

Name: _____
Chemistry 332
Third Hour Exam

1A.(10 points) Diagram, describe and give potentials for two of the three reference electrodes we talk about in class.

I was looking for diagram like the left half of figure 14-6 for the Standard Hydrogen Electrode with a potential of 0.00

-or-

A diagram like figure 14-9 for the silver-silver chloride electrode with a potential of +.222 V if filled with 1M KCl or +.197 for saturated KCl

-or-

A diagram like figure 14.10 for the calomel electrode with a potential of +.268 if it is filled with 1M KCl or +.241 if filled with saturated KCl.

1B. (5 points) If I have a potential of .15 V vs a SHE electrode, what would that potential be when measured against each of your chosen electrodes?

.15 V SHE

.072 Silver filled with 1M KCl

.047 Silver filled with saturated KCl

.118 Calomel filled with 1M KCl

.091 Calomel filled with saturated KCl

2. (10 points) Diagram and describe two different types of ion selective electrodes work

Glass electrode - Figure 15-7 - Works because a glass has been formulated that acts as if allows certain cations (most common example is H^+) can pass through the glass.

Solid State electrode Figure 15-12 Works by having an insoluble crystal that contains the ion of interest as a barrier between the reference electrode and the sensing electrode. The insoluble crystal allows only the ion of interest to pass between the two electrodes.

Liquid based Ion-selective Figure 15-14 Works by having a hydrophobic ion exchanger in a hydrophobic solution pass the ion of interest between the reference and sensing electrode.

Compound Electrode Figure 15-17 A semipermeable membrane is placed around the outside of a pH sensing glass electrode. Usually an enzyme is placed in solution in the space between the semipermeable membrane and the electrode to convert some compound into either an acid, or make a reaction to produce H^+ to make the electrode sense the presence of the compound of interest.

3. (10 points) Suppose you found a plastic that was permeable only to Cl^- . Make a diagram and describe how you would use this plastic to make a Cl^- selective electrode.

I would have a glass tube and glue a disk of this plastic on the end. Then build something that looked like the Solid State electrode shown in figure 15-12, and fill the electrode with 1M NaCl, and put a second Ag/AgCl in the solution.

4. (15 points) In class we talked about three major designs for visible spectrometers. Make a block diagram showing the major components of these three types of spectrometers, and compare and contrast these designs for accuracy, expense, speed. (You may need the back of this page for more space)

Single beam diagram like Figure 18-4

Double beam diagram like figure 19-1

Photodiode array diagram like figure 19-11

Accuracy

Most accurate - Double beam; least accurate - Single beam and Photodiode in a tie.

Expense

Most expensive - Double beam; middle- Photodiode ; least expensive-Single beam

Speed

Fastest- Photodiode; Middle Double beam; Slowest -Single beam.

5. (10 points) Define the following terms

Fluorescence When energy is lost from a Singlet excited state by the emission of light as the molecule drops directly to a Singlet ground state. This is an allowed transition so the emission of light occurs very quickly after the original excitation.

Phosphorescence When energy is lost from a Triplet excited state by the emission of light as the molecule drops directly to a Singlet ground state. This is a 'forbidden' transition so the emission of light occurs long after the original excitation.

Intersystem crossing Radiationless transition between states with different spin quantum numbers. This is a forbidden transition, so it does not occur very frequently.

Internal Conversion Radiationless transition between states with the same spin quantum number.

Luminescence Any process where light is emitted from molecule.

Singlet State A state where all electrons in a molecule are spins paired, so there is not net spin quantum number for the molecule.

Triplet State A state where at least two electrons are in a parallel spin state so there is a net spin quantum number for the molecule.

Junction potential A potential that arises when ions cannot cross a junction at the same speed, so a charge differential builds up between the ions at the junction.

Salt Bridge A junction that allows ions to pass between different solutions, or

between an electrode and the bulk solution.

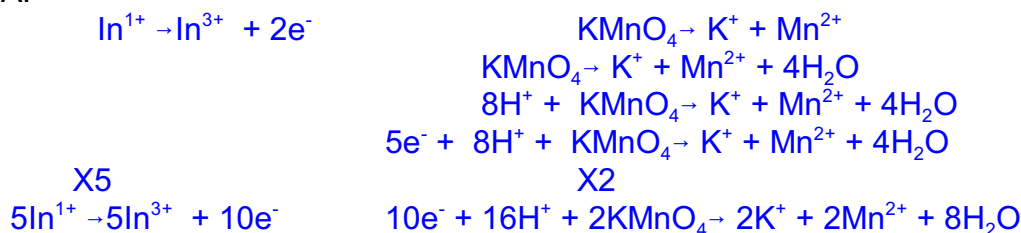
Monochromatic Light - Light of a Single wavelength

Take Home

6. (20 points) I have a 20.00 ml solution that is .1937 M In^+ , I would like to titrate this solution with .2003 M KMnO_4 . Assuming that you are going to titrate In^+ to In^{3+} , MnO_4^- to Mn^{2+} , and buffer the solution to be at pH 2, answer the following questions:

- What is the balanced net reaction for this titration?
- What is the volume of KMnO_4 required to get to the equivalence point?
- What is the potential of the solution 1/3 of the way to the equivalence point?
- What is the potential of the solution at the equivalence point?
- What is the potential of the solution 5 mls after the equivalence point?

A.



Combining equations



Removing common terms for net reaction:



B.

$$\begin{aligned} 20 \times .1937 &= 3.874 \text{ mmoles In}^{1+} \\ 3.874 \text{ mmoles In}^{1+} \times (2 \text{ moles KMnO}_4 / 5 \text{ moles In}^{1+}) &= 1.5496 \text{ mmoles KMnO}_4 \\ 1.5496 \text{ mmoles} &= X \text{ ml} \times .2003 \text{ M} \\ X &= 1.5496 / .2003 \\ &= \mathbf{7.736 \text{ ml}} \end{aligned}$$

C.

$$\begin{aligned} 7.736 \times .33333 &= 2.578 \text{ ml} \\ \text{mmoles KMnO}_4 &= 2.578 \text{ ml} \times .2003\text{M} = .5165 \text{ mmoles} \\ \text{mmoles In}^{1+} &= 20 \text{ ml} \times .1937 = 3.874 \text{ mmoles} \end{aligned}$$

Reaction Table (ignoring H^+ , K^+ and H_2O)

$$5\text{In}^{1+}(\text{aq}) + 2\text{KMnO}_4(\text{aq}) \rightarrow 2\text{Mn}^{2+}(\text{aq}) + 5\text{In}^{3+}(\text{aq})$$

Initial	3.874	.5164	0	0
Rxn	-5/2(.5164)	-.5164	+.5164	+5/2(.5164)
Net	2.583	0	.5164	1.291

Use Analyte (Indium) Nernst equation to get potential of solution



$$E = -.444 - .059/2 \log (\text{In}^{1+}/\text{In}^{3+})$$

Converting mmoles back to molarities

$$[\text{In}^{1+}] = 2.583 / (20 + 2.578) = .1144$$

$$[\text{In}^{3+}] = 1.291 / (20 + 2.578) = .05718$$

$$= -.444 - .0295 \log (.1144 / .05718)$$

$$= -.444 - .0295(.3012)$$

$$= \mathbf{-.453}$$

D.

$$E = (n_1 E^{\circ}_1 + n_2 E^{\circ}_2) / (n_1 + n_2)$$

$$E^{\circ}_1 = -.444 \text{ for the Indium}$$

$$E^{\circ}_2 = 1.507 \text{ for permanganate}$$

Your first guess is to plug the numbers directly from the table

$$E = [2(-.444) + 5(1.507)] / (2+5)$$

$$= (-.888 + 7.535) / 7$$

$$= \mathbf{.950}$$

I gave partial credit for this answer, but it is **wrong** because you have to factor the pH into E°_2 !

For the Permanganate you have the $\frac{1}{2}$ reaction



$$\text{and } E = 1.507 - .059/5 \log [(\text{Mn}^{2+})(\text{H}_2\text{O})^4 / (\text{MnO}_4^-)(\text{H}^+)^8]$$

Water is a constant so it will not change and gets lumped into the E°

Since the solution is buffered H^+ is also constant, but we need to put it into the E° ourselves

The solution is buffered at pH 2 so $[\text{H}^+] = .01$

$$E = 1.507 - .059/5 \log [(\text{Mn}^{2+}) / (\text{MnO}_4^-) (.01)^8]$$

Using properties of logs

$$E = 1.507 - .059/5 [\log (\text{Mn}^{2+}) / (\text{MnO}_4^-) + \log (1 / (.01)^8)]$$

$$E = 1.507 - .059/5 \log (\text{Mn}^{2+}) / (\text{MnO}_4^-) - .059/5 \log (1 / (.01)^8)$$

$$E = 1.507 - .059/5 \log (1 / (.01)^8) - .059/5 \log (\text{Mn}^{2+}) / (\text{MnO}_4^-)$$

$$E = 1.507 - .059/5 \log (1 / 1 \times 10^{-16}) - .059/5 \log (\text{Mn}^{2+}) / (\text{MnO}_4^-)$$

$$E = 1.507 - .059/5 \log (1 \times 10^{+16}) - .059/5 \log (\text{Mn}^{2+}) / (\text{MnO}_4^-)$$

$$E = 1.507 - .059/5 (16) - .059/5 \log (\text{Mn}^{2+}) / (\text{MnO}_4^-)$$

$$E = 1.507 - .189 - .059/5 \log (\text{Mn}^{2+}) / (\text{MnO}_4^-)$$

Lumping these first two terms together into an $E^{0'}$ for this pH

$$E^{0'} = 1.507 - .189 = 1.318$$

And this what we should plug into the equivalence point equation

$$= [2(-.444) + 5(1.318)] / (2+5)$$

$$= (-.888 + 6.590) / 7$$

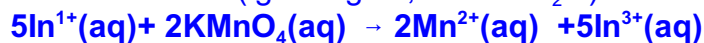
$$= \mathbf{.815}$$

E.

5 mls after the equivalence point

= 5 + 7.736 mls of KMnO_4

= 12.736 mls

mmoles $\text{KMnO}_4 = 12.736 \text{ ml} \times .2003\text{M} = 2.5510 \text{ mmoles}$ mmoles $\text{In}^{1+} = 20 \text{ ml} \times .1937 = 3.874 \text{ mmoles}$ Reaction Table (ignoring H^+ , K^+ and H_2O)

Initial	3.874	2.551	0	0
Rxn	-3.874	-2/5(3.874)	+2/5(3.874)	+3.874
Net	0	1.0014	1.5496	1.291

Use Titrant (KMnO_4) Nernst equation to get potential of solution

$$\text{and } E = 1.507 - .059/5 \log [(\text{Mn}^{2+})(\text{H}_2\text{O})^4/(\text{MnO}_4^-)(\text{H}^+)^8]$$

Here you should have recognized that pH plays a role so you should include the $[\text{H}^+] = .01$ term in your calculation.

Converting mmole of KMnO_4 and Mn^{2+} back into molarities

$$[\text{KMnO}_4] = 1.0014 \text{ mmoles} / (20 + 12.736) \text{ ml} \\ = .03059 \text{ M}$$

$$[\text{Mn}^{2+}] = 1.5496 \text{ mmoles} / (20 + 12.736) \text{ ml} \\ = .04734 \text{ M}$$

$$E = 1.507 - .059/5 \log [.04734/.03059(.01)^8] \\ = 1.507 - .0118 \log 1.547 \times 10^{16} \\ = 1.507 - .0118(16.19) \\ = 1.507 - .191 \\ = \mathbf{1.316 \text{ V}}$$

I should also be able to get this using my E° that I derived in part D

$$E = E^\circ - .059/5 \log (\text{Mn}^{2+})/(\text{MnO}_4^-)$$

$$E = 1.318 - .059/5 \log (\text{Mn}^{2+})/(\text{MnO}_4^-)$$

$$E = 1.318 - .059/5 \log .04734/.03059$$

$$= 1.318 - .059/5 (.18965)$$

$$= 1.318 - .002$$

$$= \mathbf{1.316 \text{ V}}$$

7. (20 points) Compound A has an ϵ_{300} of $3,000 \text{ M}^{-1}\text{cm}^{-1}$ and an ϵ_{250} of $35,000$. Compound B has an ϵ_{300} of $44,000 \text{ M}^{-1}\text{cm}^{-1}$ and an ϵ_{250} of $2,000$. If a mixture of these two compounds has a 77% transmittance at 250 nm and a 59% transmittance at 300 nm in a 0.1 cm cell, what are the concentrations of these two compounds in the cell?

What I did here was to make an Excel spreadsheet that uses the equations given on page 405 of your text to solve this system with minimal roundoff error

With this spreadsheet I get

$$D = -153400000$$

$$[A] = 2.957 \times 10^{-5}$$

$$[B] = 5.005 \times 10^{-5}$$