Mg}^{2+}] = 2.50 \text{ M}$

$$Q = \frac{(2.50)^3}{(1.0 \times 10^{-3})^2} = 1.56 \times 10^7$$

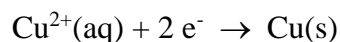
$$E_{\text{cell}} = + 2.334 \text{ v} - \frac{(8.314 \text{ J/mol}\cdot\text{K})(298.2 \text{ K})}{(6)(96485 \text{ C/mol})} \ln(1.56 \times 10^7) = + 2.26 \text{ v}$$

c) $[\text{Fe}^{3+}] = 2.00 \text{ M}$; $[\text{Mg}^{2+}] = 1.5 \times 10^{-3} \text{ M}$

$$Q = \frac{(1.5 \times 10^{-3})^3}{(2.00)^2} = 8.44 \times 10^{-10}$$

$$E_{\text{cell}} = + 2.334 \text{ v} - \frac{(8.314 \text{ J/mol}\cdot\text{K})(298.2 \text{ K})}{(6)(96485 \text{ C/mol})} \ln(8.44 \times 10^{-10}) = + 2.42 \text{ v}$$

15) Copper can be electroplated at the cathode of an electrolytic cell by the half reaction



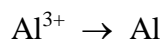
How much time would it take for 325. mg of copper metal to be plated at a current of 5.6 A?

$$\text{MW}(\text{Cu}) = 63.55 \text{ g/mol}$$

$$t = 325. \times 10^{-3} \text{ g Cu} \frac{1 \text{ mol Cu}}{63.55 \text{ g Cu}} \frac{2 \text{ mol e}^-}{1 \text{ mol Cu}} \frac{96485 \text{ C}}{1 \text{ mol e}^-} \frac{1 \text{ s}}{5.6 \text{ C}} = 176. \text{ s}$$

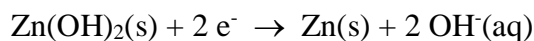
16) What mass of aluminum metal can be produced per hour in the electrolysis of molten aluminum salt (containing Al^{3+} ion) by a current of 25. A?

The reduction for aluminum ($\text{MW}(\text{Al}) = 26.98 \text{ g/mol}$) is

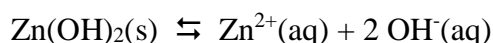


$$\text{g Al} = 1 \text{ hr} \frac{3600 \text{ s}}{1 \text{ hr}} \frac{25 \text{ C}}{1 \text{ s}} \frac{1 \text{ mol e}^-}{96485 \text{ C}} \frac{1 \text{ mol Al}}{3 \text{ mol e}^-} \frac{26.98 \text{ g Al}}{1 \text{ mol Al}} = 8.39 \text{ g Al}$$

17) The K_{sp} of $\text{Zn}(\text{OH})_2$ is 1.8×10^{-14} . Find E°_{cell} for the half reaction



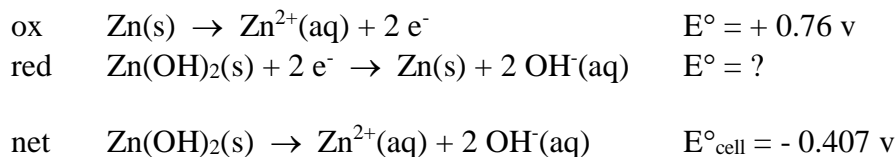
The key to doing this problem is to find a combination of an oxidation and a reduction reaction that add up to the reaction of interest, which in this case is



The cell potential can be found using

$$E^\circ_{\text{cell}} = (RT/nF) \ln K$$

$$= \frac{(8.314 \text{ J/mol}\cdot\text{K})(298.2 \text{ K}) \ln(1.8 \times 10^{-14})}{(2)(96485 \text{ C/mol})} = -0.407 \text{ v}$$

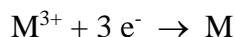


So the half-cell reduction potential for the reaction in question is

$$0.76 \text{ v} + E^\circ = -0.407 \text{ v} ; E^\circ = -0.407 \text{ v} - 0.76 \text{ v} = -1.17 \text{ v}$$

18) A metal forms from the fluoride compound MF₃. Electrolysis of molten MF₃ by a current of 3.86 A for 16.2 minutes deposits 1.25 g of metal. What is the molar mass of the metal?

Based on the formula MF₃ the reduction reaction for the metal is

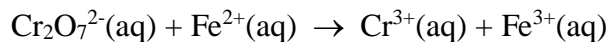


We know how many grams of metal are produced. To find the number of moles of metal we use

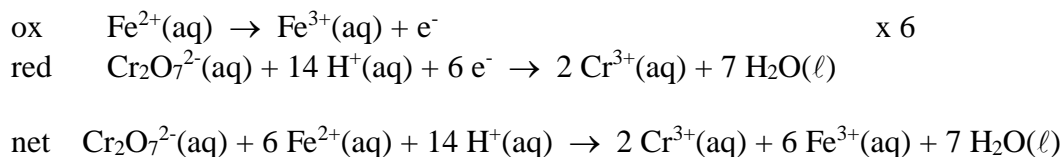
$$\text{mol M} = 16.2 \text{ min} \frac{60 \text{ s}}{1 \text{ min}} \frac{3.86 \text{ C}}{1 \text{ s}} \frac{1 \text{ mol } e^-}{96485 \text{ C}} \frac{1 \text{ mol M}}{3 \text{ mol } e^-} = 1.296 \times 10^{-2} \text{ mol M}$$

$$\text{So the molecular mass is } M = \frac{1.25 \text{ g}}{1.296 \times 10^{-2} \text{ mol}} = 96.4 \text{ g/mol}$$

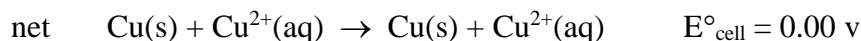
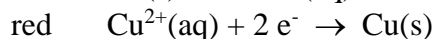
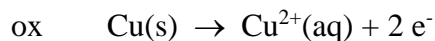
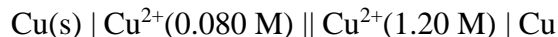
19) (18.66) The oxidation of 25.00 mL of a solution containing Fe²⁺ requires 26.00 mL of a 0.0250 M solution of K₂Cr₂O₇ in acidic solution. Balance the following equation, and calculate the molar concentration of Fe²⁺. The unbalanced redox reaction is



We first balance the redox reaction for acidic conditions



21) (18.77) Calculate the emf of the following concentration cell at 25. °C



Since the oxidation and reduction reactions are the same reaction, we know the standard cell potential will be 0.00 v. However, since the two electrodes have a different concentration of Cu^{2+} ion, a voltage can still be generated.

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{RT}{nF} \ln Q \quad Q = \frac{[\text{Cu}^{2+}]_{\text{left}}}{[\text{Cu}^{2+}]_{\text{right}}} = \frac{1.20}{0.080} = 15 \quad n = 2$$

$$E_{\text{cell}} = 0.00 \text{ v} - \frac{(8.314 \text{ J/mol}\cdot\text{K})(298.2 \text{ K}) \ln(15)}{(2)(96485. \text{ C/mol})} = -0.035 \text{ v}$$

22) (18.87) In an electrolysis experiment a student passes the same quantity of electricity through two electrolytic cells, one containing a silver salt and the other containing a gold salt. Over a certain period of time the student finds that 2.64 g of Ag and 1.61 g of Au are deposited at the cathodes. What is the oxidation state of gold in the gold salt? (NOTE: Recall that the only common oxidation number for silver is +1)

We first find the number of moles of charge in the electrolysis of the silver salt.

$$\text{moles e}^{-} = 2.64 \text{ g Ag} \times \frac{1 \text{ mol Ag}}{107.9 \text{ g Ag}} \times \frac{1 \text{ mol e}^{-}}{1 \text{ mol Ag}} = 0.02447 \text{ mol e}^{-}$$

Since the moles of e^{-} is the same in both processes, we may say for the electrolysis of the gold salt

$$\text{moles e}^{-} = 1.61 \text{ g Au} \times \frac{1 \text{ mol Au}}{197.0 \text{ g Au}} \times \frac{X \text{ mol e}^{-}}{1 \text{ mol Au}} = 0.02447 \text{ mol e}^{-}$$

$$\text{Solving for X gives} \quad \frac{X}{1 \text{ mol Au}} = 0.02447 \text{ mol e}^{-} \times \frac{197.0 \text{ g Au}}{1 \text{ mol Au}} \times \frac{1}{1.61 \text{ g Au}} = 2.99 \text{ e}^{-}/\text{mol Au}$$

So the oxidation state of gold is 3+.