## 6 - Electrochemistry

1] A spontaneous electrochemical cell would have which of the following? ${ }^{1}$
a) $\mathrm{E}_{\text {cell }}=0$
b) $\mathrm{E}_{\text {cell }}>0$
c) $\mathrm{E}_{\text {cell }}<0$
d) $\quad \mathrm{E}_{\text {cell }} \leq 0$
e) $\mathrm{E}_{\text {cell }} \geq 0$

2] The purpose of a reference electrode is to $\qquad$ ${ }^{2}$

3] Which of the following species is the strongest reducing agent? ${ }^{3}$

$$
\begin{array}{ll}
A+e^{-}=A^{-} & E^{0}=0.500 \text { Volts } \\
A^{-}+e^{-}=A^{2-} & E^{0}=0.000 \text { volts } \\
A^{2-}+e^{-}=A^{3-} & E^{0}=-0.500 \text { volts }
\end{array}
$$

4] What is $E^{0}$ for the following half reaction if $E^{0}$ for ${ }^{4}$

$$
\begin{array}{ll}
\mathrm{Zn}^{2+}+2 \mathrm{e}^{-}=\mathrm{Zn}(\mathrm{~s}) & \text { is }-0.762 \mathrm{~V} ? \\
1 / 2 \mathrm{Zn}^{2+}+\mathrm{e}^{-}=1 / 2 \mathrm{Zn}(\mathrm{~s}) &
\end{array}
$$

5] What is $E^{0}$ cell for the following reaction? ${ }^{5}$

$$
\begin{array}{ll}
2 \mathrm{Na}(\mathrm{~s})+2 \mathrm{H}^{+}=2 \mathrm{Na}^{+}+\mathrm{H}_{2}(\mathrm{~g}) \\
\mathrm{Na}^{+}+\mathrm{e}^{-}=\mathrm{Na}(\mathrm{~s}) & \mathrm{E}^{0}=-2.7143 \mathrm{~V} \\
2 \mathrm{H}^{+}+2 \mathrm{e}^{-}=\mathrm{H}_{2}(\mathrm{~g}) & \mathrm{E}^{0}=0.0000 \mathrm{~V}
\end{array}
$$

6] If $A+e^{-}=B$ has $E^{0}=0.775 V$ then the $E^{0}$ for $2 A+2 e^{-}=2 B$ is $\qquad$ .${ }^{6}$

7] The reductions take place at which electrode? ${ }^{7}$

8] The standard cell potential for the following is ${ }^{8}$

$$
\begin{array}{ll}
\mathrm{Fe}(\mathrm{~s}) / \mathrm{Fe}^{2+}(\mathrm{aq}) / / \mathrm{Sn}^{2+}(\mathrm{aq}) / \mathrm{Sn}(\mathrm{~s}) \\
\mathrm{Fe}^{2+}+2 \mathrm{e}^{-}=\mathrm{Fe}(\mathrm{~s}) & \mathrm{E}^{0}=-0.44 \mathrm{~V} \\
\mathrm{Sn}^{2+}+2 \mathrm{e}^{-}=\mathrm{Sn}(\mathrm{~s}) & \mathrm{E}^{0}=-0.141 \mathrm{~V}
\end{array}
$$

9] The $E^{0}$ for the following is ${ }^{9}$

$$
\begin{array}{ll}
\mathrm{FeCO}_{3}(\mathrm{~s})+2 \mathrm{e}^{-}=\mathrm{Fe}(\mathrm{~s})+\mathrm{CO}_{3}{ }^{2-} & \mathrm{E}^{0}=? \\
\mathrm{Fe}^{2+}+2 \mathrm{e}^{-}=\mathrm{Fe}(\mathrm{~s}) & \mathrm{E}^{0}=-0.44 \mathrm{~V} \\
\mathrm{~K}_{\mathrm{sp}}\left\{\mathrm{FeCO}_{3}(\mathrm{~s})\right\}=2.1 \mathrm{e}-11 &
\end{array}
$$

10] What is $E^{0}$ cell for the reaction below ${ }^{10}$

$$
\begin{array}{ll}
\mathrm{F}_{2}+2 \mathrm{Fe}^{2+}=2 \mathrm{~F}^{-}+2 \mathrm{Fe}^{3+} \\
\mathrm{F}_{2}+2 \mathrm{e}^{-}=2 \mathrm{~F}^{-} & \mathrm{E}_{\text {red }}=2.890 \mathrm{~V} \\
\mathrm{Fe}^{3+}+\mathrm{e}^{-}=\mathrm{Fe}^{2+} & \mathrm{E}_{\text {red }}^{0}=0.771 \mathrm{~V}
\end{array}
$$

11] What is $E^{0}$ cell for the reaction below? ${ }^{11}$

$$
\begin{array}{ll}
\mathrm{Hg}_{2} \mathrm{SO}_{4}(\mathrm{~s})+2 \mathrm{e}-=2 \mathrm{Hg}(\mathrm{I})+\mathrm{SO}_{4}^{2-} \\
\mathrm{Hg}_{2}^{2+}+2 \mathrm{e}^{-}=2 \mathrm{Hg}(\mathrm{I}) & \mathrm{E}_{\text {red }}^{0}=0.796 \mathrm{~V} \\
\mathrm{Hg}_{2} \mathrm{SO}_{4}(\mathrm{~s})=\mathrm{Hg}_{2}^{2+}+\mathrm{SO}_{4}^{2-} & \mathrm{K}_{\text {sp }}=7.4 \mathrm{e}-7
\end{array}
$$

12] What is the half reaction reduction potential for $1.00 \mathrm{e}-5 \mathrm{M} \mathrm{H}^{+}$? ${ }^{12}$

13] Which of the following species is the strongest reducing agent? ${ }^{13}$

$$
\begin{array}{ll}
\mathrm{A}^{+}+\mathrm{e}-\mathrm{A} & \mathrm{E}^{0}=0.75 \mathrm{~V} \\
\mathrm{~B}+\mathrm{e}-=\mathrm{B}^{-} & \mathrm{E}^{0}=0.25 \mathrm{~V} \\
\mathrm{D}^{2+}+\mathrm{e}-=\mathrm{D}^{+} & \mathrm{E}^{0}=-0.50 \mathrm{~V}
\end{array}
$$

14] Calculate the standard state cell potential for the following. ${ }^{14}$

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

15] What is the standard state reduction potential for the following reaction? ${ }^{15}$

$$
\begin{array}{ll}
\mathrm{AgBr}(\mathrm{~s})+\mathrm{e}^{-}=\mathrm{Ag}(\mathrm{~s})+\mathrm{Br}^{-} \\
\mathrm{Ag}^{+}+\mathrm{e}^{-}=\mathrm{Ag}(\mathrm{~s}) & \mathrm{E}^{0}=0.799 \mathrm{~V} \\
\mathrm{AgBr}(\mathrm{~s})=\mathrm{Ag}^{+}+\mathrm{Br}^{-} & \mathrm{K}_{\mathrm{sp}}=5.0 \mathrm{e}-13
\end{array}
$$

16] Calculate $\mathrm{E}_{\text {cell }}$ and K for this reaction. $\mathrm{Pt} / \mathrm{Cr}^{3+}(2.00 \mathrm{e}-4 \mathrm{M}), \mathrm{Cr}^{2+}(1.00 \mathrm{e}-3 \mathrm{M}) / / \mathrm{Pb}^{2+}(6.50 \mathrm{e}-2 \mathrm{M}) / \mathrm{Pb} .{ }^{16}$

17] What is $E$ for the following if $\mathrm{Cl}^{-}$concentration is 0.50 M ? ${ }^{17}$

$$
\mathrm{AgCl}(\mathrm{~s})+\mathrm{e}^{-}=\mathrm{Ag}(\mathrm{~s})+\mathrm{Cl}^{-} \quad \mathrm{E}^{0}=0.222 \mathrm{~V}
$$

18] Calculate $E^{0}$ for ${ }^{18} \mathrm{Ni}(\mathrm{CN})_{4}^{-}(\mathrm{aq})+2 \mathrm{e}^{-}=\mathrm{Ni}(\mathrm{s})+4 \mathrm{CN}^{-}$
Given $\mathrm{Ni}^{2+}+2 \mathrm{e}^{-}=\mathrm{Ni}(\mathrm{s}) \quad \mathrm{E}^{0}=-0.250 \mathrm{~V} \quad \beta\left\{\mathrm{Ni}(\mathrm{CN})_{4}^{-}\right\}=1.0 \mathrm{e} 22$

19] What is the Ksp of AgCl given: ${ }^{19}$

$$
\begin{array}{ll}
\mathrm{Ag}^{+}+\mathrm{e}-\mathrm{Ag}(\mathrm{~s}) & \mathrm{E}^{0}=0.799 \mathrm{~V} \\
\mathrm{AgCl}(\mathrm{~s})+\mathrm{e}-=\mathrm{Ag}(\mathrm{~s})+\mathrm{Cl}^{-} & \mathrm{E}^{0}=0.222 \mathrm{~V}
\end{array}
$$

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

20] Calculate $\mathrm{E}_{\text {cell }}$ for $\mathrm{Cd}(\mathrm{s}) /\left[\mathrm{CdCl}_{2}\right](\mathrm{aq})=1.0 \mathrm{M} / /\left[\mathrm{AgNO}_{3}\right](\mathrm{aq})=1.0 \mathrm{M} / \mathrm{Ag}(\mathrm{s})^{20}$
a] 1.201 V
b] -1.201 V
c] 0.566 V
d] 0.997 V
e] -0.566 V

21] Calculate the standard potential for the following half-reaction, given the $\mathrm{K}_{\mathrm{sp}}$ for $\mathrm{Pd}(\mathrm{OH})_{2}$ is $3.0 \times 10^{-28}$ and the standard potential for $\mathrm{Pd}^{2+}+2 \mathrm{e}^{-}=\mathrm{Pd}(\mathrm{s})$ is $0.915 \mathrm{~V}^{21}$

$$
\mathrm{Pd}(\mathrm{OH})_{2}(\mathrm{~s})+2 \mathrm{e}^{-}=\mathrm{Pd}(\mathrm{~s})+2 \mathrm{OH}
$$

22] Explain what $\mathrm{E}^{0}$ is and why is it preferred over $\mathrm{E}^{0}$ in biochemistry? ${ }^{22}$

23] Calculate $\mathrm{E}^{0}$ for $\mathrm{H}_{2} \mathrm{C}_{2} \mathrm{O}_{4}+2 \mathrm{H}^{+}+2 \mathrm{e}-=2 \mathrm{HCO}_{2} \mathrm{H} \quad \mathrm{E}^{0}=0.204 \mathrm{~V}^{23}$

## Answers

${ }^{1} \mathrm{~b}$
${ }^{2}$ To provide a stable potential in which the electrode reaction can be compared to $2 \mathrm{H}^{+}(\mathrm{aq})+2 \mathrm{e}-$ $=\mathrm{H}_{2}(\mathrm{~g}) \mathrm{E}^{0}=0.00 \mathrm{~V}$
${ }^{3} \mathrm{~A}^{3-}$
${ }^{4}-0.762 \mathrm{~V}$
${ }^{5} \mathrm{E}^{0}$ cell $=0.0000-(-2.7143) \mathrm{V}$
${ }^{6} 0.775 \mathrm{~V}$
${ }^{7}$ Cathode
${ }^{8} \mathrm{E}=-0.141-(-0.44)=0.30 \mathrm{~V}$
${ }^{9} \mathrm{E}=-0.44-(0.0592 / 2) \log 1 / \mathrm{K}_{\mathrm{sp}}=-0.756 \mathrm{~V}$
${ }^{10}$ Ecell $=$ Ecath - Eanod $=2.890-0.771=2.119$ V
${ }^{11} E=0.796-0.0592 / 2 \log 1 /\left[\mathrm{Hg}_{2}{ }^{2+}\right]$

$$
\mathrm{K}_{\mathrm{sp}}=7.4 \mathrm{e}-7=\left[\mathrm{Hg}_{2}{ }^{2+}\right]\left[\mathrm{SO}_{4}{ }^{2-}\right]
$$

```
        [Hg2 2+}]=7.4\textrm{e}-7/[\mp@subsup{\textrm{SO}}{4}{}\mp@subsup{}{}{2-}
E=0.796-0.0592/2 log[SO44 '-}]/7.4e-7=0.615 V
\mp@subsup{}{}{12}E=E E - 0.0592 log 1/[H+]=0.0000-0.0592 log 1/[1.00e-5]=-0.296 V
13 D+
\mp@subsup{}{}{14}}\mp@subsup{\textrm{E}}{\mathrm{ cell }}{}=\mp@subsup{\textrm{E}}{\mathrm{ cath }}{}-\mp@subsup{\textrm{E}}{\mathrm{ anod }}{}=-2.936-0.339=-3.275 V Use your book's table of standard reduction
potentials.
\mp@subsup{}{}{15}\textrm{E}=\mp@subsup{\textrm{E}}{}{0}(\mp@subsup{\textrm{Ag}}{}{+}/\textrm{Ag})-0.0592 log 1/[\mp@subsup{\textrm{Ag}}{}{+}]
    Realize that K}\mp@subsup{K}{\mathrm{ sp }}{}=[\mp@subsup{\textrm{Ag}}{}{+}][\mp@subsup{\textrm{Br}}{}{-}
    [Ag'] = K Spp / [Br-] sub into Nernst Eqn above
    E = E O}(\mp@subsup{\textrm{Ag}}{}{+}/\textrm{Ag})-0.0592 log [Br-]/K <splet [Br-] = 1 for standard state condition
E}=0.799-0.0592 log 1/5.00e-13=0.0708 V
16 Pt/Cr }\mp@subsup{}{}{3+}(2.00\textrm{e}-4\textrm{M}),\mp@subsup{\textrm{Cr}}{}{2+}(1.00\textrm{e}-3\textrm{M})//\mp@subsup{\textrm{Pb}}{}{2+}(6.50\textrm{e}-2\textrm{M})/\textrm{Pb
    Ecath}=-0.126-(0.0592/2)\operatorname{log}1/6.5e-2=-0.161 V
    Eanod}=-0.408-0.0592 log (1.00e-3/2.00e-4)=-0.449 V
    E
    E [cell =-0.126-(-0.408) =0.282
    \DeltaG}\mp@subsup{\textrm{G}}{}{0}=-nFE\mp@subsup{E}{}{0}=-2*96484*0.282=-5.44e4 J
    \Delta G ^ { 0 } = - R T ~ I n K
    InK =-\DeltaG0}/RT =-(-5.44e4 J) / 8.314 * 298K
K=3.43e9
\mp@subsup{}{}{17}\textrm{E}=\mp@subsup{\textrm{E}}{}{0}-0.0592\operatorname{log}[\mp@subsup{\textrm{Cl}}{}{-}]=0.222-0.0592 log (0.50)=0.240V
18}\textrm{E}=-0.250-(0.0592/2)\operatorname{log}1/[\mp@subsup{\textrm{Ni}}{}{2+}
    \beta{Ni(CN)}\mp@subsup{)}{4}{-}}=1.0e22=[Ni(CN)\mp@subsup{)}{4}{-}]/[\mp@subsup{N⿱一𫝀口}{2+}{2+}][CN-\mp@subsup{]}{}{4
    [CN-] 4}1.0\textrm{e}22/[\textrm{Ni}(\textrm{CN}\mp@subsup{)}{4}{-}]=1/[\mp@subsup{\textrm{Ni}}{}{2+}
```

$$
\begin{aligned}
& E=-0.250-(0.0592 / 2) \log \left\{[\mathrm{CN}]^{4} 1.0 \mathrm{e} 22 /\left[\mathrm{Ni}(\mathrm{CN})_{4}^{-}\right]\right\} \\
& E^{0}=-0.250-(0.0592 / 2) \log 1.0 e 22 \\
& E^{0}=-0.90 \mathrm{~V} \\
& { }^{19} \mathrm{rxn}: \mathrm{AgCl}(\mathrm{~s})=\mathrm{Ag}^{+}+\mathrm{Cl}^{-} \quad \text { add the following } \\
& \mathrm{Ag}(\mathrm{~s})=\mathrm{Ag}^{+}+\mathrm{e}-\quad \mathrm{E}^{0}=0.799 \mathrm{~V} \\
& \mathrm{AgCl}(\mathrm{~s})+\mathrm{e}-=\mathrm{Ag}(\mathrm{~s})+\mathrm{Cl}^{-} \quad \mathrm{E}^{0}=0.222 \mathrm{~V} \\
& \mathrm{E}_{\text {cell }}=0.222-0.799 \mathrm{~V}=-0.577 \mathrm{~V} \\
& \Delta G=-R T \ln K s p=-n F E \\
& K s p=10^{\wedge}(-0.577 / 0.0592)=1.79 \mathrm{e}-10 \\
& { }^{20} \text { Anode: } \mathrm{Cd}=\mathrm{Cd}^{2+}+2 \mathrm{e}-\quad \mathrm{E}^{0}=-0.402 \mathrm{~V} \\
& \text { Cathode } \mathrm{Ag}^{+}+\mathrm{e}-\mathrm{Ag}(\mathrm{~s}) \quad \mathrm{E}^{0}=0.799 \mathrm{~V} \\
& \text { All at } 1 \mathrm{M} \text { concentration } \\
& \mathrm{E}_{\text {cell }}=\mathrm{E}^{0} \text { cell }=\mathrm{E}_{\text {cath }}-\mathrm{E}_{\text {anod }}=0.799-(-0.402) \mathrm{V}=1.201 \mathrm{~V} \\
& { }^{21} \mathrm{E}=\mathrm{E}^{0}{ }_{\mathrm{Pd} 2+/ \mathrm{Pd}}-(0.0592 / 2) \log 1 /\left[\mathrm{Pd}^{2+}\right] \quad \mathrm{K}_{\text {sp }}=3.0 \times 10^{-28}=\left[\mathrm{Pd}^{2+}\right]\left[\mathrm{OH}^{-}\right]^{2} \\
& {\left[\mathrm{Pd}^{2+}\right]=3.0 \times 10^{-28} /\left[\mathrm{OH}^{-}\right]^{2}} \\
& \text { Standard potential conditions }\left[\mathrm{OH}^{-}\right]=1.0 \mathrm{M} \\
& {\left[\mathrm{Pd}^{2+}\right]=3.0 \times 10^{-28}} \\
& E=E^{0}{ }_{P d 2+/ P d}-(0.0592 / 2) \log 1 / 3.0 \times 10^{-28} \\
& E=0.915 \mathrm{~V}-(0.0592 / 2) \log 1 / 3.0 \times 10^{-28} \\
& \mathrm{E}_{\mathrm{Pd}(\mathrm{OH}-2 / \mathrm{Pd}}^{0}=-0.100 \mathrm{~V}
\end{aligned}
$$

${ }^{22} \mathrm{E}^{01}$ is the conditional from of $\mathrm{E}^{0}$ where it is assumed that the pH is 7 rather than 0 . See discussion in text
${ }^{23} \mathrm{H}_{2} \mathrm{C}_{2} \mathrm{O}_{4}$ is oxalic acid and $\mathrm{HCO}_{2} \mathrm{H}$ is formic acid.

$$
\begin{aligned}
& E=E^{0}-\frac{0.0592}{n} \log Q \\
& E=0.204-\frac{0.0592}{2} \log \frac{\left[\mathrm{HCO}_{2} \mathrm{H}\right]^{2}}{\left[\mathrm{H}^{+}\right]^{2}\left[\mathrm{H}_{2} \mathrm{C}_{2} \mathrm{O}_{4}\right]} \quad \# 1 \quad \text { assume } \mathrm{pH} 7 \text { and all else } 1 \mathrm{M}
\end{aligned}
$$

First method is an approximation:

$$
E^{0,}=0.204-\frac{0.0592}{2} \log \frac{1}{\left[10^{-7}\right]^{2}}=-0.210 \mathrm{~V}
$$

We must consider that the $\left[\mathrm{HCO}_{2} \mathrm{H}\right]$ and the $\left[\mathrm{H}_{2} \mathrm{C}_{2} \mathrm{O}_{4}\right]$ are involved in hydrolysis reactions. The relative concentrations of each are described as:

$$
\begin{aligned}
& \alpha_{\mathrm{HCO}_{2} \mathrm{H}}=\frac{\left[H C O_{2} H\right]}{F_{\mathrm{HCO}_{2} H}}=\frac{\left[H^{+}\right]}{K_{a}+\left[H^{+}\right]} \quad\left[H C O_{2} H\right]=\frac{\left[H^{+}\right] F_{\mathrm{HCO}_{2} H}}{K_{a}+\left[H^{+}\right]} \\
& {\left[\mathrm{H}_{2} \mathrm{C}_{2} \mathrm{O}_{4}\right]=\frac{\left[H^{+}\right]^{2} F_{\mathrm{H}_{2} \mathrm{C}_{2} \mathrm{O}_{4}}}{K_{a 1} K_{a 2}+K_{a 1}\left[H^{+}\right]+\left[H^{+}\right]^{2}}}
\end{aligned}
$$

\#1 now becomes

$$
\left.E=0.204-\frac{0.0592}{2} \log \frac{\left(\frac{\left[H^{+}\right] F_{H C O_{2} H}}{K_{a}+\left[H^{+}\right]}\right)^{2}}{\left[H^{+}\right]^{2}\left(\frac{\left[H^{+}\right]^{2} F_{H_{2} \mathrm{C}_{2} O_{4}}}{K_{a 1} K_{a 2}+K_{a 1}\left[H^{+}\right]+\left[H^{+}\right]^{2}}\right.}\right)
$$

$\left[\mathrm{H}^{+}\right]=1 \mathrm{e} 7$ exact, $\mathrm{K}_{\mathrm{a}}=1.80 \mathrm{e}-4, \mathrm{~K}_{\mathrm{a} 1}=5.60 \mathrm{e}-2, \mathrm{~K}_{\mathrm{a} 2}=5.42 \mathrm{e}-5, \mathrm{~F}=1 \mathrm{M}$ exact

