

CHEMISTRY 133

Spring, 2017 HW 1.3 Solutions

1.3.1. Which type of noise is best reduced by shielding the critical electronics?

Interference. *In interference electrical signals from other sources are picked up. Thus, these need shielding most.*

1.3.2. An instrument measures the concentration of a compound in a river that varies on the order of minutes. Most of the noise associated with the measurement occurs at frequencies greater than 1 Hz. Suggest a method (analog or digital) to increase the signal to noise ratio.

Since it is stated that most of the noise is associated with higher frequencies but that concentrations are expected to vary slowly, we want to decrease high frequency noise (at frequencies greater than ~0.1 Hz – too fast to affect signal). A number of approaches could be used including:

RC (low pass) filter (analog method)

Moving average or simply 1 minute average data (digital method)

1.3.3. What type of noise can be reduced by using internal amplification in a transducer?

Shot noise. *Shot noise and internal amplification are associated with current based measurements.*

1.3.4. What type of noise can be reduced by cooling electrical components?

Thermal noise.

R&R 6.13

With a bandpass of 20kHz,

a) What is the magnitude of the shot noise for a 1 μA current? For a 1 pA current?

$$I = 1 \mu\text{A}; I_{\text{noise}} = (2qIB)^{0.5} = [(2)(1.60 \times 10^{-19} \text{ C})(1.0 \times 10^{-6} \text{ A})(20,000 \text{ s}^{-1})]^{0.5}$$

$$I_{\text{noise}} = 8 \times 10^{-11} \text{ A} = 80 \text{ pA}$$

$$I = 1 \text{ pA}; I_{\text{noise}} = 8 \times 10^{-14} \text{ A} = 0.08 \text{ pA}$$

b) What fraction of the 1 A, 1 μA , and 1 pA DC current is the shot noise fluctuation?

$$I = 1 \text{ A}; I_{\text{noise}} = 8.0 \times 10^{-8} \text{ A or fraction} = 8.0 \times 10^{-8} \text{ A} / 1 \text{ A} = 8 \times 10^{-8}$$

$$\text{for } I = 1 \mu\text{A}; \text{fraction} = 8.0 \times 10^{-11} \text{ A} / 1.0 \times 10^{-6} \text{ A} = 8 \times 10^{-5}$$

$$\text{for } I = 1 \text{ pA}; \text{fraction} = 0.08 \text{ pA} / 1 \text{ pA} = 0.08$$

5. A sample is measured 12 times by a spectroscopic method. The average concentration and standard deviation in the average are found to be $5.2 \pm 0.7 \mu\text{M}$. With the assumptions made below answer the following questions:

Assume: 1) noise is purely random, 2) the noise is defined as the standard deviation, and 3) that the standard deviation is well-represented. (The third assumption allows you to avoid using t-factors in signal averaging)

a) What signal to noise ratio would be expected in a single measurement?

$$S/N = 5.2/0.7 = 7.4$$

b) What is the signal to noise in the average value for the twelve measurements?

$$[(S/N)_{n=12}/(S/N)_{n=1}] = (12/1)^{0.5} = 3.46$$

$$(S/N)_{n=12} = 7.4 * 3.46 = 26$$

c) A researcher needs to have the noise be less than 2% of the value in a particular experiment. How many measurements should she make?

$$(S/N)_n = 1/0.02 = 50 \text{ and } [(S/N)_{n=12}/(S/N)_{n=1}] = (n/1)^{0.5}$$

or $50/7.4 = (n)^{0.5}$ or $n = (50/7.4)^2 = 45.3$ so **46 measurements** will exceed the limit desired

Harris Text: Ch. 13: 1, 5, 10, 16, 19, 28, 36

1. Explain the difference between electric charge (q, coulombs), electric current (I, amperes), and electric potential (E, volts).

Electric charge is from the surplus of negative or positively charge ions or electrons. An electric current is the flow of charged species, and an electric potential is the work needed to move charged species.

5. Consider the redox reaction: $I_2 + 2S_2O_3^{2-} \leftrightarrow 2I^- + S_4O_6^{2-}$

a) Identify the oxidizing agent on the left side of the reaction and write a balanced oxidation half-reaction.

The oxidizing agent is being reduced. This is I_2 which goes from an oxidation state of 0 to -1.

Half reaction for oxidation: $2S_2O_3^{2-} \leftrightarrow S_4O_6^{2-} + 2e^-$

b) Identify the reducing agent of the left side of the reaction and write a balanced reduction half-reaction.

The reducing agent is being oxidized. This is $S_2O_3^{2-}$ in which the oxidation state of the S atoms go from +2 to +2.5 (on average). Half reaction for reduction: $I_2(s) + 2e^- \leftrightarrow 2I^-$

c) How many coulombs of charge are passed from reductant to oxidant when 1.00 g of thiosulfate reacts?

$$\text{moles } e^- = (1.00 \text{ g } S_2O_3^{2-}) / (112 \text{ g } S_2O_3^{2-} / \text{mol } S_2O_3^{2-}) (2 \text{ mol } / 2 \text{ mol } e^-) = 0.00892 \text{ mol } e^-$$

$$q = nF = 861 \text{ C}$$

d) If the rate of reaction is 1.00 g of thiosulfate consumed per minute, what current (in amperes) flows from reductant to oxidant?

$$I = (861 \text{ C/min}) (1 \text{ min}/60s) = 14.3 \text{ A}$$

10. Consider the rechargeable battery



a) Write reduction half-reactions for each electrode. From which electrode will electrons flow from the battery into a circuit if the electrode potentials are not too different from E° values?

*left half: $Zn^{2+} + 2e^- \leftrightarrow Zn(s)$ $E^\circ = -0.762 \text{ V}$; right half: $Cl_2(l) + 2e^- \leftrightarrow 2Cl^-(aq)$ $E^\circ = 1.396 \text{ V}$ (assuming $Cl_2(l)$ was supposed to actually be $Cl_2(aq)$). When the battery is being used (as opposed to being charged, $E > 0$, so Zn must be being oxidized and supplying the electrons. **The zinc electrode supplies the electrons.***

b) If the battery delivers a constant current of $1.00 \times 10^3 \text{ A}$ for 1.00 h, how many kg of Cl_2 will be consumed?

$$I = 1.00 \times 10^3 \text{ A for } 1.00 \text{ h. Thus } q = I \cdot t = 1.00 \times 10^3 \text{ C/s} \cdot 1.00 \text{ h} \cdot 3600 \text{ s/h} = 3.6 \times 10^6 \text{ C}$$

$$q = n \cdot F \text{ or } n(e^-) = q/F = 3.6 \times 10^6 \text{ C} / (96500 \text{ C/mole } e^-) = 37.3 \text{ moles of } e^-$$

$$\text{moles of } Cl_2 = 0.5 \cdot \text{moles of } e^- = 18.7 \text{ moles}$$

$$\text{Mass of } Cl_2 = 18.7 \cdot 70.9 \text{ g/mol} = 1.32 \text{ kg}$$

16. Write the Nernst equation for the following half-reaction and find E when pH = 3.00 and $P_{AsH_3} = 1.00$ mbar. $As(s) + 3H^+ + 3e^- \leftrightarrow AsH_3(g)$ $E^\circ = -0.238$ V
 $E = E^\circ - (0.05916/3)\log\{P_{AsH_3}/[H^+]^3\}$
 $= -0.238\text{ V} - 0.01972\log\{[1.00\text{ mbar}/(1013\text{ mbar/atm})]/(10^{-3})^3\}$
 $= -0.238\text{ V} - 0.01972\log[(0.000987\text{ atm})/10^{-9}] = -0.238\text{ V} - 0.1182\text{ V} = \mathbf{-0.356\text{ V}}$

19. Suppose that the concentrations of NaF and KCl were each 0.10 M in the cell:
 $Pb(s)|PbF_2(s)|F^-(aq)||Cl^-(aq)|AgCl(s)|Ag(s)$.

a) Using the half-reactions $2AgCl(s) + 2e^- \leftrightarrow 2Ag(s) + 2Cl^-$ and $PbF_2(s) + 2e^- \leftrightarrow Pb(s) + 2F^-$, calculate the cell voltage.

$E = E_{red} - E_{ox}$ (note both quantities are calculated as **reduction** potentials) with
 $E_{red} = 0.222\text{ V} - (0.05916/2)\log[Cl^-]^2 = 0.222\text{ V} + 0.05916\text{ V} = 0.281\text{ V}$
and $E_{ox} = -0.350\text{ V} - (0.05916/2)\log[F^-]^2 = -0.350\text{ V} - (0.05916/2)\log(0.10)^2 = -0.350 + 0.05916$ or $E_{ox} = -0.291\text{ V}$
 $E = E_{red} - E_{ox} = 0.281\text{ V} - (-0.291\text{ V}) = \mathbf{0.572\text{ V}}$

b) By the reasoning in Figure 13-8, in which direction do electrons flow?

The electrons are supplied by the oxidation reaction or from the Pb/PbF₂ electrode and go to the Ag/AgCl electrode.

c) Now calculate the cell voltage by using the reactions $2Ag^+ + 2e^- \leftrightarrow 2Ag(s)$ and $Pb^{2+} + 2e^- \leftrightarrow Pb(s)$. For this part you will need the solubility products for PbF₂ and AgCl.

We need to calculate $[Ag^+]$ and $[Pb^{2+}]$. $[Ag^+] = K_{sp}/[Cl^-] = 1.8 \times 10^{-10}/0.10\text{ M} = 1.8 \times 10^{-9}\text{ M}$
 $[Pb^{2+}] = 3.6 \times 10^{-8}/(0.1)^2 = 3.6 \times 10^{-6}\text{ M}$

Now, $E = E_{red} - E_{ox}$ with

$E_{red} = 0.799\text{ V} - (0.05916/2)\log(1/[Ag^+]^2) = 0.799 - 0.517\text{ V} = 0.282\text{ V}$
and $E_{ox} = -0.126\text{ V} - (0.05916/2)\log(1/[Pb^{2+}]) = -0.287\text{ V}$
 $E = E_{red} - E_{ox} = 0.282\text{ V} - (-0.287\text{ V}) = \mathbf{0.569\text{ V}}$

28. Calculate E° for the half-reaction $Pd(OH)_2(s) + 2e^- \leftrightarrow Pd(s) + 2OH^-$ given that K_{sp} for $Pd(OH)_2$ is 3×10^{-28} and $E^\circ = 0.915\text{ V}$ for the reaction $Pd^{2+} + 2e^- \leftrightarrow Pd(s)$.

Rxn: $Pd(OH)_2(s) + 2e^- \leftrightarrow Pd(s) + 2OH^- = [Pd(OH)_2(s) \leftrightarrow Pd^{2+} + 2OH^-] + [Pd^{2+} + 2e^- \leftrightarrow Pd(s)]$

For 1 mol of $Pd^{2+} + 2e^- \leftrightarrow Pd(s)$, $\Delta G^\circ = -nFE^\circ = -(2)(96,490\text{ C/mol } e)(0.915\text{ V}) = -176.6\text{ kJ/mol}$

For 1 mol of $Pd(OH)_2(s) \leftrightarrow Pd^{2+} + 2OH^-$, $\Delta G^\circ = -RT\ln K = -8.314(298)\ln(3 \times 10^{-28}) = 157.0\text{ kJ/mol}$

For 1 mol of $Pd(OH)_2(s) + 2e^- \leftrightarrow Pd(s) + 2OH^-$, $\Delta G^\circ = -176.6 + 157.0\text{ kJ/mol} = -19.6\text{ kJ/mol}$
 $E^\circ = -\Delta G^\circ/nF = 19.6/(2 \cdot 96490\text{ C/mol } e) = \mathbf{0.101\text{ V}}$

36. The quinhydrone electrode was introduced in 1921 as a way of measuring pH.

$Pt(s)|1:1\text{ mole ratio of quinone(aq) and hydroquinone(aq), unknown pH}||Cl^-(aq, 0.5\text{ M})|Hg_2Cl_2(s)|Hg(l)|Pt(s)$

The solution whose pH is to be measured is placed in the left half-cell, which also contains a 1:1 mole ratio of quinone and hydroquinone. The half-cell reaction is:

$OC_6H_4O + 2H^+ + 2e^- \leftrightarrow HOC_6H_4OH$

a) Write half-reactions and Nernst equations for each half-cell.

oxidation side: $OC_6H_4O + 2H^+ + 2e^- \leftrightarrow HOC_6H_4OH$ (note: oxidation side based on cell notation)

convention but could be reduction reaction)

$$E = E_{ox}^{\circ} - (0.05916/2)\log\{[HOC_6H_4OH]/([OC_6H_4O][H^+]^2)\}$$

reduction side: $Hg_2Cl_2(s) + 2e^- \leftrightarrow 2Hg(l) + 2Cl^-$

$$E = E_{red}^{\circ} - (0.05916/2)\log[Cl^-]^2$$

b) Ignoring activities, rearrange the Nernst equation for the net reaction to form $E(\text{cell}) = A + (B \cdot \text{pH})$, where A and B are constants. Calculate A and B at 25°C.

$$E_{ox} = 0.700 \text{ V} - (0.05916/2)\log(1/[H^+]^2) = 0.700 \text{ V} - (-0.05916\log[H^+]) = 0.700 \text{ V} - 0.05916\text{pH}$$

$$E_{red} = E_{red}^{\circ} - (0.05916/2)\log[Cl^-]^2 = 0.268 \text{ V} - 0.05916\log(0.5) = 0.268 + 0.0178 \text{ V} = 0.286 \text{ V}$$

$$E = E_{red} - E_{ox} = 0.286 - (0.700 - 0.05916\text{pH}) = -0.414 + 0.05916\text{pH} \text{ or } A = -0.414 \text{ and } B = 0.05916$$

c) If the pH were 4.50, in which direction would electrons flow through the potentiometer?

At $\text{pH} = 4.50$, $E = -0.414 + 0.05916(4.5) = -0.148 \text{ V}$. Since the potential is negative, the opposite electrodes are the oxidation and reduction electrodes. So the actual reduction electrode is the quinone/hydroquinone electrode and the electrons are produced at the Hg/Hg_2Cl_2 electrode.