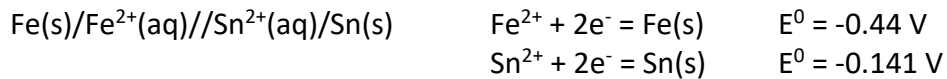


## Chem 454 - Electrochemistry Homework

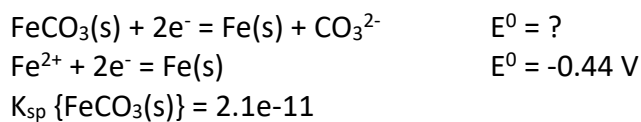
1] If  $A + e^- = B$  has  $E^0 = 0.775 \text{ V}$  then the  $E^0$  for  $2A + 2e^- = 2B$  is \_\_\_\_\_ .<sup>1</sup>

2] The standard cell potential for the following is \_\_\_\_\_<sup>2</sup>



- a) -0.030
- b) -0.581
- c) 0.581
- d) 0.44
- e) 0.30

3] The  $E^0$  for the following is \_\_\_\_\_<sup>3</sup>



- a) 0.756 V
- b) -0.124 V
- c) 0.124 V
- d) -1.07
- e) -0.756

4] An electrochemical cell will discharge spontaneously if \_\_\_\_\_<sup>4</sup>

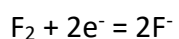
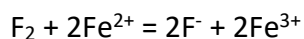
- a)  $E_{\text{cell}} < 0$     b)  $E_{\text{cell}} > 0$     c)  $E_{\text{cell}} = 0$     d) does not depend on  $E_{\text{cell}}$

5] The reductions take place at which electrode? \_\_\_\_\_<sup>5</sup>

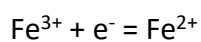
- a) anode    b) toade    c) cathode    d) alkaline    e) amphotropic

6] The purpose of a reference electrode is to provide \_\_\_\_\_ (5 points) \_\_\_\_\_<sup>6</sup>

7] What is  $E^0_{\text{cell}}$  for the reaction below? 7



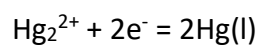
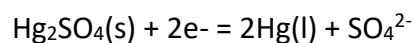
$$E^0_{\text{red}} = 2.890 \text{ V}$$



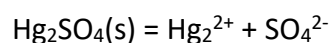
$$E^0_{\text{red}} = 0.771 \text{ V}$$

- a) -2.119 V      b) -1.348 V      c) 1.348 V      d) 0.655 V      e) 2.119 V

8] What is  $E^0_{\text{cell}}$  for the reaction below? 8



$$E^0_{\text{red}} = 0.796 \text{ V}$$



$$K_{\text{sp}} = 7.4\text{e-}7$$

9] What is  $E^0_{\text{cell}}$  for the following reaction?  $2\text{Na}(\text{s}) + 2\text{H}^+ = 2\text{Na}^+ + \text{H}_2(\text{g})$  9



- a) 5.4286 V  
b) -5.4286 V  
c) -2.7143 V  
d) 2.7143 V  
e) 1.3572 V

10] What is the half reaction potential for reduction of  $1.00\text{e-}5 \text{ M H}^+$ ? 10

- a) 0.0000 V  
b) 0.296 V  
c) -0.296 V  
d) 0.148 V  
e) -0.148 V

11] Which of the following species is the strongest reducing agent?

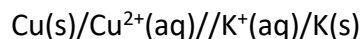
11



- a)  $A^+$
- b)  $B^-$
- c)  $B$
- d)  $D^{2+}$
- e)  $D^+$

12] Calculate the standard state cell potential for the following

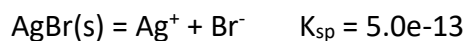
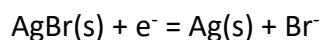
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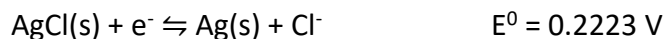
- a) -3.275 V
- b) 3.275 V
- c) 2.587 V
- d) -2.597 V
- e) 1.881 V

13] What is the standard state reduction potential for the following reaction?

13



14] A Ag/AgCl electrode is in contact with a solution that is 0.150 M in KCl(aq). What is the potential of that electrode if measured against the SHE? <sup>14</sup>



15] Based on the  $E^0$  potentials in the following table ( $E^0$  at pH 7), which is the strongest reducing agent? Which is the strongest oxidizing agent?

Strongest reducing agent \_\_\_\_\_

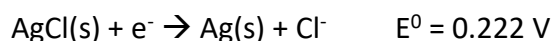
Strongest oxidizing agent \_\_\_\_\_

What would be the spontaneous balanced redox reaction between the strongest reducing agent and the strongest oxidizing agent? (5 points) What would be  $E_{\text{cell}}$  for this reaction? (5 points) <sup>15</sup>

**Table 14-2** Reduction potentials of biological interest

Reaction	$E^0$ (V)	$E^{0'}$ (V)
$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}$	+1.229	+0.816
$\text{Fe}^{3+} + \text{e}^- \rightleftharpoons \text{Fe}^{2+}$	+0.771	+0.771
$\text{I}_2 + 2\text{e}^- \rightleftharpoons 2\text{I}^-$	+0.535	+0.535
Cytochrome <i>a</i> ( $\text{Fe}^{3+}$ ) + $\text{e}^- \rightleftharpoons$ cytochrome <i>a</i> ( $\text{Fe}^{2+}$ )	+0.290	+0.290
$\text{O}_2(\text{g}) + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2\text{O}_2$	+0.695	+0.281
Cytochrome <i>c</i> ( $\text{Fe}^{3+}$ ) + $\text{e}^- \rightleftharpoons$ cytochrome <i>c</i> ( $\text{Fe}^{2+}$ )	—	+0.254
2,6-Dichlorophenolindophenol + $2\text{H}^+ + 2\text{e}^- \rightleftharpoons$ reduced 2,6-dichlorophenolindophenol	—	+0.22
Dehydroascorbate + $2\text{H}^+ + 2\text{e}^- \rightleftharpoons$ ascorbate + $\text{H}_2\text{O}$	+0.390	+0.058
Fumarate + $2\text{H}^+ + 2\text{e}^- \rightleftharpoons$ succinate	+0.433	+0.031
Methylene blue + $2\text{H}^+ + 2\text{e}^- \rightleftharpoons$ reduced product	+0.532	+0.011
Glyoxylate + $2\text{H}^+ + 2\text{e}^- \rightleftharpoons$ glycolate	—	-0.090
Oxaloacetate + $2\text{H}^+ + 2\text{e}^- \rightleftharpoons$ malate	+0.330	-0.102
Pyruvate + $2\text{H}^+ + 2\text{e}^- \rightleftharpoons$ lactate	+0.224	-0.190
Riboflavin + $2\text{H}^+ + 2\text{e}^- \rightleftharpoons$ reduced riboflavin	—	-0.208
$\text{FAD} + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{FADH}_2$	—	-0.219
(Glutathione-S) <sub>2</sub> + $2\text{H}^+ + 2\text{e}^- \rightleftharpoons 2$ glutathione-SH	—	-0.23
Safranin T + $2\text{e}^- \rightleftharpoons$ leucosafranin T	-0.235	-0.289
$(\text{C}_6\text{H}_5\text{S})_2 + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons 2\text{C}_6\text{H}_5\text{SH}$	—	-0.30
$\text{NAD}^+ + \text{H}^+ + 2\text{e}^- \rightleftharpoons \text{NADH}$	-0.105	-0.320
$\text{NADP}^+ + \text{H}^+ + 2\text{e}^- \rightleftharpoons \text{NADPH}$	—	-0.324
Cystine + $2\text{H}^+ + 2\text{e}^- \rightleftharpoons 2$ cysteine	—	-0.340
Acetoacetate + $2\text{H}^+ + 2\text{e}^- \rightleftharpoons$ L- $\beta$ -hydroxybutyrate	—	-0.346
Xanthine + $2\text{H}^+ + 2\text{e}^- \rightleftharpoons$ hypoxanthine + $\text{H}_2\text{O}$	—	-0.371
$2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2$	0.000	-0.414
Gluconate + $2\text{H}^+ + 2\text{e}^- \rightleftharpoons$ glucose + $\text{H}_2\text{O}$	—	-0.44
$\text{SO}_4^{2-} + 2\text{e}^- + 2\text{H}^+ \rightleftharpoons \text{SO}_3^{2-} + \text{H}_2\text{O}$	—	-0.454
$2\text{SO}_3^{2-} + 2\text{e}^- + 4\text{H}^+ \rightleftharpoons \text{S}_2\text{O}_4^{2-} + 2\text{H}_2\text{O}$	—	-0.527

16] (10 points) The potential of the Ag/AgCl reference electrode is 0.197 volts. Given the standard reduction potential:<sup>16</sup>



Calculate the concentration of KCl in this electrode.

17] What is  $E^0_{\text{cell}}$  for  $2\text{I}^- + 2\text{H}^+ \rightarrow \text{H}_2 + \text{I}_2$ , is this a spontaneous reaction? <sup>17</sup>

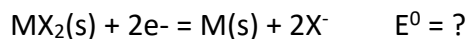
18] From the data in the Table calculate the  $K_{\text{sp}}$  of  $\text{PbSO}_4$ . <sup>18</sup>

Half Reaction	$E^0$
$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$	+1.23
$\text{Fe}(\text{CN})_6^{3-} + \text{e}^- \rightarrow \text{Fe}(\text{CN})_6^{4-}$	+0.36
$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	0.00
$\text{Pb}^{2+} + 2\text{e}^- \rightarrow \text{Pb}$	-0.126
$\text{PbSO}_4 + 2\text{e}^- \rightarrow \text{Pb} + \text{SO}_4^{2-}$	-0.355
$\text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe}$	-0.41

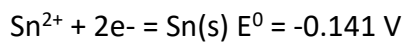
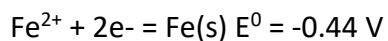
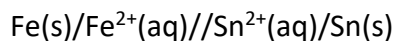
19] A silver electrode responds with a potential of 0.729 V when 25.00 mL of 0.0400 M KBr solution is mixed with 20.00 mL of 0.200 M  $\text{AgNO}_3(\text{aq})$ . What is the standard reduction potential of  $\text{Ag}^+$ ? What is the half reaction for that  $E^0$ ? <sup>19</sup>

$$\text{AgBr } K_{\text{sp}} = 5.0\text{e-}13$$

20] What is  $E^0$  for the half reaction given the following? <sup>20</sup>



21] The standard cell potential for the following is <sup>21</sup>

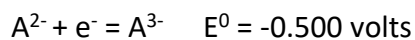
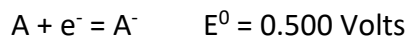


22] What is the  $K_{sp}$  of AgCl given the following? <sup>22</sup>

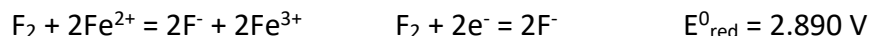


Note that  $2.303RT/nF = 0.0592 \text{ V}$ .

23] Which of the following species is the strongest oxidizing agent? <sup>23</sup>



24] What is  $E^0_{\text{cell}}$  for the reaction below? <sup>24</sup>



25] Calculate  $E_{\text{cell}}$  for  $\text{Cd(s)}/[\text{CdCl}_2](\text{aq}) = 1.0 \text{ M} // [\text{AgNO}_3](\text{aq}) = 1.0 \text{ M}/\text{Ag(s)}$  <sup>25</sup>

## Answers

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<sup>1</sup> 0.775 V

<sup>2</sup>  $E = -0.141 - (-0.44) = 0.30 \text{ V}$

<sup>3</sup>  $E = -0.44 - (0.0592/2) \log 1/K_{sp} = -0.756 \text{ V}$

<sup>4</sup> b)  $E_{\text{cell}} > 0$

<sup>5</sup> cathode

<sup>6</sup> to provide a stable potential chemical reference in which the cathode reaction can be compared.

<sup>7</sup>  $E_{\text{cell}} = E_{\text{cath}} - E_{\text{anod}} = 2.890 - 0.771 = \mathbf{2.119 \text{ V}}$

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$$^8 E = 0.796 - 0.0592/2 \log 1/[\text{Hg}_2^{2+}]$$

$$K_{sp} = 7.4e-7 = [\text{Hg}_2^{2+}][\text{SO}_4^{2-}]$$

$$[\text{Hg}_2^{2+}] = 7.4e-7/[\text{SO}_4^{2-}]$$

$$E = 0.796 - 0.0592/2 \log [\text{SO}_4^{2-}]/7.4e-7 = \mathbf{0.615 V}$$

$$^9 d: E^0_{\text{cell}} = 0.0000 - (-2.7143) V$$

$$^{10} c: E = E^0 - 0.0592 \log 1/[\text{H}^+] = 0.0000 - 0.0592 \log 1/[1.00e-5] = -0.296 V$$

$^{11} e$

$$^{12} a: E_{\text{cell}} = E_{\text{cath}} - E_{\text{anod}} = -2.936 - 0.339 = -3.275 V$$

$$^{13} \text{ Start with: } E = E^0(\text{Ag}^+/\text{Ag}) - 0.0592 \log 1/[\text{Ag}^+]$$

Realize that  $K_{sp} = [\text{Ag}^+][\text{Br}^-]$   $[\text{Ag}^+] = K_{sp} / [\text{Br}^-]$  sub into Nernst Eqn above

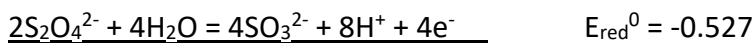
$$E = E^0(\text{Ag}^+/\text{Ag}) - 0.0592 \log [\text{Br}^-]/K_{sp} \text{ let } [\text{Br}^-] = 1 \text{ for standard state conditions}$$

$$E^0 = 0.799 - 0.0592 \log 1/5.00e-13 = 0.0708 V$$

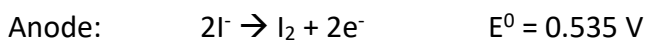
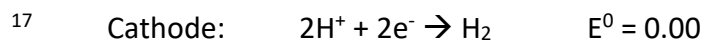
$$^{14} E = 0.2223 - 0.0592 \log 0.150 = 0.271 V$$

$^{15}$  Strongest reducing agent            $\text{S}_2\text{O}_4^{2-}$           

Strongest oxidizing agent            $\text{O}_2$           

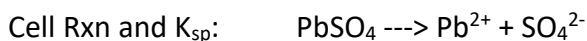
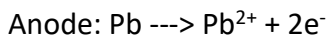
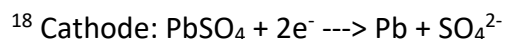


$$^{16} E = 0.222 - 0.0592 \log [\text{Cl}^-] = 0.197 [\text{Cl}^-] = 2.64 M$$



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$$E^0_{\text{cell}} = E^0_{\text{cat}} - E^0_{\text{anod}} = 0.00 - 0.535 = -0.535 \text{ V, this is an uphill reaction.}$$



$$E^0 = -0.355 + 0.126 = -0.229 \text{ V}$$

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

$$E^0 = 0.0592/n \log K$$

$$-0.229 = 0.0592/2 \log K_{\text{sp}} \quad K_{\text{sp}} = 1.8\text{e-}8$$

$$^{19} \text{ mmol Br}^- \text{ added} = 25.0 \text{ mL (0.0400 M)} = 1.00$$

$$\text{mmol Ag}^+ \text{ added} = 20.0 \text{ mL (0.200 M)} = 4.00$$

$$\text{mmol Ag}^+ \text{ left after precipitation} = 4.00 - 1.00 = 3.00$$

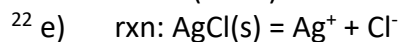
$$[\text{Ag}^+] = 3.00 \text{ mmol}/45.0 \text{ mL} = 6.67\text{e-}2$$

$$E = E^0 - 0.0592 \log (\text{Ag}^+)$$

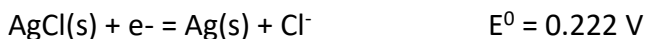
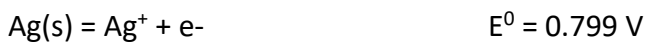
$$0.729 \text{ V} = E^0 - 0.0592 \log 1/(6.67\text{e-}2) \quad E^0 = 0.799 \text{ V} \quad \text{Ag}^+ + \text{e}^- = \text{Ag} \quad E^0 = 0.799 \text{ V}$$

$$^{20} E^0 = 0.100 - \frac{0.0592}{2} \log \frac{1}{K_{\text{sp}}}$$

$$^{21} E = -0.141 - (-0.44) = 0.30 \text{ V}$$



add the following



$$E_{\text{cell}} = 0.222 - 0.799 \text{ V} = -0.577 \text{ V}$$

$$\Delta G = -RT \ln K_{\text{sp}} = -nFE$$

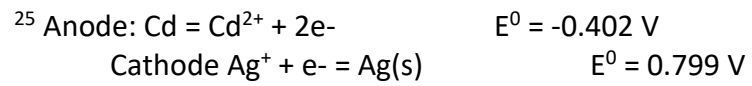
$$K_{\text{sp}} = 10^{(-0.577/0.0592)} = 1.79\text{e-}10$$



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23 b) A

24 e)  $E_{\text{cell}} = E_{\text{cath}} - E_{\text{anod}} = 2.890 - 0.771 = \mathbf{2.119 \text{ V}}$



All 1M concentration

$E_{\text{cell}} = E^0_{\text{cell}} = E_{\text{cath}} - E_{\text{anod}} = 0.799 - (-0.402) \text{ V} = 1.201 \text{ V}$