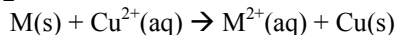


## Collected Essays Chapter 17 Answers

## 1980 - #2



For the reaction above,  $E^\circ = 0.740$  volt at  $25^\circ C$ .

(a) Determine the standard electrode potential for the reaction half-reaction  $M^{2+}(aq) + 2 e^- \rightarrow M(s)$ .

**$M \rightarrow M^{2+} + 2e^-$ , for this reaction  $E^\circ = x$ ;  $Cu^{2+} + 2e^- \rightarrow Cu$ , for this reaction  $E^\circ = 0.34$  volt**

**$0.740 \text{ v} = x + 0.34 \text{ v}$  (summation  $E^\circ_{\text{cell}}$ );  $x = 0.40$  volt (oxidation potential)**

**$-x = -0.40$  volt (for reduction)**

(b) A cell is constructed in which the reaction above occurs. All substances are initially in their standard states, and equal volumes of the solutions are used. The cell is then discharged. Calculate the value of the cell potential,  $E$ , when  $[Cu^{2+}]$  has dropped to 0.20 molar.  **$M + Cu^{2+} \rightarrow M^{2+} + Cu$**

**Standard state, original concentrations = 1.00 M**

**At point of discharge  $[M^{2+}] = 1.80$  M (correct stoichiometry)**

**$E = E^\circ - (0.0592 / n) \log Q$ : (recognition of Q)**

**$E = 0.740 - (0.0592 / 2) \log (1.80 / 0.20)$  (substitution) = 0.712 volt**

(c) Find the ratio  $[M^{2+}]_{\text{aq}} / [Cu^{2+}]_{\text{aq}}$  when the cell reaction above reaches equilibrium.

**$E = 0$  at equilibrium**

**$E^\circ = (0.0592 / 2) \log ([M^{2+}] / [Cu^{2+}])$**

**$\log [M^{2+}] / [Cu^{2+}] = [2(0.740) / 0.0592] = 25.0 = \log K$**

**$K = 1 \times 10^{25}$**

## 1981 - #5

A solution of  $CuSO_4$  was electrolyzed using platinum electrodes by passing a current through the solution. As a result, there was a decrease in both  $[Cu^{2+}]$  and the solution pH; one electrode gained in weight and a gas was evolved at the other electrode.

(a) Write the cathode half-reaction that is consistent with the observation above.  **$Cu^{2+} + 2 e^- \rightarrow Cu$**

(b) Write the anode half-reaction that is consistent with the observations above.  **$2H_2O \rightarrow O_2 + 4 H^+ + 4e^-$**

(c) Sketch an apparatus that can be used for such an experiment and label its necessary components.

**Any reasonable sketch with correct labels**

(d) List the experimental measurement that would be needed in order to determine from such an experiment the value of the faraday. **Measure mass of cathode before and after experiment; measure current; measure time**

## 1982 - #2

When a dilute solution of  $H_2SO_4$  is electrolyzed,  $O_2(g)$  is produced at the anode and  $H_2(g)$  is produced at the cathode.

(a) Write the balanced equations for the anode, cathode, and overall reaction that occur in this cell.

**Cathode:  $2H_2O + 2e^- \rightarrow H_2 + 2 OH^-$**

**Anode:  $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$**

**Overall:  $2 H_2O \rightarrow 2 H_2 + O_2$**

(b) Compute the coulombs of charge passed through the cell in 100.0 minutes at 10.0 amperes.

**Coulombs = 10.0 amp x 100 min x 60 sec/min = 6.00 x 10<sup>4</sup> coulombs**

(c) What number of moles of  $O_2$  is produced by the cell when it is operated for 100. minutes at 10.0 amperes?

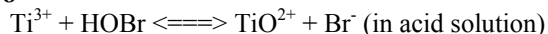
**moles of  $O_2 = (60,000 \text{ coulombs} / 96,500 \text{ coulombs/mole of } e^-) \times (1 \text{ mole } O_2 / 4 \text{ moles of } e^-) = 0.155 \text{ mole of } O_2$**

(d) The standard enthalpy of formation of  $H_2O(g)$  is -242 kilojoules per mole. How much heat is liberated by the complete combustion, at 298 K and 1.00 atmosphere, of the hydrogen produced by the cell operated as in (c)?

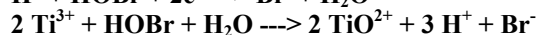
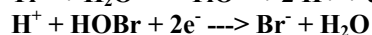
**moles of  $H_2 = (2 \text{ moles } H_2 / 1 \text{ mole } O_2) \times 0.155 \text{ mole } O_2 = 0.311 \text{ mole } H_2$ ; one mole  $H_2$  yields 1 mole  $H_2O$**

**Therefore:  $\Delta H = 0.311 \text{ mole } H_2O \times (-242 \text{ kJ} / \text{mole } H_2O) = -75.2 \text{ kJ}$**

## 1983 - #8



(a) Write the correctly balanced half-reaction and net ionic equation for the skeletal equation shown above.



(b) Identify the oxidizing agent and the reducing agent in this reaction. **HOBr is the oxidizing agent and  $\text{Ti}^{3+}$  is the reducing agent.**

(c) A galvanic cell is constructed that utilizes the reaction above. The concentration of each species is 0.10-molar. Compare the cell voltage that will be observed with the standard cell potential. Explain your reasoning.

**The observed voltage will be greater than  $E^\circ$  since  $E = E^\circ - 0.059/2 (\log [0.1]^3)$ .**

(d) Give one example of a property of this reaction, other than the cell voltage, that can be calculated from the standard cell potential,  $E^\circ$ . State the relationship between  $E^\circ$  and the property you have specified.

**Identification of the property,  $\Delta G$ , K or pH.**

**Statement of the relationship  $\Delta G^\circ = -n F E^\circ$  or  $E^\circ = 0.059/n (\log K)$ .**

## 1985 - #2

(a) Titanium can be reduced in acid solution from  $\text{TiO}^{2+}$  to  $\text{Ti}^{3+}$  with zinc metal. Write a balanced equation for the reaction of  $\text{TiO}^{2+}$  with zinc in acid solution.  **$2 \text{TiO}^{2+} + 4\text{H}^+ + \text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{Ti}^{3+} + \text{H}_2\text{O}$**

(b) What mass of zinc metal is required for the reduction of a 50.00-milliliter sample of a 0.115-molar solution of  $\text{TiO}^{2+}$ ?  **$(0.0500 \text{ liter} \times 0.115 \text{ mole TiO}^{2+} / 1 \text{ liter}) \times (1 \text{ mole Zn} / 2 \text{ mole TiO}^{2+}) \times (65.4 \text{ grams Zn} / 1 \text{ mole Zn}) = 0.188 \text{ gram Zn}$**

(c) Alternatively, the reduction of  $\text{TiO}^{2+}$  to  $\text{Ti}^{3+}$  can be carried out electrochemically. What is the minimum time, in seconds, required to reduce another 50.00-milliliter sample of the 0.115-molar  $\text{TiO}^{2+}$  solution with a direct current of 1.06 amperes?

**$0.0500 \text{ liter} \times (0.115 \text{ mole TiO}^{2+} / 1 \text{ liter}) \times (1 \text{ mole e}^- / 1 \text{ mole TiO}^{2+}) \times (96,500 \text{ coulombs} / 1 \text{ mole e}^-) \times (1 \text{ amp-sec} / 1 \text{ coulomb}) \times (1 / 1.06 \text{ amp}) = 523 \text{ sec}$**

(d) The standard reduction potential,  $E^\circ$ , for  $\text{TiO}^{2+}$  to  $\text{Ti}^{3+}$  is +0.06 volt. The standard reduction potential,  $E^\circ$ , for  $\text{Zn}^{2+}$  to  $\text{Zn}(s)$  is -0.763 volt. Calculate the standard cell potential,  $E^\circ$ , and the standard free energy change,  $\Delta G^\circ$ , for the reaction described in part(a).  **$E^\circ$  for total reaction:  $0.763\text{V} + 0.060\text{V} = 0.823 \text{ V}$**

**$\Delta G^\circ = -nFE^\circ = -(2 \text{ mole e}^-) (96,500 \text{ coulombs} / 1 \text{ mole electrons}) (0.823 / 1 \text{ mole}) (1 \text{ joule} / 1 \text{ V-coul}) = -1.59 \times 10^5 \text{ J}$**

## 1986 - #2

A direct current of 0.125 ampere was passed through 200 milliliters of a 0.25-molar solution of  $\text{Fe}_2(\text{SO}_4)_3$  between platinum electrodes for a period of 1.100 hours. Oxygen gas was produced at the anode.

The only change at the cathodes was a slight change in the color of the solution. At the end of the electrolysis, the electrolyte was acidified with sulfuric acid and was titrated with an aqueous solution of potassium permanganate. The volume of the  $\text{KMnO}_4$  solution required to reach the end point was 24.65 milliliters.

(a) How many faradays were passed through the solution?

**$1.100 \text{ hr} \times (3600 \text{ sec} / \text{hr}) = 3960 \text{ sec}$**

**$3960 \text{ sec} \times (0.125 \text{ coulomb} / \text{sec}) = 495 \text{ coulombs}$**

**$495 \text{ coulombs} \times (1 \text{ faraday} / 96500 \text{ coulombs}) = 5.13 \times 10^{-3} \text{ F}$**

(b) Write a balanced half-reaction for the process that occurred at the cathode during the electrolysis.



(c) Write a balanced net ionic equation for the reaction that occurred during the titration with potassium permanganate.  **$\text{MnO}_4^- + 8 \text{H}^+ + 5 \text{Fe}^{2+} \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O} + 5 \text{Fe}^{3+}$**

(d) Calculate the molarity of the  $\text{KMnO}_4$  solution.

**$5.13 \times 10^{-3} \text{ faraday} \times (1 \text{ mole Fe}^{2+} / 1 \text{ faraday}) = 5.13 \times 10^{-3} \text{ mole Fe}^{2+}$**

**$5.13 \times 10^{-3} \text{ mole Fe} \times (1 \text{ mole MnO}_4^- / 5 \text{ mole Fe}^{2+}) = 1.03 \times 10^{-3} \text{ mole MnO}_4^-$**

**$1.03 \times 10^{-3} \text{ mole MnO}_4^- \div 0.02465 \text{ liter} = 0.0416 \text{ M MnO}_4^- \text{ (or KMnO}_4)$**

**1987 - #6**

A dilute solution of sodium sulfate,  $\text{Na}_2\text{SO}_4$ , was electrolyzed using inert platinum electrodes. In a separate experiment, a concentrated solution of sodium chloride,  $\text{NaCl}$ , was electrolyzed also using inert platinum electrodes. In each experiment, gas formation was observed at both electrodes.

(a) Explain why metallic sodium is not formed in either experiment.  **$\text{Na}^+$  is not reduced as easily as  $\text{H}_2\text{O}$ . OR if  $\text{Na(s)}$  were formed it would immediately react with the water to reform  $\text{Na}^+$  and  $\text{H}_2(\text{g})$**

(b) Write balanced equations for the half-reactions that occur at the electrodes during electrolysis of the dilute sodium sulfate solution. Clearly indicate which half-reaction occurs at each electrode.



(c) Write balanced equations for the half-reactions that occur at the electrodes during the electrolysis of the concentrated sodium chloride solution. Clearly indicate which half-reaction occurs at each electrode.



(d) Select two of the gases obtained in these experiments, and for each gas, indicate one experimental procedure that can be used to identify it.

**$\text{H}_2$  - "pop" with a glowing splint or other suitable test**

**$\text{O}_2$  - ignite a glowing splint of other suitable test**

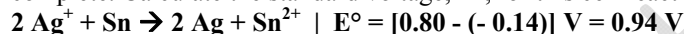
**$\text{Cl}_2$  - yellowish-green color or other suitable test**

**1988 - #3**

An electrochemical cell consists of a tin electrode in an acidic solution of 1.00-molar  $\text{Sn}^{2+}$  connected by a salt bridge to a second compartment with a silver electrode in an acidic solution of 1.00-molar  $\text{Ag}^+$ .

(a) Write the equation for the half-cell reaction occurring at each electrode. Indicate which half-reaction occurs at the anode. **Anode:  $\text{Sn} \rightarrow \text{Sn}^{2+} + 2\text{e}^-$  | Cathode:  $\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$**

(b) Write the balanced chemical equation for the overall spontaneous cell reaction that occurs when the circuit is complete. Calculate the standard voltage,  $E^\circ$ , for this cell reaction.



(c) Calculate the equilibrium constant for this cell reaction at 298 K.

**$E = (0.0591 \div n) \log K$  (or  $-nFE = -RT \ln K$ );  $\log K = (0.94 \times 2) \div 0.0591 = 31.8$ ;  $K = 6 \times 10^{31}$**

(d) A cell similar to the one described above is constructed with solutions that have initial concentrations of 1.00 molar  $\text{Sn}^{2+}$  and 0.0200-molar  $\text{Ag}^+$ . Calculate the initial voltage,  $E$ , of this cell.

**$E = E^\circ - (0.0591 \div n) \log [\text{Sn}^{2+}] / [\text{Ag}^+]^2$**

**OR**

**$E = E^\circ - (RT / nF) \ln Q$**

**$Q = [\text{Sn}^{2+}] / [\text{Ag}^+]^2$**

**$E = 0.94 = (0.0591 \div 2) \log (1 \div (0.022))$**

**$E = 0.94 - 0.10 = 0.84 \text{ V}$**

**1989 - #2**

The electrolysis of an aqueous solution of potassium iodide,  $\text{KI}$ , results in the formation of hydrogen gas at the cathode and iodine at the anode. A sample of 80.00 milliliters of a 0.150-molar solution of  $\text{KI}$  was electrolyzed for 3.00 minutes, using a constant current. At the end of this time, the  $\text{I}_2$  produced was titrated against a 0.225-molar solution of sodium thiosulfate, which reacts with iodine according to the equation below. The end point of the titration was reached when 37.2 milliliters of the  $\text{Na}_2\text{S}_2\text{O}_3$  solution had been added.  $\text{I}_2 + 2 \text{S}_2\text{O}_3^{2-} \rightarrow 2\text{I}^- + \text{S}_4\text{O}_6^{2-}$

(a) How many moles of  $\text{I}_2$  were produced during the electrolysis?  **$4.20 \times 10^{-3}$**

(b) The hydrogen gas produced at the cathode during the electrolysis was collected over water at 25 °C at a total pressure of 752 millimeters of mercury. Determine the volume of hydrogen collected. (The vapor pressure of water at 25 °C is 24 millimeters of mercury.) **0.107 L**

(c) Write the equations for the half reaction that occurs at the anode during the electrolysis.  **$2\text{I}^- \rightarrow \text{I}_2 + 2\text{e}^-$**

(d) Calculate the current used during the electrolysis. **4.49 A**

1991 - #7

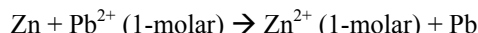
Explain each of the following.

(a) When an aqueous solution of NaCl is electrolyzed,  $\text{Cl}_2(\text{g})$  is produced at the anode, but no  $\text{Na}(\text{s})$  is produced at the cathode.  **$\text{Cl}^-$  is more easily oxidized than  $\text{H}_2\text{O}$ ;  $\text{H}_2\text{O}$  is more easily oxidized than  $\text{Na}^+$**

(b) The mass of  $\text{Fe}(\text{s})$  produced when 1 faraday is used to reduce a solution of  $\text{FeSO}_4$  is 1.5 times the mass of  $\text{Fe}(\text{s})$  produced when 1 faraday is used to reduce a solution of  $\text{FeCl}_3$ .  **$\text{Fe}^{2+}$  requires 2 Faraday / mol Fe (s)**

**$\text{Fe}^{3+}$  require 3 Faraday / mol Fe (s)**

**for equal numbers of Faraday (1/2 : 1/3 as 1.5 : 1) (Or inverse relationship is clear)**



(c) The cell that utilized the reaction above has a higher potential when  $[\text{Zn}^{2+}]$  is decreased and  $[\text{Pb}^{2+}]$  held constant, but a lower potential when  $[\text{Pb}^{2+}]$  is decreased and  $[\text{Zn}^{2+}]$  is held constant.

**Le Châtelier's argument**

**if  $[\text{Zn}^{2+}]$  goes down; reaction shifts right, i.e. cell potential goes up**

**if  $[\text{Pb}^{2+}]$  goes down; reaction shifts left, i.e. cell potential goes down**

**OR**

**Nernst Equation argument**

**$E = E^\circ - RT \ln Q$  with  $Q = [\text{Zn}^{2+}] / [\text{Pb}^{2+}]$**

**if  $[\text{Zn}^{2+}]$  goes down  $Q < 1$ , therefore  $E > E^\circ$**

**if  $[\text{Pb}^{2+}]$  goes down  $Q > 1$ , therefore  $E < E^\circ$**

(d) The cell that utilizes the reaction given in (c) has the same cell potential as another cell in which  $[\text{Zn}^{2+}]$  and  $[\text{Pb}^{2+}]$  are each 0.1-molar.

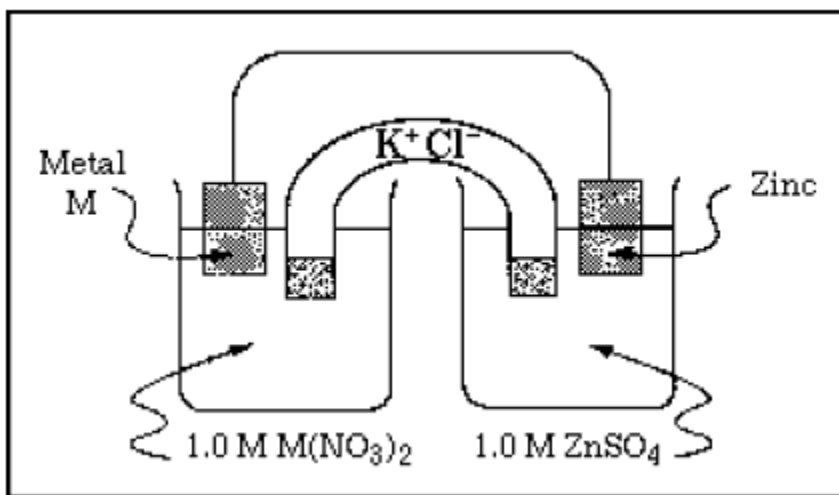
**$[\text{Zn}^{2+}] / [\text{Pb}^{2+}]$  does not change; regardless of values; i.e.  $E = E^\circ$  OR  $[\text{Zn}^{2+}] / [\text{Pb}^{2+}] = 1$  so  $\ln Q = 0$ ; i.e.  $E = E^\circ$**

1992 - #2

An unknown metal M forms a soluble compound  $\text{M}(\text{NO}_3)_2$ .

(a) A solution of  $\text{M}(\text{NO}_3)_2$  is electrolyzed. When a constant current of 2.50 amperes is applied for 35.0 minutes, 3.06 grams of the metal M is deposited. Calculate the molar mass of M and identify the metal. **112.5 g/mol**

(b) The metal identified in (a) is used with zinc to construct a galvanic cell, as shown below. Write the net ionic equation for the cell reaction and calculate the cell potential,  $E^\circ$ .  **$\text{Cd}^{2+} + \text{Zn} \rightarrow \text{Cd} + \text{Zn}^{2+}$ ;  $E^\circ = 0.36 \text{ V}$**



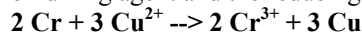
(c) Calculate the value of the standard free energy change,  $\Delta G^\circ$ , at  $25^\circ\text{C}$  for the reaction in (b) **-69 kJ**

(d) Calculate the potential,  $E$ , for the cell shown in (b) if the initial concentration of  $\text{ZnSO}_4$  is 0.10-molar, but the concentration of the  $\text{M}(\text{NO}_3)_2$  solution remains unchanged. **0.39 V**

1993 – #7

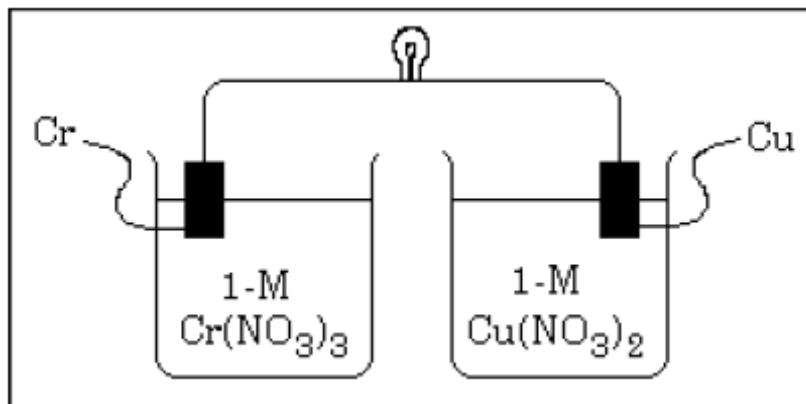
A galvanic cell is constructed using a chromium electrode in a 1.00 molar solution of  $\text{Cr}(\text{NO}_3)_3$  and a copper electrode in a 1.00 molar solution of  $\text{Cu}(\text{NO}_3)_2$ . Both solutions are at  $25^\circ\text{C}$ .

(a) Write a balanced net ionic equation for the spontaneous reaction that occurs as the cell operates. Identify the oxidizing agent and the reducing agent.



**Cr = reducing agent;  $\text{Cu}^{2+}$  = oxidizing agent**

(b) A partial diagram of the cell is shown below.



(i) Which metal is the cathode? **Cu is cathode**

(ii) What additional component is necessary to make the cell operate? **salt bridge**

(iii) What function does the component in (ii) serve? **transfer of ions or charge but not electrons**

(c) How does the potential of this cell change if the concentration of  $\text{Cr}(\text{NO}_3)_3$  is changed to 3.00 molar at  $25^\circ\text{C}$ ? Explain.

**Nernst equation use, E decreases**

1996 - #7



Consider the reaction represented above that occurs at  $25^\circ\text{C}$ . All reactants and products are in their standard states. The value of the equilibrium constant,  $K_{\text{eq}}$ , for the reaction is  $4.2 \times 10^{17}$  at  $25^\circ\text{C}$ .

(a) Predict the sign of the standard cell potential,  $E^\circ$ , for a cell based on the reaction. Explain your prediction.

**The sign of the cell potential will be positive because (any one is sufficient): K is greater than 1, the reaction is spontaneous (occurs),  $E^\circ$  for  $\text{Sr}^{2+}$  is more positive, Standard reduction potential for Sr more negative,  $E^\circ = +0.52 \text{ V}$**

(b) Identify the oxidizing agent for the spontaneous reaction. **The oxidizing agent is  $\text{Mg}^{2+}$**

(c) If the reaction were carried out at  $60^\circ\text{C}$  instead of  $25^\circ\text{C}$ , how would the cell potential change? Justify your answer. **The cell potential would increase**

**Since all ions are at 1 M, Q for the system is 1 and  $E^\circ = (RT/nF) \ln K$  so as T increases, so should  $E^\circ$  OR**

**No change, because in the Nernst equation  $E_{\text{cell}} = E^\circ - (RT/nF) \ln Q$ ;  $-\ln Q = 0$ , and  $E_{\text{cell}} = E^\circ$**

(d) How would the cell potential change if the reaction were carried out at  $25^\circ\text{C}$  with a 1.0-molar solution of  $\text{Mg}(\text{NO}_3)_2$  and a 0.10-molar solution of  $\text{Sr}(\text{NO}_3)_2$ ? Explain.  **$E_{\text{cell}}$  will increase. In the equation  $E_{\text{cell}} = E^\circ - (0.0592 / n) \log Q$ ;  $-Q = 0.1$  therefore  $\log Q$  is negative therefore term after  $E^\circ$  is positive therefore  $E_{\text{cell}}$  increases OR with the concentration of  $\text{Mg}^{2+}$  larger than that of  $\text{Sr}^{2+}$ , Le Chatelier's principle predicts the reaction will have a larger driving force to the right and a more positive  $E_{\text{cell}}$**

(e) When the cell reaction in (d) reaches equilibrium, what is the cell potential? At equilibrium,  **$E_{\text{cell}} = 0$**

1997 - #3

In an electrolytic cell, a current of 0.250 ampere is passed through a solution of a chloride of iron, producing Fe(s) and Cl<sub>2</sub>(g).

(a) Write the equation for the reaction that occurs at the anode.  $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$

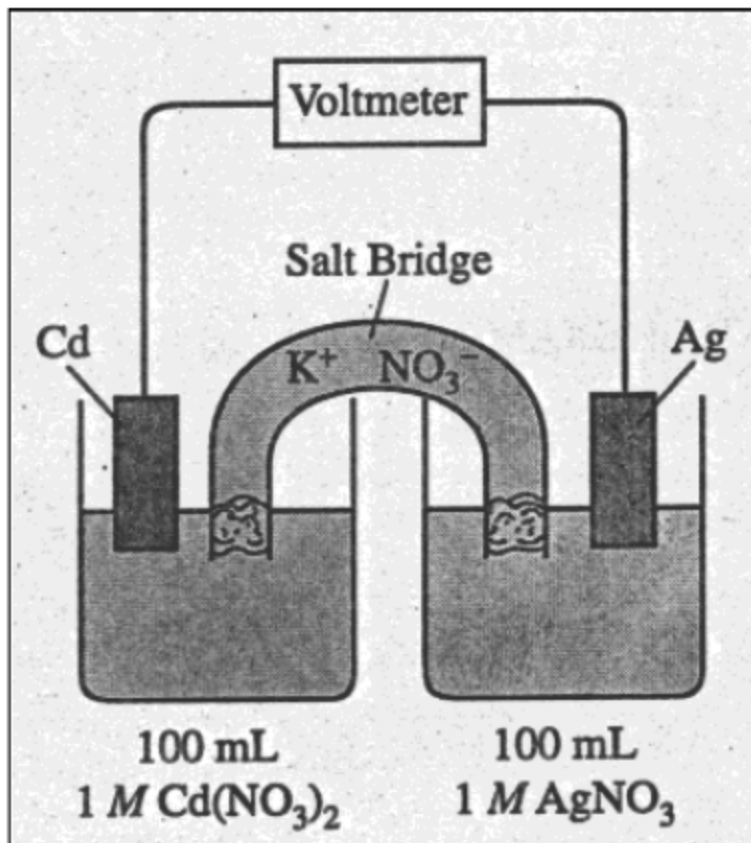
(b) When the cell operates for 2.00 hours, 0.521 gram of iron is deposited at one electrode. Determine the formula of the chloride of iron in the original solution.  $\text{FeCl}_2$

(c) Write the balanced equation for the overall reaction that occurs in the cell.  $\text{Fe}^{2+} + 2\text{Cl}^- \rightarrow \text{Fe} + \text{Cl}_2$

(d) How many liters of Cl<sub>2</sub>(g), measured at 25°C and 750 mmHg, are produced when the cell operates as described in part (b)? **0.231 L**

(e) Calculate the current that would produce chlorine gas at a rate of 3.00 grams per hour. **2.27 A**

1998 - #8



Answer the following questions regarding the electrochemical cell shown above.

(a) Write the balanced net-ionic equation for the spontaneous reaction that occurs as the cell operates, and determine the cell voltage.  $2\text{Ag}^+(\text{aq}) + \text{Cd}(\text{s}) \rightarrow 2\text{Ag}(\text{s}) + \text{Cd}^{2+}(\text{aq}); 1.20\text{ V}$

(b) In which direction do anions flow in the salt bridge as the cell operates? Justify your answer. **Anions (or NO<sub>3</sub><sup>-</sup> ions) will follow to the Cd<sup>2+</sup> solution or from the Ag<sup>+</sup> solution to balance the charges.**

(c) If 10.0 mL of 3.0-molar AgNO<sub>3</sub> solution is added to the half-cell on the right, what will happen to the cell voltage? Explain. **The cell voltage will increase. Ag<sup>+</sup> is a reactant, so increasing [Ag<sup>+</sup>] will increase the driving force (stress) for the forward (spontaneous) reaction and the potential will increase.**

(d) If 1.0 grams of solid NaCl is added to each half-cell, what will happen to the cell voltage? Explain. **The cell voltage will decrease. Adding the NaCl will have no effect on the Cd cell, but will cause AgCl to precipitate in the Ag cell (Ag<sup>+</sup> + Cl<sup>-</sup> → AgCl). Thus [Ag<sup>+</sup>] causes a decrease in voltage.**

(e) If 20.0 mL of distilled water is added to both half-cells, the cell voltage decreases. Explain. **Since  $Q = [\text{Cd}^{2+}] / [\text{Ag}^+]^2$ , diluting both solution by the same amount will increase the value of Q. According to the Nernst equation,  $E = E^\circ - (0.0592 \log Q)/n$ , if Q increases, then voltage decreases.**

2000 - #2

Answer the following questions that relate to electrochemical reactions.

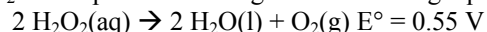
(a) Under standard conditions at 25°C, Zn(s) reacts with Co<sup>2+</sup>(aq) to produce Co(s).

(i) Write the balanced equation for the oxidation half reaction. **Zn(s) → Zn<sup>2+</sup>(aq) + 2e<sup>-</sup>**

(ii) Write the balanced net-ionic equation for the overall reaction. **Co<sup>2+</sup> + Zn → Co + Zn<sup>2+</sup>**

(iii) Calculate the standard potential, E°, for the overall reaction at 25°C. **0.48V.**

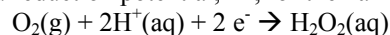
(b) At 25°C, H<sub>2</sub>O<sub>2</sub> decomposes according to the following equation.



(i) Determine the value of the standard free energy change, ΔG°, for the reaction at 25°C. **-1.1 x 10<sup>2</sup> kJ**

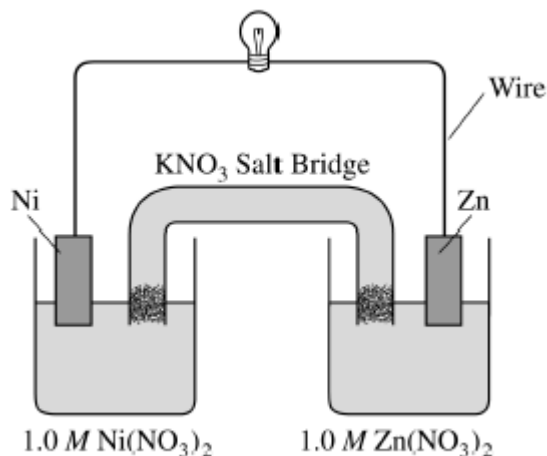
(ii) Determine the value of the equilibrium constant, K<sub>eq</sub>, for the reaction at 25°C. **K = 1.9 x 10<sup>19</sup>**

(iii) The standard reduction potential, E°, for the half reaction O<sub>2</sub>(g) + 4H<sup>+</sup>(aq) + 4e<sup>-</sup> → 2 H<sub>2</sub>O(l) has a value of 1.23 V. Using this information in addition to the information given above, determine the value of the standard reduction potential, E°, for the half reaction below. **0.68 V**



(c) In an electrolytic cell, Cu(s) is produced by the electrolysis of CuSO<sub>4</sub>(aq). Calculate the maximum mass of Cu(s) that can be deposited by a direct current of 100. amperes passed through 5.00 L of 2.00 M CuSO<sub>4</sub>(aq) for a period of 1.00 hour. **119 g Cu**

2001 - #7



Answer the following questions that refer to the galvanic cell shown in the diagram above. (Use the table of standard reduction potentials provided to you.)

(a) Identify the anode of the cell and write the half-reaction that occurs there. **Zn → Zn<sup>2+</sup> + 2e<sup>-</sup>**

(b) Write the net ionic equation for the overall reaction that occurs as the cell operates and calculate the value of the standard cell potential, E<sub>cell</sub><sup>o</sup>. **Zn + Ni<sup>2+</sup> → Zn<sup>2+</sup> + Ni, 0.51 V**

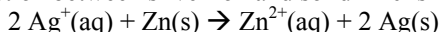
(c) Indicate how the value of E<sub>cell</sub> would be affected if the concentration of Ni(NO<sub>3</sub>)<sub>2</sub>(aq) was changed from 1.0 M to 0.10 M and the concentration of Zn(NO<sub>3</sub>)<sub>2</sub>(aq) remained at 1.0 M. Justify your answer.

**E<sub>cell</sub> would decrease. Since Ni<sup>2+</sup> is a reactant, a decrease in its concentration decreases the driving force for the forward reaction**

(d) Specify whether the value of K<sub>eq</sub> for the cell reaction is less than 1, greater than 1, or equal to 1. Justify your answer. **K > 1; E° is positive, so K > 1**

2002 - #2

Answer parts (a) through (e) below, which relate to reactions involving silver ion,  $\text{Ag}^+$ . The reaction between silver ion and solid zinc is represented by the following equation.



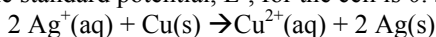
(a) A 1.50 g sample of Zn is combined with 250. mL of 0.110 M  $\text{AgNO}_3$  at 25°C.

(i) Identify the limiting reactant. Show calculations to support your answer.  **$\text{Ag}^+$  is the limiting reagent**

(ii) On the basis of the limiting reactant that you identified in part (i), determine the value of  $[\text{Zn}^{2+}]$  after the reaction is complete. Assume that volume change is negligible. **0.0550 M  $\text{Zn}^{2+}$**

(b) Determine the value of the standard potential,  $E^\circ$ , for a galvanic cell based on the reaction between  $\text{AgNO}_3(\text{aq})$  and solid Zn at 25°C. **1.56 V**

Another galvanic cell is based on the reaction between  $\text{Ag}^+(\text{aq})$  and  $\text{Cu}(\text{s})$ , represented by the equation below. At 25°C, the standard potential,  $E^\circ$ , for the cell is 0.46 V.



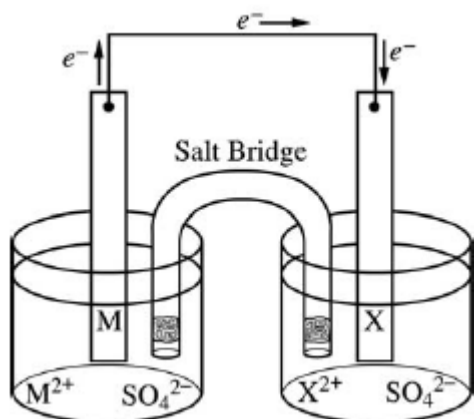
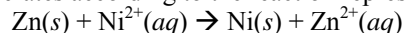
(c) Determine the value of the standard free-energy change,  $\Delta G^\circ$ , for the reaction between  $\text{Ag}^+(\text{aq})$  and  $\text{Cu}(\text{s})$  at 25°C. **-89 kJ**

(d) The cell is constructed so that  $[\text{Cu}^{2+}]$  is 0.045 M and  $[\text{Ag}^+]$  is 0.010 M. Calculate the value of the potential, E for the cell. **0.38 V**

(e) Under the conditions specified in part (d), is the reaction in the cell spontaneous? Justify your answer. **Yes; it is spontaneous because the cell potential is positive.**

2002B - #7

The diagram below shows the experimental setup for a typical electrochemical cell that contains two standard half-cells. The cell operates according to the reaction represented by the following equation.

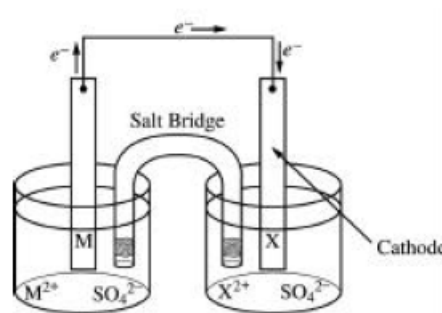


(a) Identify M and  $\text{M}^{2+}$  in the diagram and specify the initial concentration for  $\text{M}^{2+}$  in solution.

**Electrons flow from the anode to the cathode in a voltaic electrochemical cell. The anode is where oxidation occurs, and in the reaction above,  $\text{Zn}(\text{s})$  is oxidized. So, the anode electrode must be Zn (M) and the solution contains  $\text{Zn}^{2+}$  ( $\text{M}^{2+}$ ). The  $[\text{Zn}^{2+}] = 1.0 \text{ M}$  in a standard cell. Additionally, the reduction potential for the  $\text{Zn}^{2+}/\text{Zn}$  redox couple is less than that for  $\text{Ni}^{2+}/\text{Ni}$ .**

(b) Indicate which of the metal electrodes is the cathode. Write the balanced equation for the reaction that occurs in the half-cell containing the cathode.

The cathode is  $\text{Ni}(\text{s})$ , indicated by "X"



The half-reaction is  $2 e^- + \text{Ni}^{2+} \rightarrow \text{Ni}(\text{s})$ .



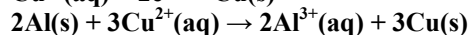
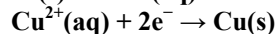
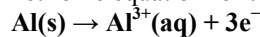
(c) What would be the effect on the cell voltage if the concentration of  $\text{Zn}^{2+}$  was reduced to  $0.100\text{ M}$  in the half-cell containing the Zn electrode? **When the  $[\text{Zn}^{2+}]$  is lowered to  $0.100\text{ M}$ , then  $Q < 1$ . The value of the cell potential under these nonstandard conditions is more positive than  $E^\circ$  (under standard conditions). The cell voltage increases. An argument involving LeChâtelier's principle is also acceptable: the decreased  $[\text{Zn}^{2+}]$  increases the "potential" for the reaction to proceed to the right.**

(d) Describe what would happen to the cell voltage if the salt bridge was removed. Explain. **The cell voltage drops to zero when the salt bridge is removed. This happens because the salt bridge is needed to allow charge balance to occur in the solutions the electrodes are immersed in. In the absence of the salt bridge, ions cannot flow to balance the buildup of cations in the anode compartment and the buildup of anions in the cathode compartment.**

### 2003B - #6

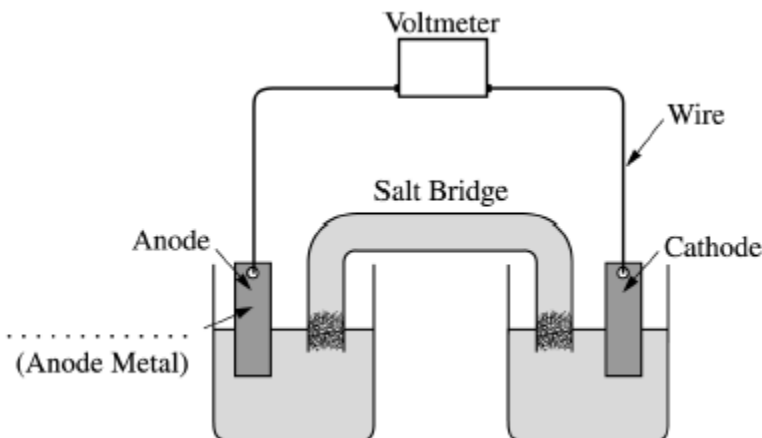
Answer the following questions about electrochemistry.

(a) Several different electrochemical cells can be constructed using the materials shown below. Write the balanced net-ionic equation for the reaction that occurs in the cell that would have the greatest positive value of  $E_{\text{cell}}^\circ$ .



(b) Calculate the standard cell potential,  $E_{\text{cell}}^\circ$ , for the reaction written in part (a).  **$2.00\text{ V}$**

(c) A cell is constructed based on the reaction in part (a) above. Label the metal used for the anode on the cell shown in the figure below. **The metal is aluminum solid.**



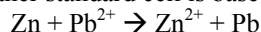
(d) Of the compounds  $\text{NaOH}$ ,  $\text{CuS}$ , and  $\text{NaNO}_3$ , which one is appropriate to use in a salt bridge? Briefly explain your answer, and for each of the other compounds, include a reason why it is not appropriate.

**$\text{NaOH}$  is not appropriate. The anion,  $\text{OH}^-$ , would migrate towards the anode. The  $\text{OH}^-$  would react with the  $\text{Al}^{3+}$  ion in solution.**

**$\text{CuS}$  is not appropriate. It is insoluble in water, so no ions would be available to migrate to the anode and cathode compartment to balance the charge.**

**$\text{NaNO}_3$  is appropriate. It is soluble in water, and neither the cation nor the anion will react with the ions in the anode or cathode compartment.**

(e) Another standard cell is based on the following reaction.



If the concentration of  $\text{Zn}^{2+}$  is decreased from 1.0 M to 0.25 M, what effect does this have on the cell potential? Justify your answer.

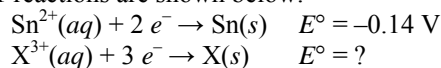
$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - 0.059 \ln \left( \frac{[\text{Zn}^{2+}]}{[\text{Pb}^{2+}]} \right)$$

If  $[\text{Zn}^{2+}]$  is reduced, then the ratio  $\left( \frac{[\text{Zn}^{2+}]}{[\text{Pb}^{2+}]} \right) < 1$ , therefore

$$\ln \left( \frac{[\text{Zn}^{2+}]}{[\text{Pb}^{2+}]} \right) < 0. \text{ Thus } E_{\text{cell}} \text{ increases (becomes more positive).}$$

#### 2004 - #6

An electrochemical cell is constructed with an open switch, as shown in the diagram above. A strip of Sn and a strip of an unknown metal, X, are used as electrodes. When the switch is closed, the mass of the Sn electrode increases. The half-reactions are shown below.



(a) In the diagram above, label the electrode that is the cathode. Justify your answer. The Sn (tin) electrode is the cathode.

**The increase in mass indicates that reduction occurs at the Sn electrode:  $\text{Sn}^{2+}(\text{aq}) + 2 e^{-} \rightarrow \text{Sn}(\text{s})$**

**Reduction occurs at the cathode.**

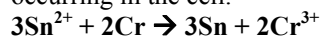
(b) In the diagram to the right, draw an arrow indicating the direction of the electron flow in the external circuit when the switch is closed.

**Diagram should have arrow showing electrons flowing from the anode towards the cathode.**

(c) If the standard cell potential,  $E_{\text{cell}}$ , is +0.60 V, what is the standard reduction potential, in volts, for the  $\text{X}^{3+}/\text{X}$  electrode? **-0.74 V**

(d) Identify metal X. **Cr**

(e) Write a balanced net-ionic equation for the overall chemical reaction occurring in the cell.



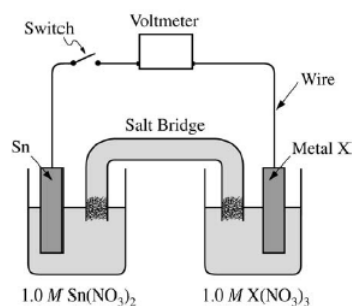
(f) In the cell, the concentration of  $\text{Sn}^{2+}$  is changed from 1.0 M to 0.50 M, and the concentration of  $\text{X}^{3+}$  is changed from 1.0 M to 0.10 M.

(i) Substitute all the appropriate values for determining the cell potential,  $E_{\text{cell}}$ , into the Nernst equation. (Do not do any calculations.)

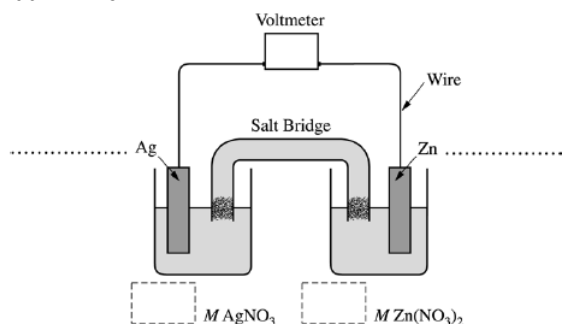
$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0592}{n} \log \frac{[\text{Cr}^{3+}]^2}{[\text{Sn}^{2+}]^3}$$

$$E_{\text{cell}} = +0.60 \text{ V} - \frac{0.0592}{6} \log \frac{[0.10]^2}{[0.50]^3}$$

(ii) On the basis of your response in part (f) (i), will the cell potential,  $E_{\text{cell}}$ , be greater than, less than, or equal to the original  $E_{\text{cell}}$ ? Justify your answer.  **$E_{\text{cell}}$  will be greater (more positive). Since the Q ratio is a number less than 1, the log of the ratio will be negative. A negative times a negative is positive.**

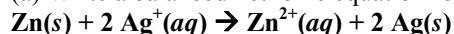


## 2004B - #6



The following questions refer to the electrochemical cell shown in the diagram above.

(a) Write a balanced net ionic equation for the spontaneous reaction that takes place in the cell.



(b) Calculate the standard cell potential,  $E^\circ$ , for the reaction in part (a). **1.56 V**

(c) In the diagram above,

(i) label the anode and the cathode on the dotted lines provided, and

**The anode is the zinc metal electrode, the cathode is the silver metal electrode.**

(ii) indicate in the boxes below the half-cells, the concentration of  $\text{AgNO}_3$  and the concentration of  $\text{Zn}(\text{NO}_3)_2$  that are needed to generate  $E^\circ$ .  **$[\text{AgNO}_3] = [\text{Zn}(\text{NO}_3)_2] = 1 \text{ M}$**

(d) How will the cell potential be affected if KI is added to the silver half-cell? Justify your answer.

**A precipitate will form as  $\text{I}^-$  ions react with  $\text{Ag}^+$  ions in solution in cathode compartment.  $[\text{Ag}^+]$  will be reduced, causing cell potential to decrease.**

## 2005 - #8d

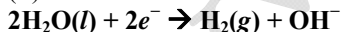
The compound NaI dissolves in pure water according to the equation  $\text{NaI}(s) \rightarrow \text{Na}^+(aq) + \text{I}^-(aq)$ . Some of the information in the table of standard reduction potentials given below may be useful in answering the questions that follow.

Half-reaction $E^\circ$	(V)
$\text{O}_2(g) + 4\text{H}^+ + 4 e^- \rightarrow 2 \text{H}_2\text{O}(l)$	1.23
$\text{I}_2(s) + 2 e^- \rightarrow 2 \text{I}^-$	0.53
$2\text{H}_2\text{O}(l) + 2 e^- \rightarrow \text{H}_2(g) + 2\text{OH}^-$	-0.83
$\text{Na}^+ + e^- \rightarrow \text{Na}(s)$	-2.71

(d) An electric current is applied to a 1.0 M NaI solution.

(i) Write the balanced oxidation half-reaction for the reaction that takes place.  **$2\text{I}^- \rightarrow \text{I}_2(s) + 2e^-$**

(ii) Write the balanced reduction half-reaction for the reaction that takes place.



(iii) Which reaction takes place at the anode, the oxidation reaction or the reduction reaction?

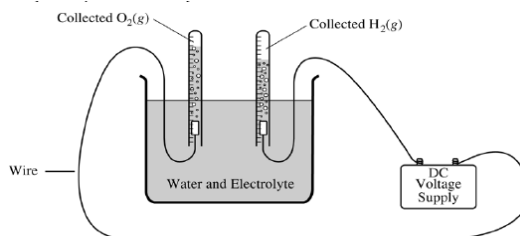
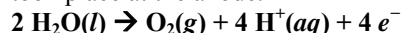
**The oxidation half-reaction occurs at the anode.**

(iv) All electrolysis reactions have the same sign for  $\Delta G^\circ$ . Is the sign positive or negative? Justify your answer. **The sign of  $\Delta G$  for all electrolysis reactions is positive. Because electrolysis reactions are non-spontaneous, energy in the form of applied electrical current (electrical work) must be applied to make the reaction occur.**

## 2005B - #2

Water was electrolyzed, as shown in the diagram to the right, for 5.61 minutes using a constant current of 0.513 ampere. A small amount of non-reactive electrolyte was added to the container before the electrolysis began. The temperature was 298 K and the atmospheric pressure was 1.00 atm.

(a) Write the balanced equation for the half reaction that took place at the anode.



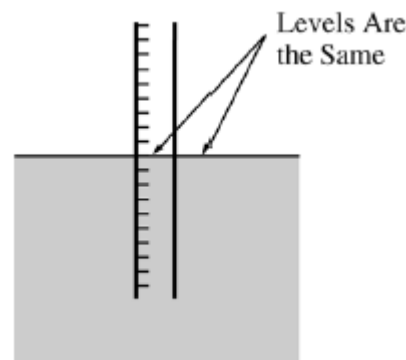
(b) Calculate the amount of electric charge, in coulombs, that passed through the solution. **173 Coulombs**  
 (c) Why is the volume of  $O_2(g)$  collected different from the volume of  $H_2(g)$  collected, as shown in the diagram? **When water decomposes according to the balanced chemical equation  $2H_2O(l) \rightarrow O_2(g) + 2H_2(g)$ , twice as many moles of hydrogen are produced than moles of oxygen.**

(d) Calculate the number of moles of  $H_2(g)$  produced during the electrolysis.

**$8.96 \times 10^{-4} \text{ mol}$**

(e) Calculate the volume, in liters, at 298 K and 1.00 atm of dry  $H_2(g)$  produced during the electrolysis. **0.0219 L**

(f) After the hydrolysis reaction was over, the vertical position of the tube containing the collected  $H_2(g)$  was adjusted until the water levels inside and outside the tube were the same, as shown in the diagram below. The volume of gas in the tube was measured under these conditions of 298 K and 1.00 atm, and its volume was greater than the volume calculated in part (e). Explain. **Because the electrolysis of water occurs in water, there is some water vapor in the tube of  $H_2(g)$  that was collected. The volume calculated in part (e) was the volume of only the  $H_2(g)$  in the tube at the given temperature and pressure. The presence of another gas (water vapor) results in a greater volume at the given temperature and pressure.**



### 2006B - #2

Answer the following questions about voltaic cells.

(a) A voltaic cell is set up using  $Al/Al^{3+}$  as one half-cell and  $Sn/Sn^{2+}$  as the other half-cell. The half-cells contain equal volumes of solutions and are at standard conditions.

(i) Write the balanced net-ionic equation for the spontaneous cell reaction.  **$3 Sn^{2+} + 2 Al \rightarrow 3 Sn + 2 Al^{3+}$**

(ii) Determine the value, in volts, of the standard potential,  $E^\circ$ , for the spontaneous cell reaction. **1.52 V**

(iii) Calculate the value of the standard free-energy change,  $\Delta G^\circ$ , for the spontaneous cell reaction. Include units with your answer. **-880 kJ/mol**

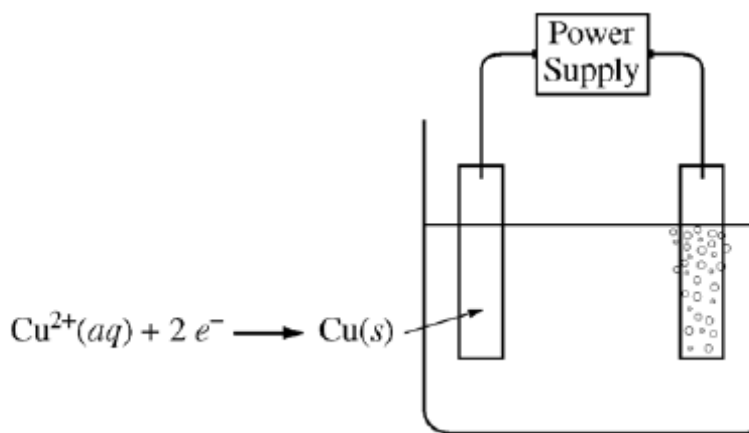
(iv) If the cell operates until  $[Al^{3+}]$  is 1.08 M in the  $Al/Al^{3+}$  half-cell, what is  $[Sn^{2+}]$  in the  $Sn/Sn^{2+}$  half-cell? **0.88 mol/L**

(b) In another voltaic cell with  $Al/Al^{3+}$  and  $Sn/Sn^{2+}$  half-cells,  $[Sn^{2+}]$  is 0.010 M and  $[Al^{3+}]$  is 1.00 M.

Calculate the value, in volts, of the cell potential,  $E_{cell}$ , at 25°C. **1.46 V**

### 2007 #3

An external direct-current power supply is connected to two platinum electrodes immersed in a beaker containing 1.0 M  $CuSO_4(aq)$  at 25°C, as shown in the diagram above. As the cell operates, copper metal is deposited onto one electrode and  $O_2(g)$  is produced at the other electrode. The two reduction half-reactions for the overall reaction that occurs in the cell are shown in the table below.



Half-Reaction	$E^\circ$ (V)
$O_2(g) + 4 H^+(aq) + 4 e^- \rightarrow 2 H_2O(l)$	+1.23
$Cu^{2+}(aq) + 2 e^- \rightarrow Cu(s)$	+0.34

(a) On the diagram, indicate the direction of electron flow in the wire.

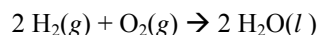
**The electron flow in the wire is from the right toward the left (counterclockwise).**

(b) Write a balanced net ionic equation for the electrolysis reaction that occurs in the cell.

**$2H_2O(l) + 2Cu^{2+}(aq) \rightarrow 4H^+(aq) + 2Cu(s) + O_2(g)$**

- (c) Predict the algebraic sign of  $\Delta G^\circ$  for the reaction. Justify your prediction. **The sign of  $\Delta G^\circ$  would be positive because the reaction is NOT spontaneous.**
- (d) Calculate the value of  $\Delta G^\circ$  for the reaction. **+340 kJ mol<sup>-1</sup>**  
 An electric current of 1.50 amps passes through the cell for 40.0 minutes.
- (e) Calculate the mass, in grams, of the Cu(s) that is deposited on the electrode. **1.19 g Cu**
- (f) Calculate the dry volume, in liters measured at 25°C and 1.16 atm, of the O<sub>2</sub>(g) that is produced. **0.197 L**

**2007B - #3**



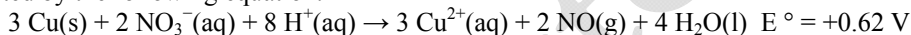
In a hydrogen-oxygen fuel cell, energy is produced by the overall reaction represented above.

- (a) When the fuel cell operates at 25°C and 1.00 atm for 78.0 minutes, 0.0746 mol of O<sub>2</sub>(g) is consumed. Calculate the volume of H<sub>2</sub>(g) consumed during the same time period. Express your answer in liters measured at 25°C and 1.00 atm. **3.65 L H<sub>2</sub>**
- (b) Given that the fuel cell reaction takes place in an acidic medium,
- write the two half reactions that occur as the cell operates,  
 $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2 \text{H}_2\text{O}$   
 $\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$
  - identify the half reaction that takes place at the cathode, and  $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2 \text{H}_2\text{O}$
  - determine the value of the standard potential,  $E^\circ$ , of the cell. **1.23 V**
- (c) Calculate the charge, in coulombs, that passes through the cell during the 78.0 minutes of operation as described in part (a).  **$2.88 \times 10^4 \text{ C}$**

**2008 - #3a-c**

Answer the following questions related to chemical reactions involving nitrogen monoxide, NO(g).

The reaction between solid copper and nitric acid to form copper(II) ion, nitrogen monoxide gas, and water is represented by the following equation.



- (a) Using the information above and in the table below, calculate the standard reduction potential,  $E^\circ$ , for the reduction of NO<sub>3</sub><sup>-</sup> in acidic solution. **0.96 V**

Half-Reaction	Standard Reduction Potential, $E^\circ$
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$	+0.34 V
$\text{NO}_3^-(\text{aq}) + 4\text{H}^+(\text{aq}) + 3\text{e}^- \rightarrow \text{NO}(\text{g}) + 2\text{H}_2\text{O}(\text{l})$	?

- (b) Calculate the value of the standard free energy change,  $\Delta G^\circ$ , for the overall reaction between solid copper and nitric acid. **-360 kJ/mol**
- (c) Predict whether the value of the standard entropy change,  $\Delta S^\circ$ , for the overall reaction is greater than 0, less than 0, or equal to 0. Justify your prediction.  **$\Delta S^\circ > 0$ . Even though there is a loss of 7 moles of ions in solution, the value of  $\Delta S^\circ$  for the overall reaction will be greater than zero because two moles of NO gas will be produced (there are no gaseous reactants).**