

Justin Chau
jc55395

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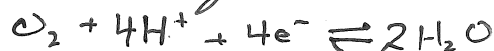
Analytical Chemistry Homework 9

13.1) Electric charge is the quantity of positive or negative particles.

Current is the quantity of charge moving past a point in a circuit each second.

Electric potential measures the work that can be done by each coulomb of charge as it moves from one point to another.

13.3) 16 mol O_2 /day

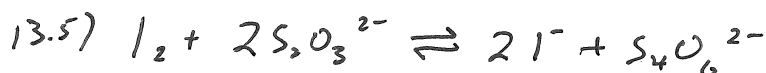


a) $64 \text{ mol } e^-/\text{day} = 7.41 \times 10^{-4} \text{ mol/s} = 71.5 \text{ C/s} = 71.5 \text{ A}$

b) $500 \text{ W} / 115 \text{ V} = 4.35 \text{ A}$

Human uses 16x more current than refrigerator.

c) $1.1 \text{ V} \times 71.5 \text{ A} = 79 \text{ W}$



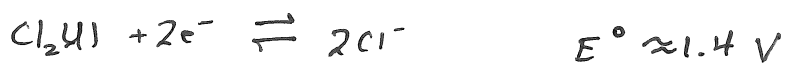
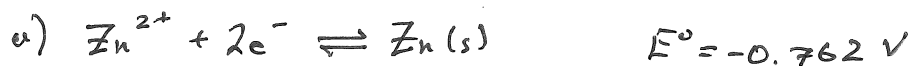
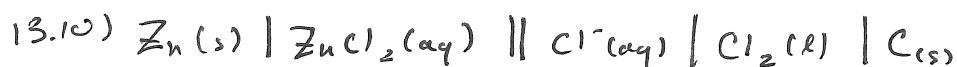
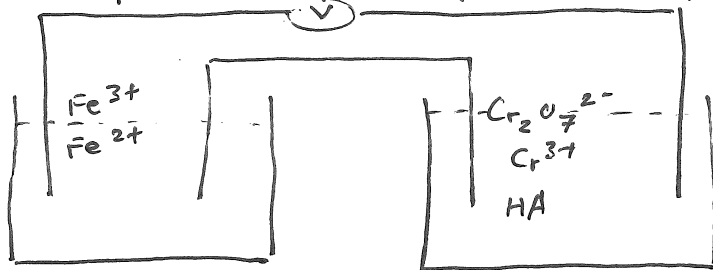
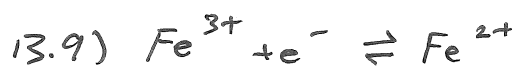
a) $I_2 + 2e^- \rightleftharpoons 2I^-$, I_2 is the oxidant.

b) $2S_2O_3^{2-} \rightleftharpoons S_4O_6^{2-} + 2e^-$, $S_2O_3^{2-}$ is the reductant.

c) $1 \text{ g } S_2O_3^{2-} / 112.13 \text{ g/mol} = 8.92 \text{ mmol } S_2O_3^{2-} = 8.92 \text{ mmol } e^-$

$(8.92 \times 10^{-3} \text{ mol}) (9.6485 \times 10^4) = 861 \text{ C}$

d) $861 \text{ C} / 60 \text{ s} = 14.3 \text{ A}$



Electrons will flow from Zn electrode to C electrode.

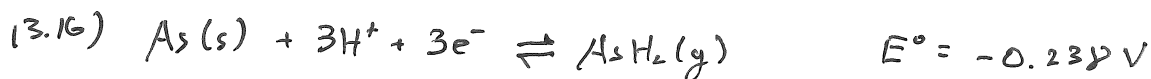


$$= \left[\frac{1}{2} (1e3) / 9.64e4 \right] (3600 \text{ s/hr})$$

$$= 18.7 \text{ mol Cl}_2$$

$$= 1.32 \text{ kg Cl}_2$$

13.12) Cl_2 , b/c it has most positive reduction potential.

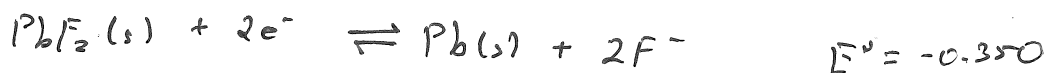


$$E = -0.238 - \frac{0.05916}{3} \log \frac{P_{\text{AsH}_3}}{[\text{H}^+]^3}$$

$$= -0.356 \text{ V}$$



$$[\text{NaF}] = [\text{KCl}] = 0.10 \text{ M}$$

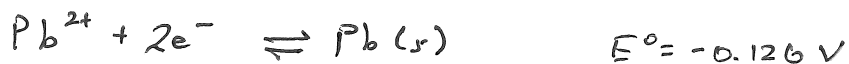
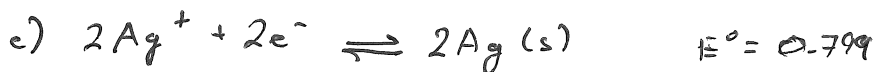


$$E_+ = 0.222 - \frac{0.05916}{2} \log [\text{Cl}^-]^2 = 0.2812 \text{ V}$$

$$E_- = -0.350 - \frac{0.05916}{2} \log [\text{F}^-]^2 = -0.2908 \text{ V}$$

$$E_{\text{cell}} = E_+ - E_- = 0.2812 + 0.2908 = 0.572 \text{ V}$$

b) Electrons flow from left half cell ($E = -0.2908 \text{ V}$) to right half cell ($E = 0.2812 \text{ V}$)



$$[\text{Pb}^{2+}] = K_{\text{sp}}(\text{PbF}_2) / [\text{F}^-]^2 = (3.6 \times 10^{-8}) / (0.10)^2 = 3.6 \times 10^{-6} \text{ M}$$

$$[\text{Ag}^+] = K_{\text{sp}}(\text{AgCl}) / [\text{Cl}^-] = (1.8 \times 10^{-10}) / (0.10) = 1.8 \times 10^{-9} \text{ M}$$

$$E_+ = 0.799 - \frac{0.05916}{2} \log \frac{1}{[\text{Ag}^+]^2} = 0.2812 \text{ V}$$

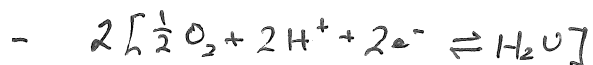
$$E_- = -0.126 - \frac{0.05916}{2} \log \frac{1}{[\text{Pb}^{2+}]} = -0.2870 \text{ V}$$

$$E_{\text{cell}} = E_+ - E_- = 0.2812 + 0.2870 = 0.568 \text{ V}$$

13.25

Calculate E° , ΔG° , K 

$$E^\circ_+ = 1.92\text{V}$$



$$E^\circ_- = 1.229\text{V}$$



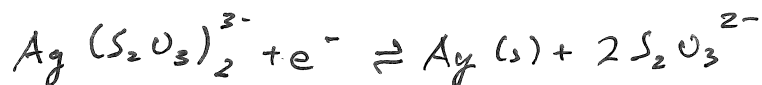
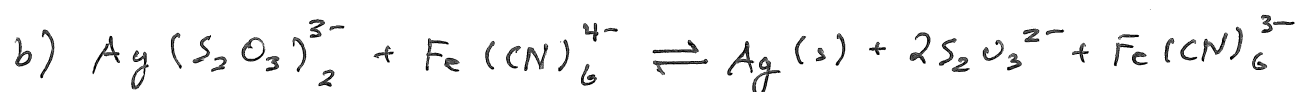
$$\Delta G^\circ = -nFE^\circ$$

$$K = 10^{nE^\circ/0.05916}$$

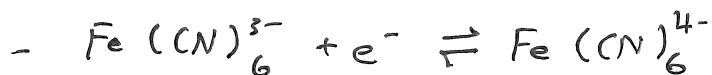
$$= -4 \cdot 96485 \cdot 0.691$$

$$= 10^{47}$$

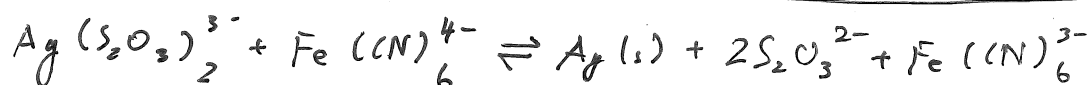
$$= -2.7 \times 10^5 \text{ J}$$



$$E^\circ_+ = 0.017\text{V}$$



$$E^\circ_- = 0.356\text{V}$$



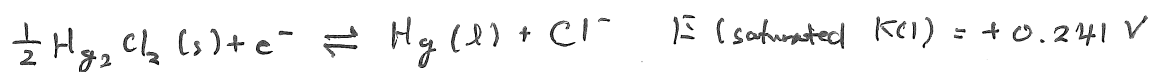
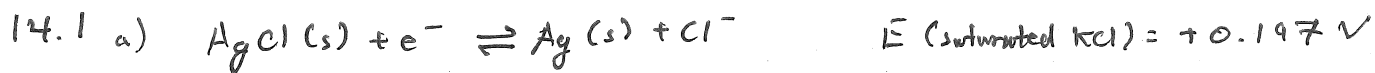
$$E^\circ = -0.339\text{V}$$

$$\Delta G^\circ = -nFE^\circ$$

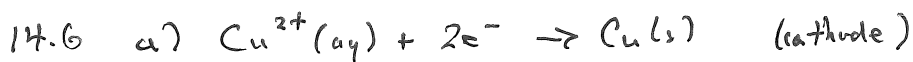
$$K = 10^{nE^\circ/0.05916}$$

$$= 32.7 \text{ kJ}$$

$$= 1.9 \times 10^{-6}$$



b) Predicted Voltage = $\cancel{0.197 - 0.241} = \cancel{-0.044 \text{ V}}$
 $0.241 - 0.197 = 0.044 \text{ V}$



b) $E = E^\circ + \frac{0.05916}{2} \log [\text{Cu}^{2+}]$
 $= 0.339 + \frac{0.05916}{2} \log (0.10)$
 $= 0.309 \text{ V}$

c) $E_{\text{cell}} = E_{\text{Cu}/\text{Cu}^{2+}} - E_{\text{SCE}} = 0.309 - 0.241$
 $= 0.068 \text{ V}$

14.12) A junction potential develops where dissimilar electrolyte solutions come into contact, and a voltage difference is observed.

This limits the accuracy of potentiometric analysis b/c the contribution of the junction potential to the measured voltage is unknown.

Figure 13-64 would not have a junction potential. b/c there are no liquid junctions.

14.13) H^+ has a greater mobility than K^+ . The HCl side HCl/KCl junction will be negative b/c H^+ diffuses into KCl region faster than K^+ diffuses into HCl region.

K^+ has a greater mobility than Na^+ , so this junction has the opposite sign.

HCl/KCl voltage is larger b/c the difference in mobility b/w H^+ and K^+ is greater than difference in mobility b/w K^+ and Na^+ .

14.26) pH of 0.025 M KH_2PO_4 / 0.025 M Na_2HPO_4 @ 20°C = 6.881

pH of 0.05 M potassium hydrogen phthalate @ 20°C = 4.002

$$\frac{E_{\text{unknown}} - E_{S1}}{\text{pH}_{\text{unknown}} - \text{pH}_{S1}} = \frac{E_{S2} - E_{S1}}{\text{pH}_{S2} - \text{pH}_{S1}}$$

$$\frac{E_{\text{unk}} - (-18.3 \text{ mV})}{\text{pH}_{\text{unk}} - 6.881} = \frac{(146.3 \text{ mV}) - (-18.3 \text{ mV})}{4.002 - 6.881} = -57.173 \text{ mV/pH unit}$$

$$\text{pH}_{\text{unk}} = \frac{E_{\text{unk}} - (-18.3 \text{ mV})}{-57.173} + 6.881$$

$$= 5.686$$

$$\text{observed slope} = -57.173 \text{ mV/pH unit}$$

$$\text{theoretical slope} = \frac{-RT \ln 10}{F}$$

$$= \frac{(8.31447 \text{ J } (293.15 \text{ K}) \ln 10)}{9.64853 \text{ e4 C/mol}}$$

$$= -0.05817 \text{ V}$$

$$\beta = \frac{\text{observed}}{\text{theoretical}} = \frac{-57.173}{-58.17} = 0.983$$

$$14.33 \quad E = \text{constant} - 0.05916 \log [CN^-]$$

$$a) \quad -0.230 \text{ V} = \text{constant} - 0.05916 \log (1e^{-3})$$

$$\text{constant} = -0.407 \text{ V}$$

$$b) \quad -0.300 = -0.407 - 0.05916 \log x$$

$$x = 1.55e^{-2} \text{ M}$$

$$c) \quad -0.230 = \text{constant} - 0.05916 \log (1e^{-3})$$

$$- \quad -0.300 = \text{constant} - 0.05916 \log x$$

$$0.070 = -0.05916 \log \frac{1e^{-3}}{x}$$

$$x = 1.52e^{-2} \text{ M}$$

$$14.35) \quad [F^-]_{\text{providence}} = 1.00 \text{ mg } F_{1/2} = 5.26e^{-5} \text{ M}$$

$$E_{\text{providence}} = \text{constant} - 0.05916 \log (5.26e^{-5})$$

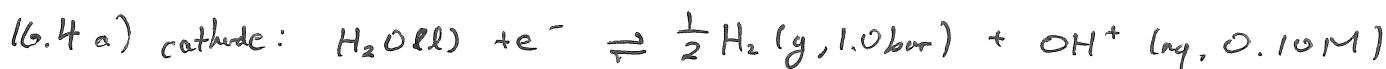
$$E_{\text{Forburn}} = \text{constant} - 0.05916 \log [F^-]_{\text{Forburn}}$$

$$\Delta E = E_{\text{Forburn}} - E_{\text{providence}} = 0.0400 \text{ V}$$

$$= -0.05916 \log \frac{[F^-]_{\text{Forburn}}}{5.26e^{-5}}$$

$$[F^-]_{\text{Forburn}} = 1.11e^{-5} \text{ M}$$

$$= 0.211 \text{ mg } / 2$$



$$E = E_+ - E_-$$

$$= \left[E_{\text{cath}}^\circ - 0.05916 \log \left(P_{\text{H}_2}^{\frac{1}{2}} [\text{OH}^-] \right) \right] - \left[E_-^\circ - 0.05916 \log ([\text{Br}^-]) \right]$$

$$= \left[-0.828 - 0.05916 \log (1.0^{\frac{1}{2}} \cdot 0.1) \right] - \left[1.078 - 0.05916 \log (0.1) \right]$$

$$= -1.906 \text{ V}$$

b) $R = 2.0 \Omega$, $I = 100 \text{ mA}$

$$\text{Ohmic potential} = IR = (0.1)(2.0) = 0.20 \text{ V}$$

c) $E = E_+ - E_- - IR - \text{Overpotentials}$

$$= -1.906 - 0.2 - (0.20 + 0.40)$$

$$= -2.71 \text{ V}$$

d) $E_+ = E_+^\circ - 0.05916 \log \left(P_{\text{H}_2}^{\frac{1}{2}} [\text{OH}^-] \right)$

$$= -0.828 - 0.05916 \log (1.0^{\frac{1}{2}} \cdot 1.0)$$

$$= -0.828 \text{ V}$$

$$E_- = E_-^\circ - 0.05916 \log ([\text{Br}^-])$$

$$= 1.078 - 0.05916 \log (1.0^{\frac{1}{2}} \cdot 0.010)$$

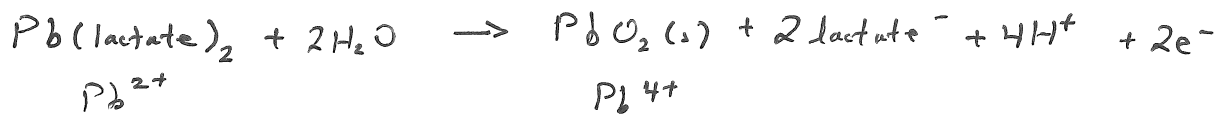
$$= 1.196 \text{ V}$$

$$E = E_+ - E_- - IR - \text{Overpotentials}$$

$$= -0.828 - 1.196 - 0.20 - (0.20 + 0.40)$$

$$= -2.82 \text{ V}$$

16.9



lead is oxidized to PbO_2 at the anode.

$$\frac{385.3}{239.2} \cdot 0.1111\text{g} = 0.1790\text{g}$$

$$\% \text{ Pb(lactate)} = \frac{0.1790}{0.3268} \cdot 100 = 54.77\%$$

16.13 When excess Br_2 is in solution, current flows at a low applied potential difference (0.25 V) in the detector circuit by virtue of the reactions:



16.15 5 mA delivered for 0.1 s

$$\text{a) } (0.005\text{ A})(0.1) = 0.0005\text{ C}$$

$$\frac{0.0005\text{ C}}{96485\text{ C/mol}} = 5.2 \times 10^{-9}\text{ mol } \frac{1}{2}\text{e}^-$$

b) $0.02\text{ mol e}^-/\text{L}$ delivered.

$$\frac{5.2 \times 10^{-9}\text{ mol}}{0.02\text{ mol/L}} = 2.6 \times 10^{-7}\text{ L} = 0.00026\text{ mL}$$

$$= 0.26\text{ nL}$$

16.23

- a) The glucose monitor has a test strip w/ 2 carbon indicator electrodes, and a $\text{Ag}|\text{AgCl}$ reference electrode.

When blood is placed on the test strip, glucose is oxidized near indicator electrode 1 by mediator to gluconolactone and the mediator is reduced.

With a potential of $+0.2\text{ V}$ on the indicator electrode, reduced mediator is re-oxidized at the indicator electrode.

The current b/w indicator electrode 1 and the reference electrode is \propto to the rate of oxidation of the mediator, which is \propto to the conc. of glucose + interfering species in the blood.

Indicator electrode 2 has mediator but not glucose oxidase.

Current measured b/w indicator electrode 2 and reference electrode is \propto to the conc. of interfering species in the blood.

This difference b/w the two currents is then \propto to the conc. of glucose in the blood.

- b) w/o a mediator, rate of oxidation of glucose is dependent on conc. of O_2 in the blood.

If O_2 levels in the blood are low, a low, inaccurate reading of glucose conc. will be taken.

A conc. of mediator that is constant and high will ensure that ~~as~~ variations in current are mainly due to glucose conc. variations.

- c) Glucose oxidase is replaced by glucose dehydrogenase, which does not use O_2 as a reactant.

The enzyme oxidizes glucose and reduces PQQ cofactor to PQQH_2 , which is then oxidized back to PQQ by nearby Os^{3+} bound to the polymer chain.

By moving from Os to Os , e^- can reach the carbon electrode.

The coulometric sensor measures the total # of e^- needed to oxidize the glucose in the blood sample.

d) Amperometry measures current during enzyme-enabled oxidation of glucose.

Current is \propto to rate of oxidation.

The rates of most reactions increase w/ increasing temperature.

Therefore, current will increase w/ increasing temperature of the blood sample.

Coulometry measures the total # of e^- released in oxidation.

Glucose releases $2e^-$ per molecule, independent of temperature.

The coulometric signal should not have any temperature dependence.

e) $1.00 \text{ g glucose} / \text{L} = 5.55 \text{ mM glucose}$.

$0.300 \times 10^{-6} \text{ L}$ contains $1.665 \text{ nmol glucose}$.

1 mol glucose releases $2e^-$, $2H^+$ in oxidation.

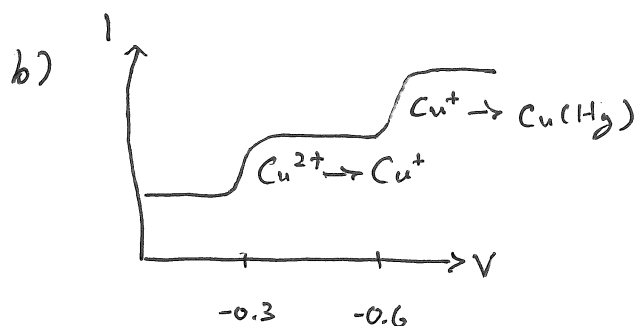
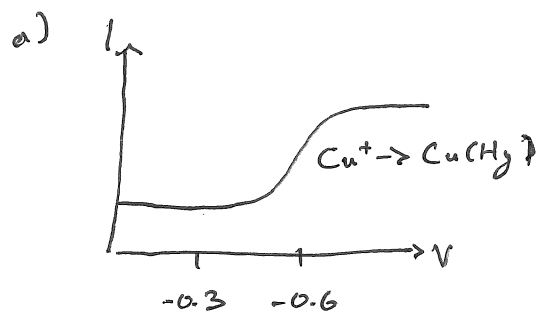
$\Rightarrow 2 \times 1.665 \text{ nmol} = 3.33 \text{ nmol } e^- \text{ released}$.

$Q = nF = (3.33 \times 10^{-9}) (96485) = 321 \mu\text{C}$.

16.25 $1\text{M NH}_3 / 1\text{M NH}_4\text{Cl}$ solution

Cu^{2+} reduced to Cu^+ near -0.3 V

$\text{Cu}^+ \rightarrow \text{Cu(Hg)}$ near -0.6 V



c) The potential for $\text{Cu(I)} \rightarrow \text{Cu(Hg)}$ will change, if Pt is used, since product cannot be Cu amalgam.

16.32) Peak B: $\text{RNH}_2\text{OH} \rightarrow \text{RNO} + 2\text{H}^+ + 2\text{e}^-$

Peak C: $\text{RNO} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{RNH}_2\text{OH}$

Peak C was not seen in the initial scan b/c RNO was not initially present.