

Name: _____

Chem 2113

Test 4

Summer 2002

Questions are worth 25 points each. OMIT ONE QUESTION by clearly writing OMIT in the space provided for your work. If you fail to mark OMIT on a question I will omit the last question of the test. Show your work and circle your answers for full credit.

1. To determine the amount of manganese in a sample, 0.9421 g of that sample was dissolved in nitric acid and diluted to 500.0 mL in a volumetric flask. From this solution, two 50.00 mL aliquots were taken and treated as follows:

<u>Vol. 74.1 ppm Mn</u>	<u>Mass KIO₄</u>	<u>Final Volume</u>	<u>%T for the solution</u>
0.00	0.80 g	100.0	61.3%
5.00	0.80 g	100.0	19.6%

Calculate the percent manganese in the original sample.

Absorbance for the solutions: $2 - \log(61.3) = 0.212_5$
 $2 - \log(19.6) = 0.707_7$

Concentration from standard: $74.1 * 5.00 / 100 = 3.70_5$ ppm

$$\text{Slope} = \frac{\text{rise}}{\text{run}} = \frac{(0.7077 - 0.2125)}{3.705} = 0.133_7 = m$$

$$\text{y-intercept} = 0.212_5 = b$$

$$\text{-x intercept} = b / m = 0.212_5 / 0.133_7 = 1.59_0 \text{ ppm from the unknown}$$

$$\text{Concentration in the unknown} = 1.59_0 * 100 / 50 = 3.18_0 \text{ ppm}$$

$$3.18_0 \text{ mg/L} * 0.500 \text{ L} = 1.59_0 \text{ mg Mn}$$

$$(1.59_0 \text{ mg Mn} / 942.1 \text{ mg sample}) * 100\% = \underline{0.169\% \text{ Mn}}$$

2. Nickel can be determined by complexation with 8-hydroxyquinolinol followed by measurement of the absorption of the solution at 365 nm. Solutions of nickel were treated appropriately, and the following data were obtained:

$[\text{Ni}^{2+}]$	% T	A
0.00	100%	0
5.0×10^{-5}	69.4%	0.158 ₆
1.0×10^{-4}	49.2%	0.308 ₀
2.0×10^{-4}	22.3%	0.651 ₇

Calculate the following quantities for the **linearly related** data. [HINT: Do you have to manipulate any of the given values?] Using the A values we calculated for y...

$$\Sigma x = 3.5 \times 10^{-4}$$

$$\Sigma y = 1.118_3$$

$$\Sigma x^2 = 5.25 \times 10^{-8}$$

$$\Sigma y^2 = 0.54475887$$

$$\Sigma xy = 1.69075 \times 10^{-4}$$

$$n = 4$$

Determine the values for the following:

$$S_{xx} = 2.1875 \times 10^{-8}$$

$$S_{yy} = 0.2320706876$$

$$S_{xy} = 7.12171 \times 10^{-5}$$

$$m = 325_6$$

$$b = -0.005_2$$

$$r = 0.9995$$

An unknown containing nickel was analyzed using the above method. A 0.100 g sample of the unknown was dissolved and diluted to 250.0 mL. A 50.00 mL aliquot of this solution was then treated with the 8-hydroxyquinolinol, and diluted to 100.0 mL. The transmittance for this treated solution was determined to be 12.7%T. Calculate the percent nickel in the original sample.

$$A = 2 - \log(12.7) = 0.896_2, \therefore x = (y - b) / m = (0.896_2 - (-0.005_2)) / 325_6 = 2.7_7 \times 10^{-4} \text{ M}$$

$$2.7_7 \times 10^{-4} \times 100 / 50 = 5.5_4 \times 10^{-4} \text{ M in the original solution}$$

$$5.5_4 \times 10^{-4} \times 0.250 = 1.3_8 \times 10^{-4} \text{ moles of nickel}$$

$$1.3_8 \times 10^{-4} \times 58.7 = 8.1_2 \times 10^{-3} \text{ g Ni}$$

$$(8.1_2 \times 10^{-3} \text{ g Ni} / 0.100 \text{ g sample}) \times 100\% = \underline{8.1\% \text{ Ni}}$$

3. Species M and R are present in a mixture. The following information has been compiled for M and R

	ϵ_M	ϵ_R	A
425 nm	5700	2940	0.488 ₁
600 nm	150	3500	0.306 ₃

At 425 nm, the solution has 32.5 %T, while at 600 nm the solution has 49.4 %T. Calculate the concentration of M and R in the solution. [NOTE: All measurements in a 1.00 cm cell.]

At 425 nm: $0.488_1 = 5700M + 2940R$

At 600 nm: $0.306_3 = 150M + 3500R$

Solving for R using 600 nm: $R = (0.306_3 - 150M) / 3500$

Substituting into 425 nm: $0.488_1 = 5700M + 2940 [(0.306_3 - 150M) / 3500]$

Simplifying: $0.488_1 = 5700M + 0.257_3 - 126M$

Rearranging: $0.488_1 - 0.257_3 = 5700M - 126M$

$0.230_8 = 5574M$

$M = 4.14 \times 10^{-5}$

Substituting into our earlier equation: $R = (0.306_3 - (150 * 4.14 \times 10^{-5})) / 3500$

$R = 8.57 \times 10^{-5}$

4. A potentiometric determination was used to measure the nitrate ion concentration in well water using a nitrate-specific membrane electrode as the indicator electrode and a SCE as the reference electrode. When pNO_3 (x axis) was plotted vs. cell potential in mV (y axis) for a series of standards in a constant ionic strength buffer the following values were obtained:

$$\Sigma x = 20; \Sigma y = -75.6; \Sigma x^2 = 82.5; \Sigma y^2 = 10,002.3; \Sigma xy = -451.05; n = 5$$

What is the slope, the y-intercept, and the correlation coefficient from this data?

$$S_{xx} = 82.5 - (20^2/5) = 2.5; S_{yy} = 10,002.3 - ((-75.6)^2 / 5) = 8859.228$$

$$S_{xy} = -451.05 - [20 * -75.6] / 5 = -148.65$$

$$m = -148.65 / 2.5 = -59.46$$

$$b = -75.6/5 - (20/5)*(-59.46) = 222.72$$

$$r = \frac{-148.65}{\sqrt{(2.5)(8859.228)}} = -0.998$$

A sample of well water was obtained for determination of nitrate ion concentration. A 25.00 mL aliquot was treated with a constant ionic strength buffer and diluted to 50.00 mL. The potential of this solution was measured 4 times, and the average of these readings was determined to be -4.2 mV. According to EPA regulations, the maximum nitrate ion concentration for potable water is 1.6×10^{-4} M in the nitrate ion. Calculate the concentration and the standard deviation for the nitrate ion in the well water, and determine if the sample can be considered potable.

Concentration: $y-b/m = x = (-4.2 - 222.72) / -59.46 = 3.81_6$, but this is pNO_3
 $[\text{NO}_3^-] = 10^{-3.816} = 1.5_3 \times 10^{-4}$ M
 $1.5_3 \times 10^{-4}$ M * 50/25 = $3.0_6 \times 10^{-4}$ M NO_3^-

Standard deviation: $s_x = \sqrt{\frac{S_{yy} - m^2 S_{xx}}{n - 2}} = \sqrt{\frac{8859.228 - (-59.46^2)(2.5)}{5 - 2}} = 2.614$

$$s_c = \frac{s_x}{m} \sqrt{\frac{1}{M} + \frac{1}{N} + \frac{(\bar{y}_c - \bar{y})^2}{m^2 S_{xx}}} = \left(\frac{2.614}{-59.46} \right) \sqrt{\frac{1}{4} + \frac{1}{5} + \frac{(-15.12 - (-4.2))^2}{(-59.46)^2 (2.5)}} = -0.03_0$$

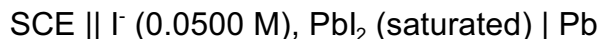
But, this is the standard deviation of a logarithmic value, and we know $s_y/y = 2.303s_a$

$$\therefore s_y / 3.0_6 \times 10^{-4} = (2.303)(-0.03_0) = -0.0689$$

$$s_y = (-0.0689)(3.0_6 \times 10^{-4}) = 2 \times 10^{-5}$$

$\therefore 3.1(\pm 0.2) \times 10^{-4}$ M NO_3^- ; the water is NOT POTABLE.

5. a) Determine the K_{sp} for lead iodide (PbI_2) from the following electrochemical cell:



if the measured cell potential is $-0.533 V$. (Assume $E_j = 0$)

$$E_{cell} = E_{indicator} - E_{reference}, \therefore -0.533 = x - 0.244, \text{ and } x = -0.533 + 0.244 = -0.289V$$

For the lead $\frac{1}{2}$ cell, $-0.289 = (-0.126) - (0.05916/2) \log (1/[Pb^{2+}])$

Since $\log (1/[Pb^{2+}]) = pPb$, $\therefore pPb = 2(-0.289 + 0.126) / -0.05916 = 5.51$

$$\therefore [Pb^{2+}] = 10^{-5.51} = 3.0_9 \times 10^{-6}$$

For the reaction $PbI_2 \rightleftharpoons Pb^{2+} + 2I^-$; $K_{sp} = [Pb^{2+}][I^-]^2$

$$K_{sp} = [3.0_9 \times 10^{-6}][0.0500]^2$$

$$\underline{K_{sp} = 7.7 \times 10^{-9}}$$

Mercury



Lead



b) The potential of a sulfate specific ion electrode (SCE reference electrode) was measured as $-213 mV$ in a solution that contained $1.00 \times 10^{-5} M$ sulfate ion, while the potential was $-156 mV$ in a $1.00 \times 10^{-4} M$ sulfate ion solution. A solution containing an unknown concentration of sulfate ion was measured with a potential of $-187 mV$. What is the concentration of sulfate ion in the unknown solution?

Since the potential is linearly related to the log of the concentration, we know that the $-213 mV$ is associated with -5.00 , and $-156 mV$ is with -4.00

$$\text{Slope} = ((-156) - (-213)) / ((-4.00) - (-5.00)) = 57$$

$$\text{y-intercept} = -184.5 - (57)(-4.5) = 72$$

$$x = (-187 - 72) / 57 = -4.54$$

$$[SO_4^{2-}] = 10^{-4.54}; \therefore \underline{[SO_4^{2-}] = 2.9 \times 10^{-5}}$$