

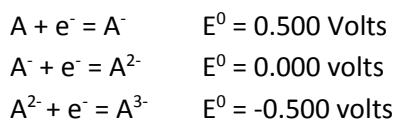
6 – Electrochemistry

1] A spontaneous electrochemical cell would have which of the following? ¹

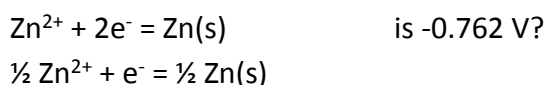
- a) $E_{\text{cell}} = 0$
- b) $E_{\text{cell}} > 0$
- c) $E_{\text{cell}} < 0$
- d) $E_{\text{cell}} \leq 0$
- e) $E_{\text{cell}} \geq 0$

2] The purpose of a reference electrode is to _____ ²

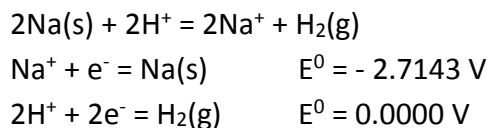
3] Which of the following species is the strongest reducing agent? ³



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



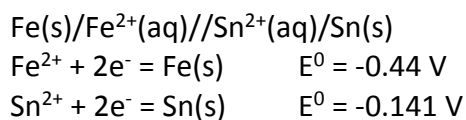
5] What is E^0_{cell} for the following reaction? ⁵



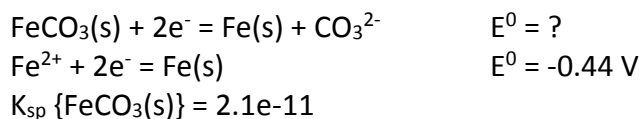
6] If $A + e^- = B$ has $E^0 = 0.775 \text{ V}$ then the E^0 for $2A + 2e^- = 2B$ is _____ ⁶

7] The reductions take place at which electrode? ⁷

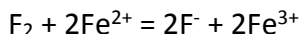
8] The standard cell potential for the following is ⁸



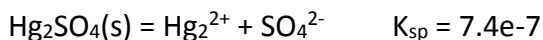
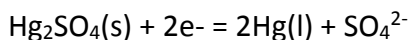
9] The E^0 for the following is ⁹



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



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

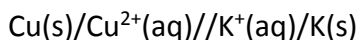


12] What is the half reaction reduction potential for $1.00\text{e-}5 \text{ M H}^+$? ¹²

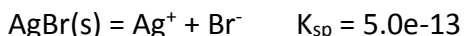
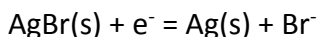
13] Which of the following species is the strongest reducing agent? ¹³



14] Calculate the standard state cell potential for the following. ¹⁴

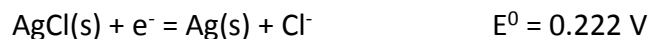


15] What is the standard state reduction potential for the following reaction? ¹⁵

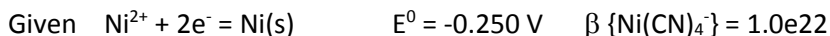


16] Calculate E_{cell} and K for this reaction. $\text{Pt}/\text{Cr}^{3+}(2.00\text{e-}4\text{M}), \text{Cr}^{2+}(1.00\text{e-}3\text{M})//\text{Pb}^{2+}(6.50\text{e-}2\text{M})/\text{Pb}$. ¹⁶

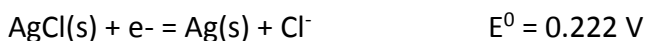
17] What is E for the following if Cl^- concentration is 0.50 M ? ¹⁷



18] Calculate E^0 for ¹⁸ $\text{Ni}(\text{CN})_4^-(\text{aq}) + 2\text{e}^- = \text{Ni}(\text{s}) + 4 \text{CN}^-$



19] What is the K_{sp} of AgCl given: ¹⁹

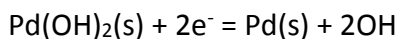


Note that $2.303RT/nF = 0.0592 \text{ V}$.

20] Calculate E_{cell} for $\text{Cd(s)}/[\text{CdCl}_2](\text{aq}) = 1.0 \text{ M} // [\text{AgNO}_3](\text{aq}) = 1.0 \text{ M}/\text{Ag(s)}$ 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 K_{sp} for $\text{Pd}(\text{OH})_2$ is 3.0×10^{-28} and the standard potential for $\text{Pd}^{2+} + 2\text{e}^- = \text{Pd(s)}$ is 0.915 V. ²¹



22] Explain what E° is and why is it preferred over E^0 in biochemistry? ²²

23] Calculate E° for $\text{H}_2\text{C}_2\text{O}_4 + 2\text{H}^+ + 2\text{e}^- = 2\text{HCO}_2\text{H}$ $E^0 = 0.204 \text{ V}$ ²³

Answers

¹ b

² To provide a stable potential in which the electrode reaction can be compared to $2\text{H}^+(\text{aq}) + 2\text{e}^- = \text{H}_2(\text{g})$ $E^0 = 0.00 \text{ V}$

³ A^{3-}

⁴ -0.762 V

⁵ $E^{\circ}_{\text{cell}} = 0.0000 - (-2.7143) \text{ V}$

⁶ 0.775 V

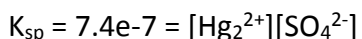
⁷ Cathode

⁸ $E = -0.141 - (-0.44) = 0.30 \text{ V}$

⁹ $E = -0.44 - (0.0592/2) \log 1/K_{\text{sp}} = -0.756 \text{ V}$

¹⁰ $E_{\text{cell}} = E_{\text{cath}} - E_{\text{anod}} = 2.890 - 0.771 = \mathbf{2.119 \text{ V}}$

¹¹ $E = 0.796 - 0.0592/2 \log 1/[\text{Hg}_2^{2+}]$



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

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

$$^{12} E = E^0 - 0.0592 \log 1/[\text{H}^+] = 0.0000 - 0.0592 \log 1/[1.00\text{e-}5] = -0.296 \text{ V}$$

¹³ D+

¹⁴ $E_{\text{cell}} = E_{\text{cath}} - E_{\text{anod}} = -2.936 - 0.339 = -3.275 \text{ V}$ Use your book's table of standard reduction potentials.

$$^{15} E = E^0(\text{Ag}^+/\text{Ag}) - 0.0592 \log 1/[\text{Ag}^+]$$

Realize that $K_{\text{sp}} = [\text{Ag}^+][\text{Br}^-]$

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

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

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

¹⁶ Pt/Cr³⁺(2.00e-4M), Cr²⁺(1.00e-3M)//Pb²⁺(6.50e-2M)/Pb

$$E_{\text{cath}} = -0.126 - (0.0592/2) \log 1/6.5\text{e-}2 = -0.161 \text{ V}$$

$$E_{\text{anod}} = -0.408 - 0.0592 \log (1.00\text{e-}3/2.00\text{e-}4) = -0.449 \text{ V}$$

$$E_{\text{cell}} = -0.161 - (-0.449) = 0.288 \text{ V}$$

$$E^0_{\text{cell}} = -0.126 - (-0.408) = 0.282$$

$$\Delta G^0 = -nFE^0 = -2*96484*0.282 = -5.44\text{e}4 \text{ J}$$

$$\Delta G^0 = -RT \ln K$$

$$\ln K = -\Delta G^0 / RT = -(-5.44\text{e}4 \text{ J}) / 8.314 * 298\text{K}$$

$$K = 3.43\text{e}9$$

$$^{17} E = E^0 - 0.0592 \log [\text{Cl}^-] = 0.222 - 0.0592 \log (0.50) = 0.240 \text{ V}$$

$$^{18} E = -0.250 - (0.0592/2) \log 1/[\text{Ni}^{2+}]$$

$$\beta \{[\text{Ni}(\text{CN})_4]^{-}\} = 1.0\text{e}22 = [\text{Ni}(\text{CN})_4]^{-} / [\text{Ni}^{2+}][\text{CN}^-]^4$$

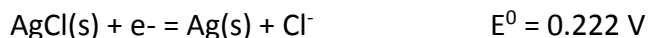
$$[\text{CN}^-]^4 1.0\text{e}22 / [\text{Ni}(\text{CN})_4]^{-} = 1/[\text{Ni}^{2+}]$$

$$E = -0.250 - (0.0592/2) \log \{[\text{CN}^-]^4 / [\text{Ni}(\text{CN})_4^-]\}$$

$$E^0 = -0.250 - (0.0592/2) \log 1.0 \times 10^{22}$$

$$E^0 = -0.90 \text{ V}$$

¹⁹ rxn: $\text{AgCl}(s) = \text{Ag}^+ + \text{Cl}^-$ add the following

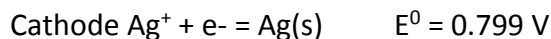


$$E_{\text{cell}} = 0.222 - 0.799 \text{ V} = -0.577 \text{ V}$$

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

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

²⁰ Anode: $\text{Cd} = \text{Cd}^{2+} + 2e^-$ $E^0 = -0.402 \text{ V}$



All at 1M concentration

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

²¹ $E = E^0_{\text{Pd}^{2+}/\text{Pd}} - (0.0592 / 2) \log 1 / [\text{Pd}^{2+}]$ $K_{\text{sp}} = 3.0 \times 10^{-28} = [\text{Pd}^{2+}][\text{OH}^-]^2$

$$[\text{Pd}^{2+}] = 3.0 \times 10^{-28} / [\text{OH}^-]^2$$

Standard potential conditions $[\text{OH}^-] = 1.0 \text{ M}$

$$[\text{Pd}^{2+}] = 3.0 \times 10^{-28}$$

$$E = E^0_{\text{Pd}^{2+}/\text{Pd}} - (0.0592 / 2) \log 1 / 3.0 \times 10^{-28}$$

$$E = 0.915 \text{ V} - (0.0592 / 2) \log 1 / 3.0 \times 10^{-28}$$

$$E^0_{\text{Pd}(\text{OH})_2/\text{Pd}} = -0.100 \text{ V}$$

²² E^0' is the conditional from of E^0 where it is assumed that the pH is 7 rather than 0. See discussion in text

²³ $\text{H}_2\text{C}_2\text{O}_4$ is oxalic acid and HCO_2H is formic acid.

$$E = E^0 - \frac{0.0592}{n} \log Q$$

$$E = 0.204 - \frac{0.0592}{2} \log \frac{[HCO_2H]^2}{[H^+]^2 [H_2C_2O_4]} \quad \#1 \quad \text{assume pH 7 and all else 1 M}$$

First method is an approximation:

$$E^{0'} = 0.204 - \frac{0.0592}{2} \log \frac{1}{[10^{-7}]^2} = -0.210V$$

We must consider that the $[HCO_2H]$ and the $[H_2C_2O_4]$ are involved in hydrolysis reactions. The relative concentrations of each are described as:

$$\alpha_{HCO_2H} = \frac{[HCO_2H]}{F_{HCO_2H}} = \frac{[H^+]}{K_a + [H^+]} \quad [HCO_2H] = \frac{[H^+] F_{HCO_2H}}{K_a + [H^+]}$$

$$[H_2C_2O_4] = \frac{[H^+]^2 F_{H_2C_2O_4}}{K_{a1} K_{a2} + K_{a1} [H^+] + [H^+]^2}$$

#1 now becomes

$$E = 0.204 - \frac{0.0592}{2} \log \frac{\left(\frac{[H^+] F_{HCO_2H}}{K_a + [H^+]} \right)^2}{[H^+]^2 \left(\frac{[H^+]^2 F_{H_2C_2O_4}}{K_{a1} K_{a2} + K_{a1} [H^+] + [H^+]^2} \right)}$$

$$[H^+] = 1e-7 \text{ exact, } K_a = 1.80e-4, K_{a1} = 5.60e-2, K_{a2} = 5.42e-5, F = 1 \text{ M exact}$$

$$E^{0'} = -0.268 \text{ V}$$