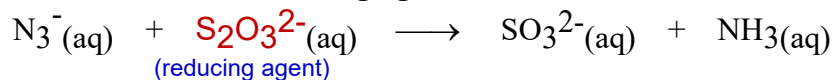


1. (10 points) Use the ion-electron method to balance the following redox reaction that occurs in *basic* solution. Write **complete, balanced equations** for the individual half-reactions and for the overall net ionic equation. Also, **circle the reducing agent** in this reaction.



**Reduction Half Reaction:**



**Oxidation Half Reaction:**



**Net Ionic Equation:**



2. (3 points) A compound sometimes called "calcium cerium selenate" has the formula  $\text{CaCe}(\text{SeO}_4)_3$ . Give the oxidation states of all four elements in this compound.



3. (10 points) **SHOW ALL WORK.** A 100.0 mL sample of a solution of  $\text{Sn}^{2+}$  required 42.15 mL of 0.1100 M  $\text{KMnO}_4$  to reach the equivalence point in a titration. Assuming that the main products of the redox reaction are  $\text{Sn}^{4+}$  and  $\text{Mn}^{2+}$ , determine the molarity of the  $\text{Sn}^{2+}$  solution. (**Note:** Your answer must include the **balanced, net-ionic equation** for the titration reaction, in acidic solution.)



$$(0.04215 \text{ L}) (0.110 \text{ mole MnO}_4^- / \text{L}) (5 \text{ mole Sn}^{2+} / 2 \text{ mole MnO}_4^-)$$

$$= 0.01159 \text{ mole Sn}^{2+}$$

$$(0.01159 \text{ mole Sn}^{2+}) / (0.100 \text{ L}) = 0.116 \text{ M Sn}^{2+}$$

4. (6 points) Write **balanced ionic equations** for the half-reactions.

(a) The **cathode** reaction in the electrolysis of *aqueous*  $\text{KNO}_3$ .



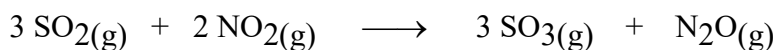
(b) The **anode** reaction in the electrolysis of *molten*  $\text{Al}_2\text{O}_3$ .



(c) The **anode** reaction in the electrolysis of *aqueous*  $\text{Na}_2\text{SO}_4$ .



5. Consider the following reaction and the related thermodynamic data below.



Compound	Standard Heat of Formation ( $\Delta H^\circ_f$ ) in kJ/mole	Standard Entropy ( $S^\circ$ ) in J/mole·K
$\text{NO}_2(\text{g})$	33	240
$\text{N}_2\text{O}(\text{g})$	82	221
$\text{SO}_2(\text{g})$	- 297	248
$\text{SO}_3(\text{g})$	- 396	257

(a) (10 points) **SHOW ALL WORK.** Is the above reaction spontaneous at 25 °C? Determine the appropriate thermodynamic quantity that is required in order to answer this question.

$$\Delta H^\circ = 3(- 396) + 82 - [ 3(- 297) + 2(33) ] = - 281 \text{ kJ}$$

$$\Delta S^\circ = 3(257) + 221 - [ 3(248) + 2(240) ] = - 232 \text{ J/K} = - 0.232 \text{ kJ/K}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = - 281 \text{ kJ} - (298 \text{ K})(- 0.232 \text{ kJ/K}) = - 212 \text{ kJ}$$

Negative  $\Delta G^\circ$  indicates that the reaction is spontaneous at 25 °C.

(b) (10 points) **SHOW ALL WORK.** Determine the **equilibrium constant** ( $K_p$ ) for the above reaction at 600 °C. ( $600 + 273 = 873 \text{ K}$ )

Since  $\Delta H^\circ$  and  $\Delta S^\circ$  are relatively independent of temp, their values at 298 K can be used to estimate  $\Delta G^\circ$  (and K) at another temp. At 873 K:

$$\Delta G = (- 281 \text{ kJ}) - (873 \text{ K})(- 0.232 \text{ kJ/K}) = - 78.5 \text{ kJ}$$

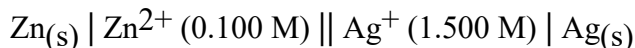
$$\Delta G = - RT \ln K$$

$$\ln K = - \Delta G / RT = - (- 78.5 \text{ kJ / mole}) / (8.314 \times 10^{-3} \text{ kJ/mole}\cdot\text{K})(873 \text{ K})$$

$$\ln K = 10.81$$

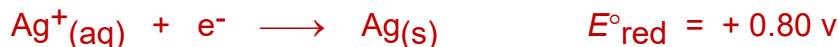
$$K = 4.95 \times 10^4$$

6. A Zn/Ag **battery** is constructed based on the following electrochemical cell in which the volume of solution in each half-cell is 0.500 L.



- (a) (6 points) Write **balanced chemical equations** for the half-reactions and the overall **cell reaction** occurring in this device. Also, determine the **standard cell potential** ( $E^\circ_{\text{cell}}$ ).

**cathode reaction:**



**anode reaction:**



**cell reaction:**



$$E^\circ_{\text{cell}} = 0.80 + 0.76 = 1.56 \text{ v}$$

- (b) (10 points) **SHOW ALL WORK.** This battery is pronounced "dead" when 98 % of its chemical capacity is used up (i.e., when the concentration of the major reactant has dropped to 2.00 % of its initial value). Calculate the cell potential (in volts) of the battery at this point.

$$\text{Initially, moles Ag}^+ = (0.500 \text{ L}) (1.50 \text{ mole/L}) = 0.750 \text{ moles}$$

$$\text{moles Zn}^{2+} = (0.500 \text{ L}) (0.100 \text{ mole/L}) = 0.0500 \text{ moles}$$

$$\text{moles Ag}^+ \text{ remaining} = 2.00 \% \text{ of } 0.750 = (0.020) (0.750) = 0.015 \text{ moles}$$

$$[\text{Ag}^+] = 0.015 \text{ mole} / 0.500 \text{ L} = 0.0300 \text{ M}$$

$$\text{moles Ag}^+ \text{ consumed} = 0.750 \text{ moles} - 0.015 \text{ moles} = 0.735 \text{ moles}$$

$$\begin{aligned} \text{moles Zn}^{2+} \text{ formed} &= (0.735 \text{ mole Ag}^+) (1 \text{ mole Zn}^{2+} / 2 \text{ mole Ag}^+) \\ &= 0.3675 \text{ moles} \end{aligned}$$

$$\text{moles Zn}^{2+} \text{ remaining} = 0.0500 + 0.3675 = 0.4175 \text{ moles}$$

$$[\text{Zn}^{2+}] = 0.4175 \text{ mole} / 0.500 \text{ L} = 0.835 \text{ M}$$

$$Q = [\text{Zn}^{2+}] / [\text{Ag}^+]^2 = 0.835 / (0.0300)^2 = 927.8$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - (0.0592/n) \log Q = 1.56 - (0.0592 / 2) \log(927.8)$$

$$E_{\text{cell}} = 1.56 - 0.088 = 1.47 \text{ v}$$

- (c) (8 points) **SHOW ALL WORK.** Determine the current (in amps) that this battery could produce if it is operated continuously for 24 hours until it dies (based on the same 98 % definition of "dead"). (**Note:** The cell potentials from parts a and/or b above are not required here!)

$$\text{moles Ag}^+ \text{ consumed} = 0.735 \text{ moles}$$

$$(0.735 \text{ mole Ag}^+) (1 \text{ mole e}^- / 1 \text{ mole Ag}^+) = 0.735 \text{ mole e}^-$$

$$(0.735 \text{ mole e}^-) (96,500 \text{ coul} / \text{mole e}^-) (1 \text{ amp}\cdot\text{sec} / \text{coul}) = 7.093 \times 10^4 \text{ amp}\cdot\text{sec}$$

$$(7.093 \times 10^4 \text{ amp}\cdot\text{sec}) / (24 \text{ hr}) (3600 \text{ sec/hr}) = 0.82 \text{ amps}$$

7. (8 points) **SHOW ALL WORK.** A solution containing tungsten (W) ion in an unknown oxidation state was electrolyzed with a current of 1.25 amp for 6.00 hours. During this process, 12.86 g of metallic tungsten was deposited at the cathode. Determine the oxidation state of the tungsten ion in the original solution.



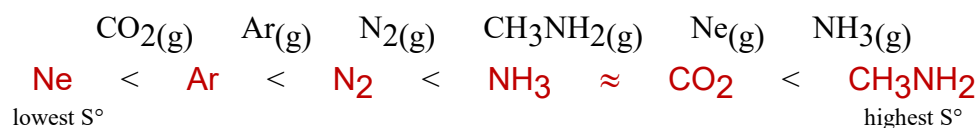
$$(1.25 \text{ amp}) (6 \text{ hr}) (3600 \text{ sec/hr}) = 27,000 \text{ amp}\cdot\text{sec} = 27,000 \text{ coul}$$

$$(27,000 \text{ coul}) (1 \text{ mole } e^{-} / 96,500 \text{ coul}) = 0.280 \text{ mole } e^{-}$$

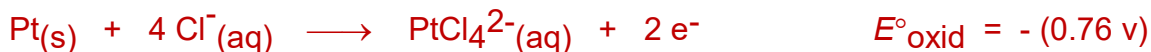
$$(12.86 \text{ g } W) (1 \text{ mole } W / 183.85 \text{ g}) = 0.0700 \text{ mole } W$$

$$n = 0.280 / 0.0700 = 4 \quad \therefore \text{oxidation state is } W^{4+}$$

8. (4 points) Arrange the following substances in order of increasing standard molar entropy ( $S^{\circ}$ ).



9. (8 points) **SHOW ALL WORK.** Use appropriate electrochemical data to determine the *formation constant* ( $K_f$ ) for  $\text{PtCl}_4^{2-}(\text{aq})$ . *Include balanced chemical equations for all relevant reactions.*



$$E^{\circ}_{\text{cell}} = 1.18 - 0.76 = 0.42 \text{ v}$$

$$\log K_f = n E^{\circ}_{\text{cell}} / 0.0592 = 2 (0.42) / 0.0592 = 14.19$$

$$K_f = 1.55 \times 10^{14}$$

10. (7 points) **SHOW ALL WORK.** Acetone (a common organic liquid) has a normal boiling point of 56.1 °C, a heat of vaporization of 31.3 kJ/mole, and a standard molar entropy [ $S^{\circ}(\text{liq})$ ] of 200.4 J/mole·K. Calculate the standard molar entropy [ $S^{\circ}(\text{g})$ ] of gaseous acetone (in J/mole·K).

$$\Delta G = \Delta H - T\Delta S = 0 \quad (\text{at equilibrium})$$

$$\Delta S = \Delta H / T = 31,300 \text{ J} / (56.1 + 273.15) \text{ K} = 95.1 \text{ J/K}$$

$$\Delta S = 95.1 \text{ J/K} = S^{\circ}(\text{g}) - S^{\circ}(\text{liq}) = S^{\circ}(\text{g}) - 200.4 \text{ J/mole}\cdot\text{K}$$

$$S^{\circ}(\text{g}) = 296 \text{ J/mole}\cdot\text{K}$$

