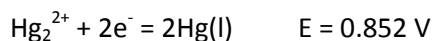


Chem 454 – Exam 1 – February 11, 2009

1] An analysis of chloride ion was conducted by the method of standard addition with an ISE. That electrode responded to a 10.0 mL sample solution with a potential of - 434.1 mV. An aliquot of 1.00 mL of $1.11 \times 10^{-3} \text{ M KCl(aq)}$ was added. The electrode now responded with a potential of -533.1 mV. What is the concentration Cl^- in that sample? (20 points)

2] Calculate potential of the SCE based on the following (20 points):



$$K_{\text{sp}} (\text{Hg}_2\text{Cl}_2) = 1.2 \times 10^{-18}$$

$$[\text{KCl}]_{\text{saturated}} = 4.5 \text{ M}$$

3] What is anodic stripping voltammetry? How does it work? Why does it achieve such a low LOD when compared with standard polarographic analyses? (20 points)

4] What is cyclic voltammetry? Describe the potential waveform (E vs. t) that is applied to the electrode to achieve voltammogram. Sketch a voltammogram and label the axes and the major electrode reactions involved with a reversible redox species $\text{Ox} + \text{e}^- = \text{Red}$. Assume that the solution contains $[\text{Ox}] = 1 \text{ mM}$ and $[\text{Red}] = 0$. Why is it only a moderate success as an analytical technique? Why is it so popular with chemists outside of analytical interests? (20 points)

5] A new analytical technique was measured against a standard one. The new technique is being considered as it offers a much faster analysis time. To compare the two 10 analyses of Pb was conducted on a sample. The follow was found:

	Average	Std. Dev.
Standard	19.5 ppm	1.7 ppm
New	22.1 ppm	2.8 ppm

When comparing the two techniques it is apparent the new technique gives a higher average. What is the expected percentage of results from the standard method of analysis that will fall above the average of the new method (22.1 ppm)? (20 points)

$$y = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{(x-\mu)^2}{2\sigma^2}} = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{z^2}{2}}$$

Table 4-1 Ordinate and area for the normal (Gaussian) error curve,

$$y = \frac{1}{\sqrt{2\pi}} e^{-z^2/2}$$

$ z ^a$	y	Area ^b	$ z $	y	Area	$ z $	y	Area
0.0	0.398 9	0.000 0	1.4	0.149 7	0.419 2	2.8	0.007 9	0.497 4
0.1	0.397 0	0.039 8	1.5	0.129 5	0.433 2	2.9	0.006 0	0.498 1
0.2	0.391 0	0.079 3	1.6	0.110 9	0.445 2	3.0	0.004 4	0.498 650
0.3	0.381 4	0.117 9	1.7	0.094 1	0.455 4	3.1	0.003 3	0.499 032
0.4	0.368 3	0.155 4	1.8	0.079 0	0.464 1	3.2	0.002 4	0.499 313
0.5	0.352 1	0.191 5	1.9	0.065 6	0.471 3	3.3	0.001 7	0.499 517
0.6	0.333 2	0.225 8	2.0	0.054 0	0.477 3	3.4	0.001 2	0.499 663
0.7	0.312 3	0.258 0	2.1	0.044 0	0.482 1	3.5	0.000 9	0.499 767
0.8	0.289 7	0.288 1	2.2	0.035 5	0.486 1	3.6	0.000 6	0.499 841
0.9	0.266 1	0.315 9	2.3	0.028 3	0.489 3	3.7	0.000 4	0.499 904
1.0	0.242 0	0.341 3	2.4	0.022 4	0.491 8	3.8	0.000 3	0.499 928
1.1	0.217 9	0.364 3	2.5	0.017 5	0.493 8	3.9	0.000 2	0.499 952
1.2	0.194 2	0.384 9	2.6	0.013 6	0.495 3	4.0	0.000 1	0.499 968
1.3	0.171 4	0.403 2	2.7	0.010 4	0.496 5			

Table 4-6 Values of Q for rejection of data

Q (90% confidence) ^a	Number of observations
0.76	4
0.64	5
0.56	6
0.51	7
0.47	8
0.44	9
0.41	10

Table 4-2 Values of Student's t

Degrees of freedom	Confidence level (%)						
	50	90	95	98	99	99.5	99.9
1	1.000	6.314	12.706	31.821	63.657	127.32	636.619
2	0.816	2.920	4.303	6.965	9.925	14.089	31.598
3	0.765	2.353	3.182	4.541	5.841	7.453	12.924
4	0.741	2.132	2.776	3.747	4.604	5.598	8.610
5	0.727	2.015	2.571	3.365	4.032	4.773	6.869
6	0.718	1.943	2.447	3.143	3.707	4.317	5.959
7	0.711	1.895	2.365	2.998	3.500	4.029	5.408
8	0.706	1.860	2.306	2.896	3.355	3.832	5.041
9	0.703	1.833	2.262	2.821	3.250	3.690	4.781
10	0.700	1.812	2.228	2.764	3.169	3.581	4.587
15	0.691	1.753	2.131	2.602	2.947	3.252	4.073
20	0.687	1.725	2.086	2.528	2.845	3.153	3.850
25	0.684	1.708	2.060	2.485	2.787	3.078	3.725
30	0.683	1.697	2.042	2.457	2.750	3.030	3.646
40	0.681	1.684	2.021	2.423	2.704	2.971	3.551
60	0.679	1.671	2.000	2.390	2.660	2.915	3.460
120	0.677	1.658	1.980	2.358	2.617	2.860	3.373
∞	0.674	1.645	1.960	2.326	2.576	2.807	3.291

Table 4-5 Critical values of $F = s_1^2/s_2^2$ at 95% confidence level

Degrees of freedom for s_2	Degrees of freedom for s_1													
	2	3	4	5	6	7	8	9	10	12	15	20	30	∞
2	19.0	19.2	19.2	19.3	19.3	19.4	19.4	19.4	19.4	19.4	19.4	19.4	19.5	19.5
3	9.55	9.28	9.12	9.01	8.94	8.89	8.84	8.81	8.79	8.74	8.70	8.66	8.62	8.53
4	6.94	6.59	6.39	6.26	6.16	6.09	6.04	6.00	5.96	5.91	5.86	5.80	5.75	5.63
5	5.79	5.41	5.19	5.05	4.95	4.88	4.82	4.77	4.74	4.68	4.62	4.56	4.50	4.36
6	5.14	4.76	4.53	4.39	4.28	4.21	4.15	4.10	4.06	4.00	3.94	3.87	3.81	3.67
7	4.74	4.35	4.12	3.97	3.87	3.79	3.73	3.68	3.64	3.58	3.51	3.44	3.38	3.23
8	4.46	4.07	3.84	3.69	3.58	3.50	3.44	3.39	3.35	3.28	3.22	3.15	3.08	2.93
9	4.26	3.86	3.63	3.48	3.37	3.29	3.23	3.18	3.14	3.07	3.01	2.94	2.86	2.71
10	4.10	3.71	3.48	3.33	3.22	3.14	3.07	3.02	2.98	2.91	2.84	2.77	2.70	2.54
11	3.98	3.59	3.36	3.20	3.10	3.01	2.95	2.90	2.85	2.79	2.72	2.65	2.57	2.40
12	3.88	3.49	3.26	3.11	3.00	2.91	2.85	2.80	2.75	2.69	2.62	2.54	2.47	2.30
13	3.81	3.41	3.18	3.02	2.92	2.83	2.77	2.71	2.67	2.60	2.53	2.46	2.38	2.21
14	3.74	3.34	3.11	2.96	2.85	2.76	2.70	2.65	2.60	2.53	2.46	2.39	2.31	2.13
15	3.68	3.29	3.06	2.90	2.79	2.71	2.64	2.59	2.54	2.48	2.40	2.33	2.25	2.07
16	3.63	3.24	3.01	2.85	2.74	2.66	2.59	2.54	2.49	2.42	2.35	2.28	2.19	2.01

Selected Answers

1]

$$E = \text{const} - 0.0592 \log [\text{Cl}^-] \quad \text{let } x = [\text{Cl}^-]_{\text{unknown}}$$

$$-0.4341 \text{ V} = \text{const} - 0.0592 \log (x)$$

$$-0.5331 \text{ V} = \text{const} - 0.0592 \log ((10.0/11.0)x + (1.00/11.0) 1.11\text{e-}3)$$

Subtract the 2 equations to get:

$$0.099 = 0.0592 (\log (0.909x+1.01\text{e-}4) - \log (x))$$

$$1.67 = \log ((0.909x+1.01\text{e-}4) /x)$$

$$X = 2.20\text{e-}6 \text{ M KCl}$$

2]

$$E = 0.852 - (0.0592/2) \log (1/[\text{Hg}_2^{2+}])$$

$$\text{From } K_{\text{sp}} (\text{Hg}_2\text{Cl}_2) = 1.2\text{e-}18 = [\text{Hg}_2^{2+}][\text{Cl}^-]^2 \quad [\text{Hg}_2^{2+}] = 1.2\text{e-}18/[\text{Cl}^-]^2$$

$$E = 0.852 - (0.0592/2) \log ([\text{Cl}^-]^2/1.2\text{e-}18)$$

$$E = 0.282 \text{ V}$$

5]

$$Z = (19.5-22.1)/1.7 = 1.52 \quad \text{area} = 0.433 \quad \text{percent over} = 100*(0.5-0.433) = 6.6\%$$

Chem 454 – Exam 2 – March 11, 2009

- 1] a. Draw a Jablonski-type diagram illustrating the concept of fluorescence. (8 points)
- b. Using the concepts above sketch the excitation and emission fluorescence spectra. (8 points)
- c. How does fluorescence differ from phosphorescence? (4 points)
- 2] Sketch in as much detail as you can provide, **the components** of a Michelson interferometer. Label each component. Indicate with arrows the direction of how light passes through the device. **A discussion of how this device works is not necessary.** (20 points)
- 3] Draw an interferogram of **a) single wave length** and **b) broadband** sources for the Michelson interferometer. Label the axes. (10 points)
- 4] **a)** Using a Jablonski-type diagram, discuss how fluorescence becomes an interference in Raman spectroscopy. (10 points) **b)** Explain how fluorescence can it be minimized in the Raman experiment (5 points) **c)** Illustrate and label the Stokes and Antistokes lines in that Jablonski-type diagram. (5 points)
- 5] Suppose you are a chemist on staff at a brewing company. You are asked to develop a technique for the quick analysis of the alcohol content of their beer. The ethanol content of beer is expected to be 3-6% m/m. Which technique would you select out of the ones discussed since Exam 1 and why? For full or partial credit you must justify your answer with plausible arguments (10 points)
- 6] The UV-vis absorbance analysis of Fe^{3+} was conducted by complexation with 1,10 phenanthroline. The maximum absorption was found to be 510 nm. A 56.2 mg solution of $\text{Fe}(\text{NO}_3)_3(\text{aq})$ (MW 179.86) was treated with 1,10 phenanthroline and diluted to 1.00 L. The absorbance of the complex was found to be 0.447. An unknown solution was treated with 1,10 phenanthroline and its absorbance was found to be 0.361. What is the concentration of iron in the unknown? (10 points)
- 7] Explain the Doppler broadening effect in flame AAS. Which species are blue shifted? Which are red shifted? (10 points)

Answer to 6]

$$56.2\text{e-3 (mol/179.86 g)}(1/1 \text{ L}) = 3.12\text{e-4M}$$

$$A = \text{ebc} \quad \text{eb} = 0.447/3.12\text{e-4} = 1433$$

$$0.361 = 1433(\text{c}) \quad \text{c} = 0.361/1433 = 2.52\text{e-4M}$$

PLEASE READ -- Answer each essay question to the extent that demonstrates your knowledge of the topic. Use one page of blank paper per question. Number each question and write your name on each page.

- 1]** Describe the process of chemical ionization for mass spectrometry. What type of ions does it produce? What type of molecular information does it yield? 15 POINTS
- 2]** Using the van Deemter Equation, $H = A + B/u + C_u$ explain why the number of theoretical plates for CE is much greater than for HPLC systems. 15 POINTS
- 3]** Again using the van Deemter Equation, $H = A + B/u + C_u$ explain how capillary GC columns achieve more theoretical plates over older packed GC column designs. 15 POINTS
- 4]** Describe the chemical process involved in flame ionization detector used for GC. Sketch a diagram of the device. What class of analytes does it detect? 15 POINTS
- 5]** What is meant by “reversed phase” separation in the terminology used for HPLC? 10 POINTS
- 6]** What is a bulk property detector? Give an example. What design compromises are necessary to implement this sort of detector for CE or HPLC? How does this compromise affect the separation quality of CE and HPLC? 15 POINTS
- 7]** A series of GC-ECD injections were made for the determination of 4-chlorophenol. The results follow:

		<u>t_r</u>	<u>peak area</u>
Injection 1	12.2 ppb 4-chlorophenol	12.44 mins	22,335
	15.0 ppm dichloromethane	5.56	15,441
Injection 2	unknown conc. 4-chlorophenol	12.67	18,667
	15.0 ppm dichloromethane	5.73	16,189

What is the concentration of 4-chlorophenol in the unknown? 15 POINTS

Answer] 12.2 ppb * (15,441/22,335) * (18,667/16,169) = 9.74 ppb