

1. Which of the following statements are true and which – false? For the false statements, provide a brief explanation why they are false. (12 points)

a. Based on the table on p. 13, Mg is the best oxidizing agent of all the substances listed there.

False - highest oxidation potential, s- less reducing agent.

b. It is possible to make an electrode from  $F_2(g)$ .

False - it does not conduct electricity.

c. The standard molar entropy  $S^\circ$  of  $CO_2(g)$  must be higher than  $S^\circ$  of  $CO(g)$ .

True.

d. Fusion (melting) is an enthalpy-driven (enthalpy-favored) process.

False - it is an entropy-driven process.

e. It is not possible for a process with  $\Delta S_{\text{surroundings}} < 0$  to occur spontaneously.

False - as long as  $\Delta S_{\text{universe}} > 0$ , it is possible.

f. During the electroplating of Cu metal on a Zn electrode, reduction of  $Zn^{2+}$  happens at the cathode.

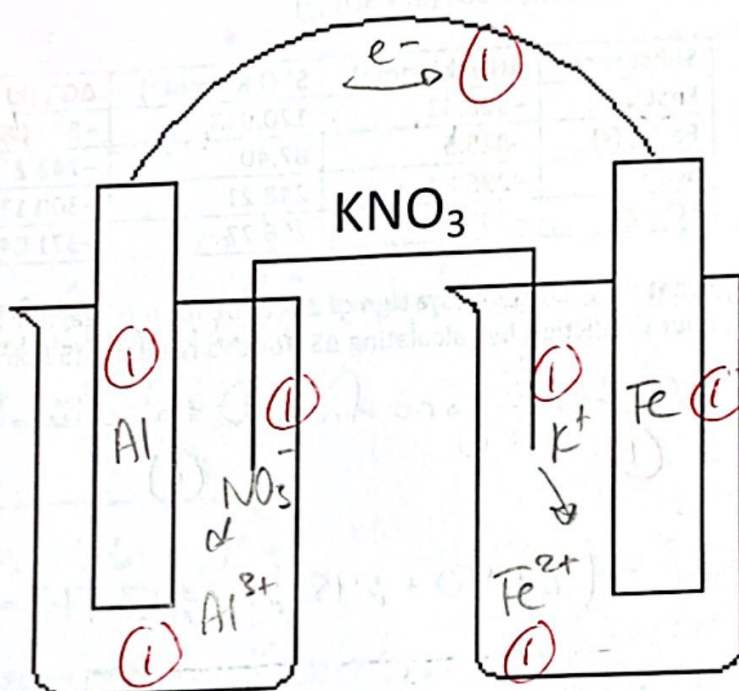
False - reduction of  $Cu^{2+}$  to Cu happens at the cathode.

g. All substances have  $S = 0$  at 0 K.

True \*

\* I gave credit to responses saying "False, this only holds for perfect crystals". This was not meant to be a trick question :)

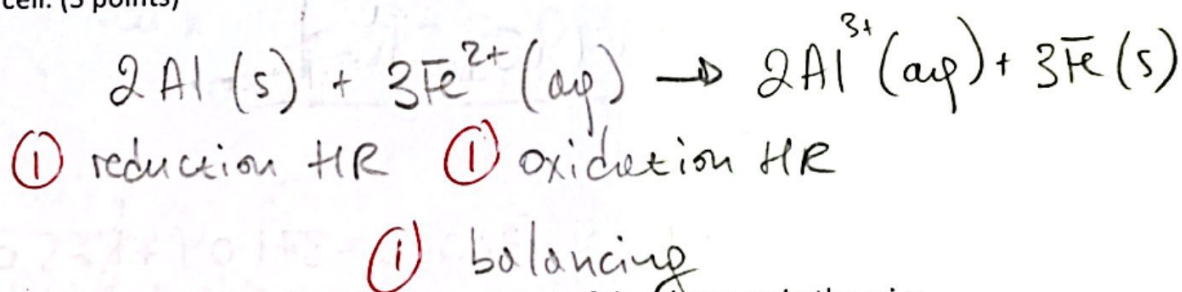
2. Consider the following unlabeled voltaic cell. One of the half-cells is  $\text{Al (s)} | \text{Al}^{3+} (\text{aq}, 1.0 \text{ M})$ ; the other half-cell is  $\text{Fe (s)} | \text{Fe}^{2+} (\text{aq}, 1.0 \text{ M})$ .



Anode/cathode      anode (1)      cathode (1)

Oxidation/reduction      oxidation (1)      reduction (1)

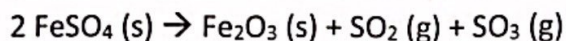
- a. Clearly label the electrodes and solutions with appropriate metal and ion symbols. Label the electrodes as the anode and the cathode. At which electrode does the oxidation reaction happen? The reduction reaction? (8 points)
- b. Write the balanced chemical equation for the reaction that occurs in this voltaic cell. (3 points)



- c. Clearly show the direction of the movement of the electrons in the wire (external circuit) and  $\text{K}^+$  and  $\text{NO}_3^-$  ions in the  $\text{KNO}_3$  salt bridge on the diagram. (3 points)



3. Consider the following reaction:



Substance	$\Delta H_f^\circ (\text{kJ mol}^{-1})$	$S^\circ (\text{J K}^{-1} \text{mol}^{-1})$	$\Delta G_f^\circ (\text{kJ mol}^{-1})$
$\text{FeSO}_4 (\text{s})$	-928.43	120.918	-825.08
$\text{Fe}_2\text{O}_3 (\text{s})$	-825.5	87.40	-742.2
$\text{SO}_2 (\text{g})$	-296.84	248.21	-300.13
$\text{SO}_3 (\text{g})$	-395.77	256.77	-371.04

- a. What do you expect the sign of  $\Delta S^\circ$  to be for this reaction? Briefly explain. Verify your prediction by calculating  $\Delta S^\circ$  for this reaction. (5 points)

$\Delta S^\circ > 0$  - goes from 0 to 2 moles gas.  
 (1) (1)

$$\Delta S^\circ = (87.40 + 248.21 + 256.77 - 2 \cdot 120.918) \text{ J K}^{-1} \text{ mol}^{-1}$$

$$= \boxed{350.54 \text{ J K}^{-1} \text{ mol}^{-1}}$$

- b. Calculate  $\Delta H^\circ$  and  $\Delta G^\circ$  for this reaction at 25 °C. (6 points)

$$\Delta H^\circ = (-825.5 - 296.84 - 395.77 + 2 \cdot 928.43) \text{ kJ mol}^{-1}$$

$$= \boxed{+338.7 \text{ kJ mol}^{-1}}$$

$$\Delta G^\circ = (-742.2 - 300.13 - 371.04 + 825.08 \cdot 2) \text{ kJ mol}^{-1}$$

$$= \boxed{+236.8 \text{ kJ mol}^{-1}}$$

- c. Is this reaction product-favored at relatively high or low temperatures? Briefly explain. (4 points)

①  $\Delta S > 0, \Delta H > 0$

①  $\Delta G = \Delta H - T\Delta S$

① For  $\Delta G$  to become negative,  $T\Delta S$  term must be maximized.

- d. Above/below which temperature does this reaction becomes product-favored? (3 points)

①  $\Delta H - T\Delta S = 0 \Rightarrow T = \frac{\Delta H}{\Delta S} = \frac{338.7 \text{ kJ mol}^{-1}}{0.35054 \text{ kJ K}^{-1} \text{ mol}^{-1}}$

①  $T = 966.4 \text{ K}$  (above 966.4 K it becomes product-favored)

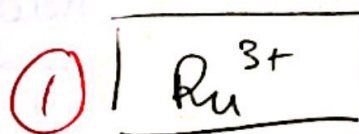
4. An aqueous solution of an unknown salt of ruthenium is electrolyzed by a current of 2.50 A passing for 50.0 min. If 2.618 g Ru is produced at the cathode, what is the charge on the ruthenium ions in solution? (1 A = 1 C/s) (8 points)

$50.0 \text{ min} \times \frac{60 \text{ s}}{1 \text{ min}} \times \frac{2.50 \text{ C}}{1 \text{ s}} \times \frac{1 \text{ mol } e^{-}}{96485 \text{ C}}$

$= 0.0777 \text{ mol } e^{-}$

$2.618 \text{ g Ru} \times \frac{1 \text{ mol}}{101.07 \text{ g}} = 0.0257 \text{ mol Ru}$

①  $\frac{0.0777 \text{ mol } e^{-}}{0.0257 \text{ mol Ru}} = 3 \text{ mol } e^{-} / \text{mol Ru}$

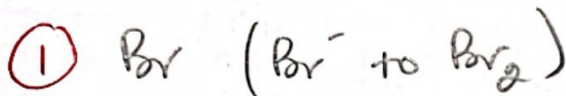




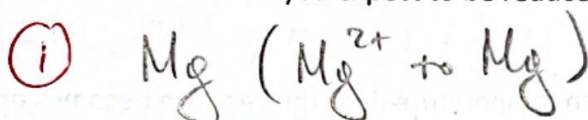
5.

a. Consider the electrolysis of *molten* (pure, liquid)  $\text{MgBr}_2$ .

i. Which element do you expect to be oxidized during this process? (1 point)



ii. Which element do you expect to be reduced during this process? (1 point)

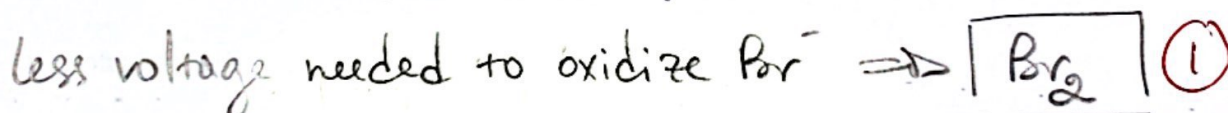
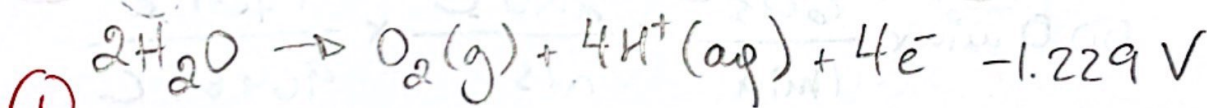
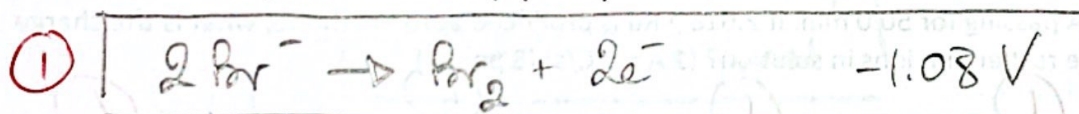


iii. What is the voltage that needs to be applied to make this electrolysis happen? (2 points)

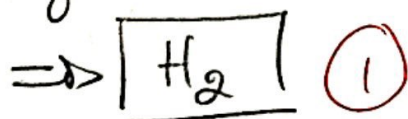
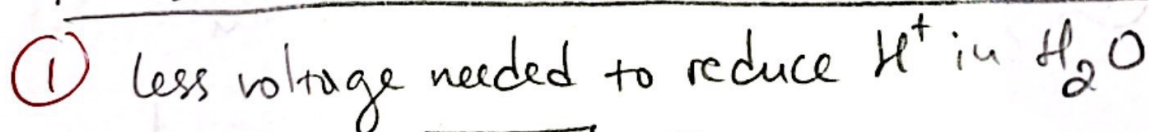
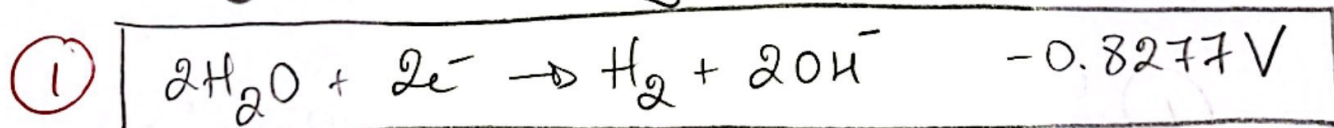
①  $2.37 \text{ V} + 1.08 \text{ V} = \boxed{3.45 \text{ V}}$

b. Now consider the electrolysis of *aqueous*  $\text{MgBr}_2$ .

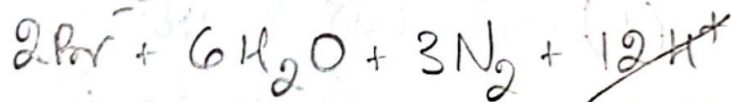
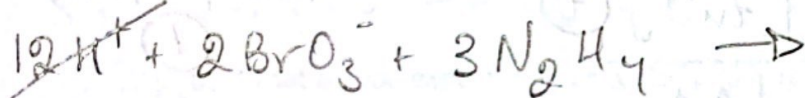
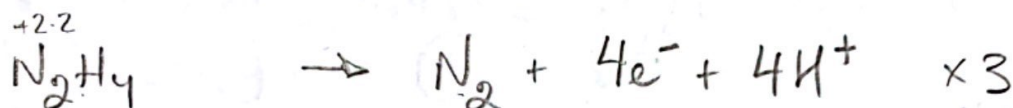
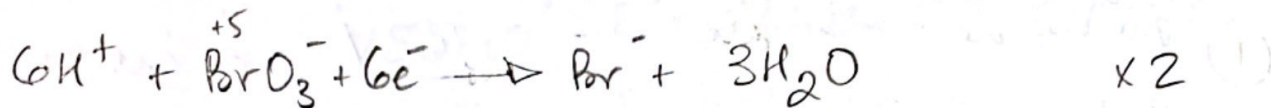
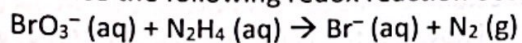
i. What reaction do you expect to occur at the anode and what is the product produced there? (3 points)



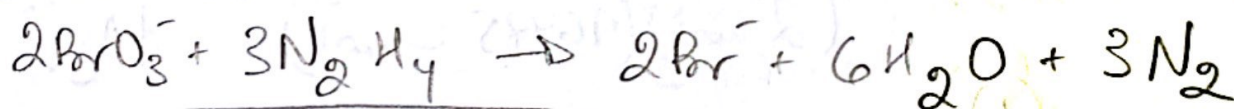
ii. What reaction do you expect to occur at the cathode and what is the product produced there? (3 points)



6. Balance the following redox reaction occurring in acidic solution. (8 points)

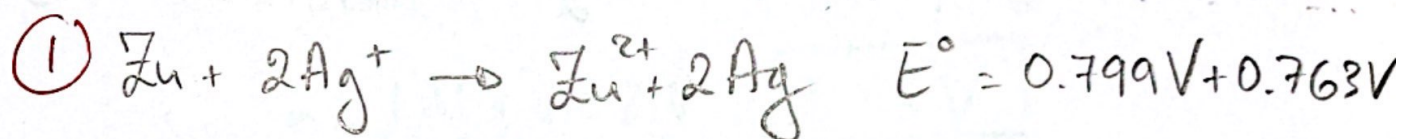
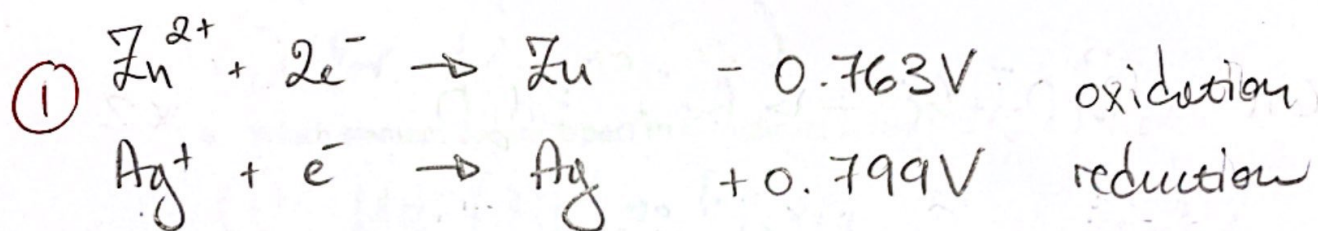


simplify





7. A voltaic cell is set up with silver and zinc half-cells at 25 °C. In the zinc half-cell,  $[Zn^{2+}] = 1.00 \text{ M}$ , while the  $Ag^+$  concentration is unknown. If the cell potential is 1.250 V, what must be  $[Ag^+]$ ? (10 points)



$$= 1.562V$$

$$\textcircled{1} \quad 2e^- \quad Q = \frac{[Zn^{2+}]}{[Ag^+]^2} \quad \textcircled{1}$$

$$\textcircled{1} \quad E = E^\circ - \frac{RT}{nF} \ln Q \Rightarrow$$

$$1.250V = 1.562V - \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298K)}{(2 \text{ mol})(96485 \text{ C mol}^{-1})} \ln \frac{(1.00M)}{[Ag^+]^2}$$

$$\ln \frac{1.00M}{[Ag^+]^2} = 24.3 \Rightarrow \frac{1.00}{[Ag^+]^2} = 3.58 \times 10^{10} \quad \textcircled{1}$$

$$\Rightarrow [Ag^+]^2 = 2.8 \times 10^{-11} \Rightarrow [Ag^+] = 5.3 \times 10^{-6} \text{ M}$$

$\textcircled{1}$

8. Consider the reaction  $\text{Cl}_2(\text{g}) + 2\text{I}^-(\text{aq}) \rightleftharpoons 2\text{Cl}^-(\text{aq}) + \text{I}_2(\text{s})$ .

a. Calculate  $\Delta G^\circ$  and  $K$  for this reaction at 25 °C. Is this reaction product-favored as written? (7 points)

$$\textcircled{1} \Delta G^\circ = -nFE^\circ \quad \textcircled{1} E^\circ = 1.36\text{ V} - 0.535\text{ V} = 0.825\text{ V}$$

$$n = 2e^- \quad \textcircled{1}$$

$$\Delta G^\circ = -(2\text{ mol})(96485\text{ C mol}^{-1})(0.825\text{ J C}^{-1})$$

$$= -160\text{ kJ} \quad \textcircled{1}$$

$$\Delta G^\circ = -RT \ln K \Rightarrow \textcircled{1} (8.314\text{ J K}^{-1}\text{ mol}^{-1})(298\text{ K}) \ln K =$$

$$-160000\text{ J} \Rightarrow \ln K = 64 \Rightarrow \boxed{K = 8.1 \times 10^{27}} \quad \textcircled{1}$$

b. What do you expect the sign of  $\Delta S^\circ$  of this reaction to be? Briefly explain. (2 points)

$$\textcircled{1} \Delta S < 0$$

$\textcircled{1}$  loss of gas, formation of solid

c. Will the standard cell potential of a voltaic cell described by this reaction ( $E^\circ_{\text{cell}}$ ) increase or decrease when the temperature is raised above 25 °C? Briefly explain. (4 points)

$$\text{At } 25^\circ\text{C}, \Delta G^\circ < 0, \Delta S < 0$$

$$\Delta H \text{ must be } < 0 \quad \textcircled{1}$$

for the process to be product-favored.

$$\Delta G = \Delta H - T\Delta S, \text{ as } T \uparrow, T\Delta S \uparrow \quad \textcircled{1}$$

and  $\Delta G$  becomes less negative

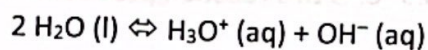
$$\text{Since } \Delta G = -nFE^\circ, \boxed{E^\circ \text{ will decrease.}} \quad \textcircled{1}$$

$\textcircled{1}$

$\textcircled{1}$



9. In previous chapters you learned about autoionization of water and  $K_w$ .



a. Calculate  $\Delta G^\circ$  for this process at 25 °C in  $\text{kJ mol}^{-1}$ . (3 points)

$$\Delta G^\circ = -RT \ln K = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K}) \ln(1.0 \times 10^{-14}) = \boxed{+79.9 \text{ kJ mol}^{-1}}$$

b. Calculate  $\Delta G$  for this process at 25 °C when  $[\text{H}_3\text{O}^+] = 1.0 \times 10^{-12} \text{ M}$  and  $[\text{OH}^-] = 1.0 \times 10^{-8} \text{ M}$ . Is autoionization of water spontaneous under these conditions? (4 points)

$$\Delta G = \Delta G^\circ + RT \ln Q \quad (1)$$

$$Q = [\text{H}_3\text{O}^+][\text{OH}^-] \quad (1)$$

$$\Delta G = (79900 \text{ J mol}^{-1}) + (8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K}) \ln(1.0 \times 10^{-12} \cdot 1.0 \times 10^{-8})$$
$$= -34.2 \text{ kJ mol}^{-1} \quad (1)$$

(1) Spontaneous