**Chem 454 - Electrochemistry Homework**

1] If $A + e^- = B$ has $E^0 = 0.775$ V then the $E^0$ for $2A + 2e^- = 2B$ is ___________________. [1]

2] The standard cell potential for the following is [2]

| | | |
|---|---|---|
| $Fe(s)/Fe^{2+}(aq)//Sn^{2+}(aq)/Sn(s)$ | $Fe^{2+} + 2e^- = Fe(s)$ | $E^0 = -0.44$ V |
| | $Sn^{2+} + 2e^- = Sn(s)$ | $E^0 = -0.141$ V |

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

3] The $E^0$ for the following is [3]

| | |
|---|---|
| $FeCO_3(s) + 2e^- = Fe(s) + CO_3^{2-}$ | $E^0 = ?$ |
| $Fe^{2+} + 2e^- = Fe(s)$ | $E^0 = -0.44$ V |

$K_{sp}$ {$FeCO_3(s)$} = 2.1e-11

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 [4]

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

5] The reductions take place at which electrode? [5]

a) anode b) toade c) cathode d) alkaline e) amphiprotic

6] The purpose of a reference electrode is to provide____________ (5 points) [6]

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

$F_2 + 2Fe^{2+} = 2F^- + 2Fe^{3+}$ $F_2 + 2e^- = 2F^-$ $E^0_{red} = 2.890$ V

$Fe^{3+} + e^- = Fe^{2+}$ $E^0_{red} = 0.771$ V

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

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

$Hg_2SO_4(s) + 2e- = 2Hg(l) + SO_4^{2-}$

$Hg_2^{2+} + 2e^- = 2Hg(l)$ $E^0_{red} = 0.796$ V

$Hg_2SO_4(s) = Hg_2^{2+} + SO_4^{2-}$ $K_{sp} = 7.4e-7$

9] What is $E^0_{cell}$ for the following reaction? $2Na(s) + 2H^+ = 2Na^+ + H_2(g)$ 9

$Na^+ + e^- = Na(s)$ $E^0 = -2.7143$ V

$2H^+ + 2e^- = H_2(g)$ $E^0 = 0.0000$ V

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 1.00e-5 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]

$A^+ + e^- = A$ $E^0 = 0.75$ V

$B + e^- = B^-$ $E^0 = 0.25$ V

$D^{2+} + e^- = D^+$ $E^0 = -0.50$ V

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

12] Calculate the standard state cell potential for the following [12]

$Cu(s)/Cu^{2+}(aq)//K^+(aq)/K(s)$

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 reduct n potential for the following reaction? [13]

$AgBr(s) + e^- = Ag(s) + Br^-$

$Ag^+ + e^- = Ag(s)$ $E^0 = 0.799$ V

$AgBr(s) = Ag^+ + Br^-$ $K_{sp} = 5.0e-13$

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? [14]

$AgCl(s) + e^- \leftrightharpoons Ag(s) + Cl^-$ $E^0 = 0.2223$ V

15] Based on the $E^{0\prime}$ 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 reducing agent? (5 points) What would be $E_{cell}$ for this reaction? (5 points) [15]

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

| Reaction | $E°$ (V) | $E°'$ (V) |
|---|---|---|
| $O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$ | +1.229 | +0.816 |
| $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ | +0.771 | +0.771 |
| $I_2 + 2e^- \rightleftharpoons 2I^-$ | +0.535 | +0.535 |
| Cytochrome *a* ($Fe^{3+}$) + $e^-$ ⇌ cytochrome *a* ($Fe^{2+}$) | +0.290 | +0.290 |
| $O_2(g) + 2H^+ + 2e^- \rightleftharpoons H_2O_2$ | +0.695 | +0.281 |
| Cytochrome *c* ($Fe^{3+}$) + $e^-$ ⇌ cytochrome *c* ($Fe^{2+}$) | — | +0.254 |
| 2,6-Dichlorophenolindophenol + $2H^+ + 2e^-$ ⇌ reduced 2,6-dichlorophenolindophenol | — | +0.22 |
| Dehydroascorbate + $2H^+ + 2e^-$ ⇌ ascorbate + $H_2O$ | +0.390 | +0.058 |
| Fumarate + $2H^+ + 2e^-$ ⇌ succinate | +0.433 | +0.031 |
| Methylene blue + $2H^+ + 2e^-$ ⇌ reduced product | +0.532 | +0.011 |
| Glyoxylate + $2H^+ + 2e^-$ ⇌ glycolate | — | −0.090 |
| Oxaloacetate + $2H^+ + 2e^-$ ⇌ malate | +0.330 | −0.102 |
| Pyruvate + $2H^+ + 2e^-$ ⇌ lactate | +0.224 | −0.190 |
| Riboflavin + $2H^+ + 2e^-$ ⇌ reduced riboflavin | — | −0.208 |
| FAD + $2H^+ + 2e^-$ ⇌ $FADH_2$ | — | −0.219 |
| (Glutathione-S)$_2$ + $2H^+ + 2e^-$ ⇌ 2 glutathione-SH | — | −0.23 |
| Safranine T + $2e^-$ ⇌ leucosafranine T | −0.235 | −0.289 |
| $(C_6H_5S)_2 + 2H^+ + 2e^- \rightleftharpoons 2C_6H_5SH$ | — | −0.30 |
| $NAD^+ + H^+ + 2e^- \rightleftharpoons$ NADH | −0.105 | −0.320 |
| $NADP^+ + H^+ + 2e^- \rightleftharpoons$ NADPH | — | −0.324 |
| Cystine + $2H^+ + 2e^-$ ⇌ 2 cysteine | — | −0.340 |
| Acetoacetate + $2H^+ + 2e^-$ ⇌ L-β-hydroxybutyrate | — | −0.346 |
| Xanthine + $2H^+ + 2e^-$ ⇌ hypoxanthine + $H_2O$ | — | −0.371 |
| $2H^+ + 2e^- \rightleftharpoons H_2$ | 0.000 | −0.414 |
| Gluconate + $2H^+ + 2e^-$ ⇌ glucose + $H_2O$ | — | −0.44 |
| $SO_4^{2-} + 2e^- + 2H^+ \rightleftharpoons SO_3^{2-} + H_2O$ | — | −0.454 |
| $2SO_3^{2-} + 2e^- + 4H^+ \rightleftharpoons S_2O_4^{2-} + 2H_2O$ | — | −0.527 |

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

$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-$ $E^0 = 0.222$ V

Calculate the concentration of KCl in this electrode.

17] What is $E^0_{cell}$ for $2I^- + 2H^+ \rightarrow H_2 + I_2$, is this a spontaneous reaction? [17]

18] From the data in the Table calculate the $K_{sp}$ of $PbSO_4$. [18]

| Half Reaction | $E^0$ |
| --- | --- |
| $O_2 + 4H^+ + 4e^-$ ---> $2H_2O$ | +1.23 |
| $Fe(CN)_6^{3-} + e^-$ ---> $Fe(CN)_6^{4-}$ | +0.36 |
| $2H^+ + 2e^-$ ---> $H_2$ | 0.00 |
| $Pb^{2+} + 2e^-$ ---> Pb | -0.126 |
| $PbSO_4 + 2e^-$ ---> $Pb + SO_4^{2-}$ | -0.355 |
| $Fe^{2+} + 2e^-$ ---> 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 $AgNO_3$(aq). What is the standard reduction potential of $Ag^+$? What is the half reaction for that $E^0$? [19]

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

20] What is $E^0$ for the half reaction given the following? [20]

$MX_2(s) + 2e- = M(s) + 2X^-$ $E^0$ = ?

$M^{2+} + 2e = M(s)$ $E^0$ = 0.100 V

$MX_2(s) = M^{2+} + 2X^-$ $K_{sp}$ = 1.0e-10

21] The standard cell potential for the following is [21]

$Fe(s)/Fe^{2+}(aq)//Sn^{2+}(aq)/Sn(s)$

$Fe^{2+} + 2e- = Fe(s)$ $E^0$ = -0.44 V

$Sn^{2+} + 2e- = Sn(s)$ $E^0$ = -0.141 V

22] What is the Ksp of AgCl given the following? [22]

$Ag^+ + e- = Ag(s)$ $E^0 = 0.799$ V

$AgCl(s) + e- = Ag(s) + Cl^-$ $E^0 = 0.222$ V

Note that 2.303RT/nF = 0.0592 V.

23] Which of the following species is the strongest oxidizing agent? [23]

$A + e^- = A^-$ $E^0 = 0.500$ Volts

$A^- + e^- = A^{2-}$ $E^0 = 0.000$ volts

$A^{2-} + e^- = A^{3-}$ $E^0 = -0.500$ volts

24] What is $E^0_{cell}$ for the reaction below? [24]

$F_2 + 2Fe^{2+} = 2F^- + 2Fe^{3+}$ $F_2 + 2e^- = 2F^-$ $E^0_{red} = 2.890$ V

$Fe^{3+} + e^- = Fe^{2+}$ $E^0_{red} = 0.771$ V

25] Calculate $E_{cell}$ for Cd(s)/[$CdCl_2$](aq) = 1.0 M//[$AgNO_3$](aq) = 1.0 M/Ag(s) [25]

**Answers**

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[1] 0.775 V

[2] E = -0.141 –(-0.44) = 0.30 V

[3] E = -0.44 – (0.0592/2) log $1/K_{sp}$ = -0.756 V

[4] b) $E_{cell} > 0$

[5] cathode

[6] to provide a stable potential chemical reference in which the cathode reaction can be compared.

[7] Ecell = Ecath – Eanod = 2.890 – 0.771 = **2.119 V**

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[8] $E = 0.796 – 0.0592/2 \log 1/[Hg_2^{2+}]$

$K_{sp} = 7.4e\text{-}7 = [Hg_2^{2+}][SO_4^{2-}]$

$[Hg_2^{2+}] = 7.4e\text{-}7/[SO_4^{2-}]$

$E = 0.796 – 0.0592/2 \log [SO_4^{2-}]/7.4e\text{-}7 =$ **0.615 V**

[9] d: $E^0_{cell} = 0.0000 – (-2.7143)$ V

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

[11] e

[12] a: $E_{cell} = E_{cath} – E_{anod} = -2.936 – 0.339 = -3.275$ V

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

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

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

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

[14] $E = 0.2223 – 0.0592 \log 0.150 = 0.271$ V

[15] Strongest reducing agent ________$S_2O_4^{2-}$________

Strongest oxidizing agent _______$O_2$_________

$O_2 + 4H^+ + 4e^- = 2H_2O$ $E_{red}^0 = 1.229$ V

$\underline{2S_2O_4^{2-} + 4H_2O = 4SO_3^{2-} + 8H^+ + 4e^-}$ $E_{red}^0 = -0.527$

$O_2 + 2S_2O_4^{2-} + 2H_2O = 4SO_3^{2-} + 4H^+$ $E_{cell} = 1.229 –(-0.527) = 1.756$

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

[17] Cathode: $2H^+ + 2e^- \rightarrow H_2$ $E^0 = 0.00$

Anode: $2I^- \rightarrow I_2 + 2e^-$ $E^0 = 0.535$ V

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

[18] Cathode: $PbSO_4 + 2e^- \text{--->} Pb + SO_4^{2-}$

Anode: $Pb \text{--->} Pb^{2+} + 2e^-$

Cell Rxn and $K_{sp}$: $PbSO_4 \text{--->} Pb^{2+} + SO_4^{2-}$

$E^0$ = - 0.355 + 0.126 = -0.229 V

ΔG = -nFE = -RT ln K

$E^0$ = 0.0592/n log K

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

[19] mmol $Br^-$ added = 25.0 mL (0.0400 M) = 1.00

mmol $Ag^+$ added = 20.0 mL (0.200 M) = 4.00

mmol $Ag^+$ left after precipitation = 4.00 – 1.00 = 3.00

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

E = $E^0$ – 0.0592 log ($Ag^+$)

0.729 V = $E^0$ – 0.0592 log 1/(6.67e-2) $E^0$ = 0.799 V $Ag^+$ + e- = Ag $E^0$ = 0.799 V

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

[21] E = -0.141 –(-0.44) = 0.30 V
[22] e) rxn: AgCl(s) = $Ag^+ + Cl^-$

add the following

Ag(s) = $Ag^+$ + e- $E^0$ = 0.799 V

AgCl(s) + e- = Ag(s) + $Cl^-$ $E^0$ = 0.222 V

$E_{cell}$ = 0.222 – 0.799 V = -0.577 V

ΔG = -RT ln Ksp = -nFE

Ksp = 10^(-0.577/0.0592) = 1.79e-10

[23] b) A

[24] e) Ecell = Ecath – Eanod = 2.890 – 0.771 = **2.119 V**

[25] Anode: $Cd = Cd^{2+} + 2e^-$ $E^0 = -0.402$ V
Cathode $Ag^+ + e^- = Ag(s)$ $E^0 = 0.799$ V

All 1M concentration

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