

# PRACTICE EXAM 3-B

## CHEMISTRY E-1b

### ANSWERS

LAST NAME: \_\_\_\_\_

FIRST NAME: \_\_\_\_\_

**Answer Key Note: Explanations for the conceptual problems (multiple choice etc.) are given at the end of the answer key.**

#### NOTES:

1. This exam has **6** pages with **6** problems, plus the cover sheet, useful information, periodic table, and scrap paper.
2. Note the point values of each exam question, and consider where you can best spend your time.
3. Answer all questions on the exam sheets. **Put your final answers in the boxes provided.** If you must use the back, then please indicate that **clearly!**
4. Do not use red pen!
5. For full credit, **show all calculations**; this also helps us award partial credit.
6. All numerical answers **must include correct units** for full credit.

1. \_\_\_\_\_

2. \_\_\_\_\_

3. \_\_\_\_\_

4. \_\_\_\_\_

5. \_\_\_\_\_

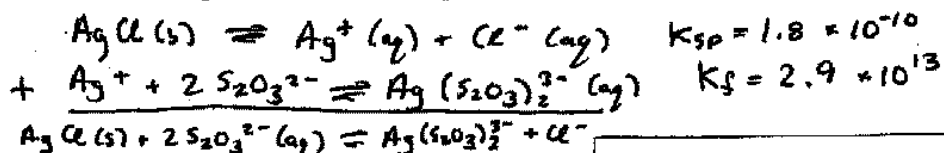
6. \_\_\_\_\_

**TOTAL: \_\_\_\_\_ / 100**

1

1. Silver chloride,  $\text{AgCl}$ , is practically insoluble in pure water. However,  $\text{AgCl}$  will dissolve in a solution that contains the thiosulfate ion,  $\text{S}_2\text{O}_3^{2-}$ , due to the formation of the complex ion  $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$ .

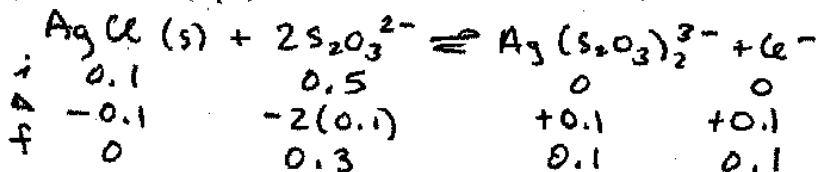
- a) Determine the equilibrium constant for the following reaction at  $25^\circ\text{C}$ : (4 pts)



$$K = K_{\text{sp}} \cdot K_f = 5220$$

$$K = 5220$$

- b) In 1.00 L of solution, you combine 0.100 moles of  $\text{AgCl (s)}$  with 0.500 moles of  $\text{Na}_2\text{S}_2\text{O}_3$ . In the space below, use the reaction quotient,  $Q$ , to show that all of the  $\text{AgCl}$  will dissolve. (5 pts) RUN ALL THE WAY TO THE RIGHT!



$$Q = \frac{[\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}][\text{Cl}^-]}{[\text{S}_2\text{O}_3^{2-}]^2} = \frac{(0.1)(0.1)}{(0.3)^2} = 0.11$$

$Q < K$  so REACTION WOULD GO RIGHT  
so ALL SOLID STAYS DISSOLVED

- c) Determine the final concentrations of each of the indicated species in this solution at equilibrium. (Hint: What reactions are at equilibrium?) (8 pts)

$[\text{S}_2\text{O}_3^{2-}]$  AND  $[\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}]$  AND  $[\text{Cl}^-]$  FROM ABOVE

FIND  $\text{Ag}^+$ :

$$K_f = \frac{[\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}]}{[\text{Ag}^+][\text{S}_2\text{O}_3^{2-}]^2}$$

$$2.9 \times 10^{13} = \frac{(0.1)}{[\text{Ag}^+](0.3)^2}$$

$$[\text{Ag}^+] = 3.8 \times 10^{-14} \text{ M}$$

$$[\text{Ag}^+] = 3.8 \times 10^{-14} \text{ M}$$

$$[\text{Cl}^-] = 0.1 \text{ M}$$

$$[\text{S}_2\text{O}_3^{2-}] = 0.3 \text{ M}$$

$$[\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}] = 0.1 \text{ M}$$

(\_\_\_\_ / 17 pts)

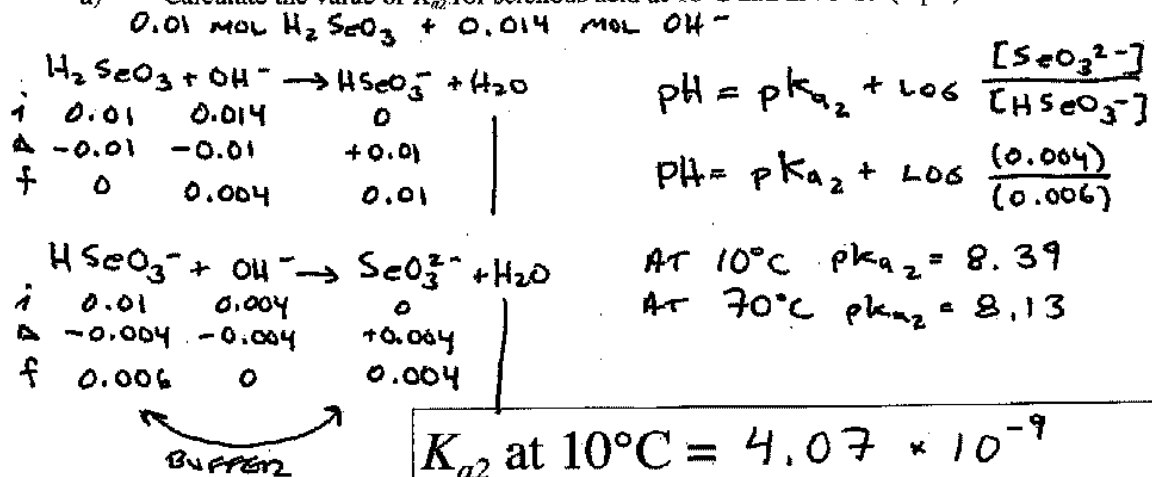
2

2. Selenous acid,  $\text{H}_2\text{SeO}_3$ , is a weak diprotic acid. A solution is prepared by mixing 100.0 mL of 0.100 M  $\text{H}_2\text{SeO}_3$  with 100.0 mL of 0.140 M NaOH. The pH of the resulting solution is measured at 10°C and at 70°C:

At 10°C, pH = 8.21

At 70°C, pH = 7.95

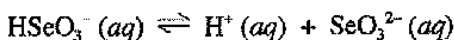
- a) Calculate the value of  $K_{a2}$  for selenous acid at 10°C and at 70°C. (8 pts)



$$K_{a2} \text{ at } 10^\circ\text{C} = 4.07 \times 10^{-9}$$

$$K_{a2} \text{ at } 70^\circ\text{C} = 7.41 \times 10^{-9}$$

- b) Determine  $\Delta H^\circ$  and  $\Delta S^\circ$  for the following reaction (the  $K_{a2}$  reaction):



(You may assume that  $\Delta H^\circ$  and  $\Delta S^\circ$  remain constant over this temperature range.) (8 pts)

$$\ln \frac{K_1}{K_2} = \frac{\Delta H^\circ}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\ln \frac{4.07 \times 10^{-9}}{7.41 \times 10^{-9}} = \frac{\Delta H^\circ}{8.314} \left( \frac{1}{343} - \frac{1}{293} \right) \Rightarrow \Delta H^\circ = 8059 \text{ J/mol}$$

$$\Delta G^\circ = -RT \ln K \Rightarrow \Delta G_{10}^\circ = 45460 \text{ J/mol} \text{ or } \Delta G_{70}^\circ = 53310 \text{ J/mol}$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} = -132 \text{ J/mol}\cdot\text{K}$$

$$\Delta H^\circ = 8.06 \text{ kJ/mol}$$

$$\Delta S^\circ = -132 \text{ J/mol}\cdot\text{K}$$

( / 16 pts)

63

3. The following reaction can be used in the laboratory to generate small quantities of oxygen gas:



- a) Given this information, and using any data from the Useful Information page, calculate the standard molar entropy,  $S^\circ$ , for oxygen gas at  $25^\circ\text{C}$ . (12 pts)

Find  $\Delta H^\circ$ :

$$\begin{aligned} \Delta H^\circ &= \sum \Delta H_f^\circ \text{ PROD} - \sum \Delta H_f^\circ \text{ REACT} \\ &= 2 \text{KCl} + 3 \text{O}_2 - 2 \text{KClO}_3 \\ &= 2(-435.9) + 3(0) - 2(-391.2) \\ \Delta H^\circ &= -89.4 \text{ kJ/mol} \end{aligned}$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$$

$$-236.8 = -89.4 - 298(\Delta S^\circ)$$

$$\Delta S^\circ = 0.495 \text{ kJ/mol}\cdot\text{K} = 495 \text{ J/mol}\cdot\text{K}$$

$$\begin{aligned} \Delta S^\circ &= \sum S^\circ \text{ PROD} - \sum S^\circ \text{ REACT} \\ 495 &= 2 \text{KCl} + 3 \text{O}_2 - 2 \text{KClO}_3 \\ 495 &= 2(82.7) + 3(S^\circ_{\text{O}_2}) - 2(143.0) \end{aligned}$$

$$S^\circ_{\text{O}_2} = 205 \text{ J/mol}\cdot\text{K}$$

$$S^\circ (\text{O}_2 (g) \text{ at } 25^\circ\text{C}) = 205 \text{ J/mol}\cdot\text{K}$$

- b) Determine  $\Delta G$  (nonstandard) at  $25^\circ\text{C}$  if the partial pressure of  $\text{O}_2$  gas is 200 torr. (4 pts)

$$P_{\text{O}_2} = 200 \text{ torr} = 0.263 \text{ atm}$$

$$Q = P_{\text{O}_2}^3 = (0.263)^2 = 0.01819$$

$$\begin{aligned} \Delta G &= \Delta G^\circ + RT \ln Q \\ &= -236800 + (8.314)(298) \ln(0.01819) \end{aligned}$$

$$\Delta G = -246700 \text{ J/mol} = -246.7 \text{ kJ/mol}$$

$$\Delta G (\text{nonstandard}) = -246.7 \text{ kJ/mol}$$

(\_\_\_\_\_/ 16 pts)

84

4.

- a) For each of the following processes, predict whether you expect the **standard** enthalpy, entropy, and free energy changes to be positive or negative. Circle the appropriate choice. (2 pts for each box)

i) Water evaporates from an open container at 25°C:

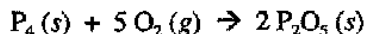


$\Delta H^\circ < 0$     $\Delta H^\circ > 0$  (circle)

$\Delta S^\circ < 0$     $\Delta S^\circ > 0$  (circle)

$\Delta G^\circ < 0$     $\Delta G^\circ > 0$  (circle)

ii) White phosphorous is exposed to air at 1 atm total pressure and 25°C and it immediately bursts into flames:

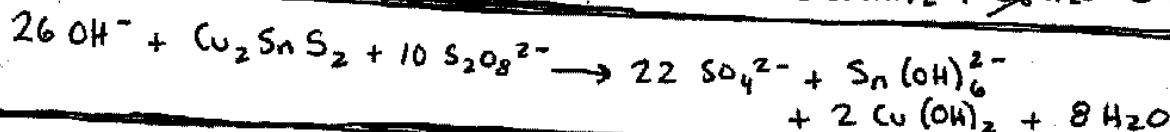
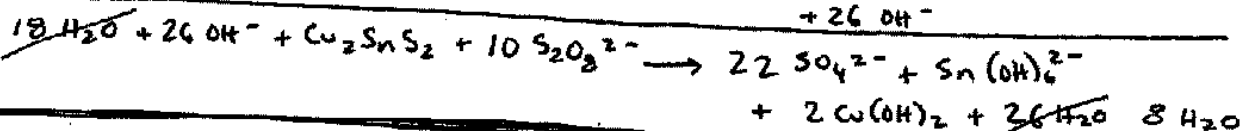
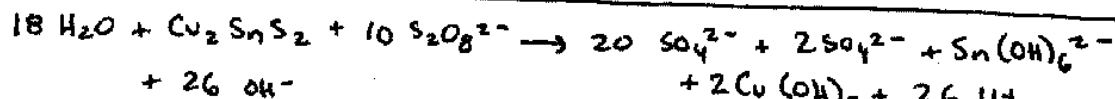
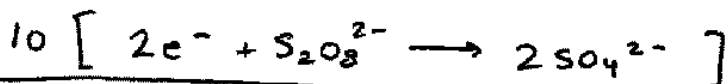
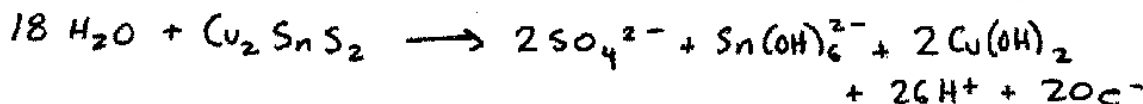
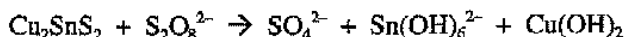


$\Delta H^\circ < 0$     $\Delta H^\circ > 0$  (circle)

$\Delta S^\circ < 0$     $\Delta S^\circ > 0$  (circle)

$\Delta G^\circ < 0$     $\Delta G^\circ > 0$  (circle)

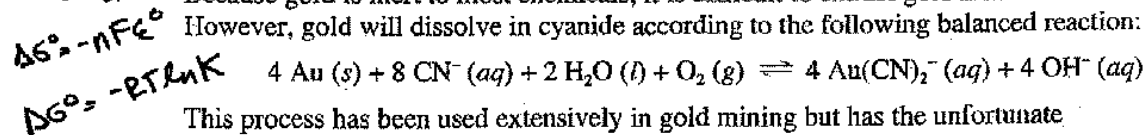
- b) Balance the following redox reaction in **basic solution**. Please **draw a box** around your final balanced equation, and make sure it is **clearly legible**. (6 pts)



( \_\_\_\_\_ / 18 pts)

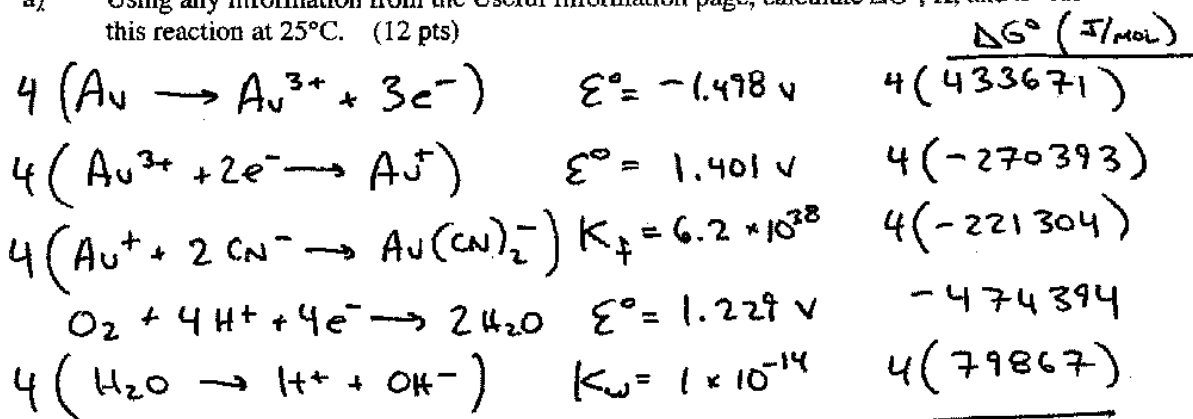
5

Because gold is inert to most chemicals, it is difficult to extract gold from ore. However, gold will dissolve in cyanide according to the following balanced reaction:



This process has been used extensively in gold mining but has the unfortunate consequence of poisoning the local environment with cyanide.

- a) Using any information from the Useful Information page, calculate  $\Delta G^\circ$ ,  $K$ , and  $E^\circ$  for this reaction at  $25^\circ\text{C}$ . (12 pts)



OVERALL R+X

$$\Delta G^\circ = -387030 \text{ J/mol}$$

$$= -387 \text{ kJ/mol}$$

$$\Delta G^\circ = -RT \ln K$$

$$(-387000) = -(8.314)(298) \ln K$$

$$K = 6.96 \times 10^{67}$$

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

$$n = 4$$

$$(-387000) = -(4)(96500) E^\circ$$

$$E^\circ = 1.003 \text{ V}$$

$$\Delta G^\circ = -387 \text{ kJ/mol}$$

$$K = 6.96 \times 10^{67}$$

$$E^\circ = 1.003 \text{ V}$$

- b) Determine  $\Delta G$  (nonstandard) for this reaction at  $25^\circ\text{C}$  under the following conditions: (4 pts)

$[\text{CN}^-] = 0.100 \text{ M}$      $P(\text{O}_2) = 159 \text{ torr} \rightarrow 0.209 \text{ atm}$      $[\text{Au}(\text{CN})_2^-] = 0.250 \text{ M}$      $\text{pH} = 10$

$$Q = \frac{[\text{OH}^-]^4 [\text{Au}(\text{CN})_2^-]^4}{[\text{CN}^-]^8 P_{\text{O}_2}} = \frac{(10^{-4})^4 (0.250)^4}{(0.1)^8 (0.209)} = 1.87 \times 10^{-10}$$

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

$$\Delta G = (-387000) + (8.314)(298) \ln (1.87 \times 10^{-10})$$

$$\Delta G = -442498 \text{ J/mol}$$

$$\Delta G = -442 \text{ kJ/mol}$$

(\_\_\_\_\_/ 16 pts)

6.

6.6

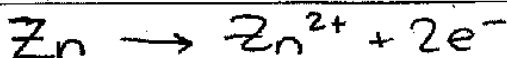
A voltaic cell is constructed by connecting the following two beakers with a voltmeter and a salt bridge at 25°C:

**Left Beaker:** A silver electrode immersed in 1.00 L of 1.00 M AgNO<sub>3</sub> solution.

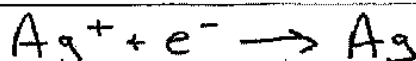
**Right Beaker:** A zinc electrode immersed in 1.00 L of 1.00 M Zn(NO<sub>3</sub>)<sub>2</sub> solution.

- a) Write the anode and cathode half-reactions and the overall balanced equation, and determine the standard potential ( $E^\circ$ ) for this cell at 25°C. (2 pts per box)

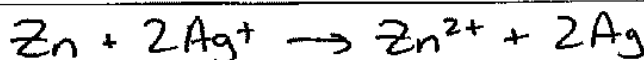
anode:



cathode:



overall:



$$0.800\text{ V} + 0.763\text{ V} = 1.563\text{ V}$$

$$E^\circ = 1.563\text{ V}$$

- b) 1.00 L of 2.00-molar NaCl is added to the left beaker causing AgCl (s) to precipitate. Calculate the new (nonstandard) potential for this cell at 25°C. (Note: The total volume of solution in the left beaker is now 2.00 liters!) (6 pts)

IN LEFT BEAKER: INITIALLY  $[\text{Cl}^-] = 1.0\text{ M}$   $[\text{Ag}^+] = 0.5\text{ M}$   
 0.5 M AgCl (s) ppt (ACTUALLY 1.0 MOLES PPT)  
 LEAVES AgCl (s) w/  $[\text{Cl}^-] = 0.5\text{ M}$   $[\text{Ag}^+] = 0\text{ M}$

SMALL AMOUNT REDISSOLVES:

$$[\text{Ag}^+][\text{Cl}^-] = K_{sp} = 1.8 \times 10^{-10}$$

$$[\text{Ag}^+](0.5) = 1.8 \times 10^{-10}$$

$$[\text{Ag}^+] = 3.6 \times 10^{-10}$$

$$Q = \frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2} = \frac{(1)}{(3.6 \times 10^{-10})^2} = 7.716 \times 10^{18}$$

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

$$= 1.563\text{ V} - \frac{0.0592}{2} \log 7.716 \times 10^{18}$$

$$E = 1.004\text{ V}$$

$$E = 1.004\text{ V}$$

- c) The AgCl precipitate formed in part (b) is then re-dissolved by the addition of sodium thiosulfate, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, due to the formation of the complex ion Ag(S<sub>2</sub>O<sub>3</sub>)<sub>2</sub><sup>3-</sup>. Would you expect that the voltage would return towards the original standard potential calculated in part (a)? Please explain your answer. (No calculations are necessary.) (4 pts)

NO,  $E$  WILL DECREASE MORE.

AS AgCl DISSOLVES,  $[\text{Cl}^-]$  INCREASES

SO  $[\text{Ag}^+]$  MUST DECREASE FURTHER.

(\_\_\_\_\_/ 18 pts)

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

## Explanations:

- 4(a): i)  $\Delta H^\circ > 0$ : The evaporation of water is an endothermic process (i.e. you must put heat in to convert liquid to gas) so  $\Delta H^\circ$  for this reaction is greater than zero.

$\Delta S^\circ > 0$ : A liquid is being converted to a gas, so entropy is increasing, and  $\Delta S^\circ$  is greater than zero.

$\Delta G^\circ > 0$ : This is a phase change reaction. We know that for a phase change reaction at the normal phase change temperature,  $\Delta G^\circ = 0$ . For this reaction, liquid water converted to gaseous water, the normal phase change temperature is the boiling point of water, which is  $100^\circ\text{C}$ . Thus, at  $100^\circ\text{C}$ ,  $\Delta G^\circ = 0$  for this reaction. At a temperature below  $100^\circ\text{C}$ ,  $\Delta G^\circ$  will be greater than 0 (not spontaneous at standard states), and at a temperature above  $100^\circ\text{C}$ ,  $\Delta G^\circ$  will be less than 0 (spontaneous at standard states). Thus, at  $25^\circ\text{C}$ ,  $\Delta G^\circ$  for this reaction is greater than zero.

- ii)  $\Delta H^\circ < 0$ : This is a combustion reaction, so it must be exothermic, and so  $\Delta H^\circ$  is less than 0.

$\Delta S^\circ < 0$ : The reactants include a solid and 5 moles of a gas, and the products contain no gas, just 2 moles of a solid. Because a gas is being converted to a solid, the entropy is decreasing, and  $\Delta S^\circ$  is less than 0.

$\Delta G^\circ < 0$ : By the description given, this reaction is spontaneous in air at  $25^\circ\text{C}$ , and the total pressure of air is 1 atm, so the pressure of oxygen gas must be less than 1 atm. (Because there are other gases in air, like nitrogen and carbon dioxide, etc...) But if this reaction is spontaneous under the conditions described, with a  $P(\text{O}_2)$  less than 1 atm, then an increase in the pressure of the **reactant** to 1 atm (standard conditions) will only make this reaction "*more spontaneous*", so the reaction must still be spontaneous at standard conditions, so  $\Delta G^\circ$  must be less than zero.

- 6(c): See from the calculations in part (b) and the Nernst equation that if the  $[\text{Ag}^+]$  decreases, the voltage will decrease, but if the  $[\text{Ag}^+]$  increases, then the voltage will increase. Adding the thiosulfate ion to the solution with the solid AgCl will cause the AgCl to re-dissolve because of the formation of the complex ion  $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$ . Although the AgCl is redissolving, the  $\text{Ag}^+$  ions are not ending up free in the solution, they are bound up in the complex ion. However, the  $\text{Cl}^-$  ions are ending up free in the solution as the AgCl dissolves. According to the  $K_{\text{sp}}$ :

$$K_{\text{sp}}(\text{AgCl}(s)) = 1.8 \times 10^{-10} = [\text{Ag}^+][\text{Cl}^-]$$

If the concentration of  $\text{Cl}^-$  ions increases as the  $\text{AgCl}(s)$  dissolves, then the concentration of  $\text{Ag}^+$  ions must decrease, and so the voltage must decrease further.



# Useful Information

$$\text{Avogadro's Number} = 6.02 \times 10^{23}$$

$$R = 0.0821 \text{ L}\cdot\text{atm/mol}\cdot\text{K} = 8.31 \text{ J/mol}\cdot\text{K}$$

$$1 \text{ Joule (J)} = 1 \frac{\text{kg}\cdot\text{m}^2}{\text{s}^2}$$

$$\text{Speed of light} = 3.00 \times 10^8 \text{ m/s}$$

$$\text{Mass of electron} = 9.11 \times 10^{-28} \text{ g}$$

$$1 \text{ \AA} = 10^{-10} \text{ m}$$

$$1 \text{ atm} = 760 \text{ torr} = 760 \text{ mmHg}$$

$$1 \text{ mL} = 1 \text{ cm}^3$$

## *Selected Aqueous Equilibrium Constants at 25°C*

$$K_w = 1.0 \times 10^{-14}$$

$$K_a(\text{HCN}) = 4.9 \times 10^{-10}$$

$$K_a(\text{HF}) = 6.6 \times 10^{-4}$$

$$K_{sp}(\text{Cd}(\text{OH})_2) = 2.5 \times 10^{-14}$$

$$K_{sp}(\text{AgCl}) = 1.8 \times 10^{-10}$$

$$K_f(\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}) = 2.9 \times 10^{13}$$

$$K_f(\text{Au}(\text{CN})_2^-) = 6.2 \times 10^{38}$$

## *Selected Standard Thermodynamic Values at 25°C*

| <i>Substance</i>      | $\Delta H_f^\circ$ (kJ/mol) | $S^\circ$ (J/mol·K) |
|-----------------------|-----------------------------|---------------------|
| KCl (s)               | -435.9                      | 82.7                |
| KClO <sub>3</sub> (s) | -391.2                      | 143.0               |

| <i>Standard Reduction Potentials at 25°C</i>   | $E^\circ$ |
|--|-----------|
| $2 \text{ H}^+ (\text{aq}) + 2 \text{ e}^- \rightarrow \text{H}_2 (\text{g})$                                    | 0.000 V   |
| $\text{O}_2 (\text{g}) + 4 \text{ H}^+ (\text{aq}) + 4 \text{ e}^- \rightarrow 2 \text{ H}_2\text{O} (\text{l})$ | 1.229 V   |
| $\text{Au}^{3+} (\text{aq}) + 3 \text{ e}^- \rightarrow \text{Au} (\text{s})$                                    | 1.498 V   |
| $\text{Au}^{3+} (\text{aq}) + 2 \text{ e}^- \rightarrow \text{Au}^+ (\text{aq})$                                 | 1.401 V   |
| $\text{Ag}^+ (\text{aq}) + \text{e}^- \rightarrow \text{Ag} (\text{s})$  | 0.800 V   |
| $\text{Zn}^{2+} (\text{aq}) + 2 \text{ e}^- \rightarrow \text{Zn} (\text{s})$                                    | -0.763 V  |