CHEM 241
April 18, 2003

Final Exam

Name: Answer Key

1. True/False----Indicate whether the following statements are **True** or **False** in the space next to the statement. Make sure you carefully read each statement ! (2 points each)

True a) In gas chromatography, use of a quadrupole mass spectrometer as a detector will normally provide better detection limits for determining the concentration of given volatile organic solutes than a thermal conductivity detector.

False b) The method of "standard addition" for quantitating analytes is often used when the sensitivity of the analytical instrument changes quickly over time and/or it is difficult to inject the exact same amount of sample each time into the instrument.

False c) The currents observed with amperometric and voltammetric methods rely on the mass transport of analyte species to the surface of the electrode by electrostatic attraction forces, once the potential of the working electrode is made positive or negative enough to pull the species toward the surface.

True d) In fluorescence spectroscopy instruments, it is typical to have two separate monochromators to select the wavelengths of excitation and emission for the fluorescent analyte species.

True e) Ethylammonium ion is the conjugate acid of ethylamine.

False f) The true pH of a 0.01 M HCl solution will be lower in the presence of 0.05 M Mg_2SO_4 added to the same solution than if it was absent.

False g) The common ion effect will always cause the solubility of an insoluble salt to increase, owing to the desire for the ion in common with one ion of the salt to attract the oppositely charge ion of the insoluble salt.

True h) Flameless atomic absorption is typically more sensitive than flame atomic absorption because the atomization efficiency in the furnace method is much greater than in the flame-based method.

False or True i) When propagating errors in multiplying or dividing two numbers with a certain degree of uncertainty, the final uncertainty will be the square root of the sum of the two % relative uncertainties squared for the respective numbers.

False j) Systematic or determinate errors in an analytical methods due to limited selectivity, matrix effects, improper calibration, etc., will always cause a positive error in measuring the concentration of a given analyte, because such errors are not random.

2. For the following glass membrane based galvanic cell, indicate whether the overall cell potential (EMF) would increase, decrease, or remain the same, for the actions indicated. Assume that activities equal concentrations, that the glass membrane is perfectly selective for hydrogen ions, neglect any liquid junction potentials, and assume that the volumes of solution in each compartment are no more than 25 ml. (**hint:** recall that E_{cell} for such a cell consists of three separate potentials, in which the working electrode voltage includes the potential of the inner reference electrode and the so-called membrane potential; also note that the acetic acid is essentially the sample in which thepH electrode and external reference electrode are placed!) (2 points each)

$Ag/AgCl_{(s)}$, KCl (0.1 M)/ acetic acid (0.1 M) / glass pH membrane / buffer, pH 7.0, KCl (0.1 M), $AgCl_{(s)}$ /Ag

↓ Decrease Adding 1 mL of concentrated NaOH (10 M) to the acetic acid solution (sample)

↓ Decrease Adding 2 mL of concentrated HCl to a weak buffer (pH 7.0) solution used as the internal reference solution of the glass pH electrode.

↓ Decrease Addition of 5 grams of sodium acetate salt (FM = 66) into the acetic acid sample solution.

↑ Increase Addition of 2 g of $AgNO_3$ into the weak buffer (pH 7.0) solution used as the internal reference solution of the glass pH electrode.

3. Multiple Choice Questions:--Please circle the letter next to the best answer for each question (3 points each).

1. The Student *t*-test can be used for comparison of an experimental mean with the true value, at a certain confidence level. When the *t*-test reveals no significant differences between the mean and the true value at the accepted confidence level, the implication is that

(A) no significant systematic error is likely to be present.
(B) a random error is not likely to be present.
(C) the random error is likely to be less than the systematic error.
(D) a different confidence level should be tested.

2. Which does *not* affect the solubility (in $g \cdot L^{-1}$) of an insoluble salt in a solution ?

(A) the number of grams of the salt placed in the solution
(B) the temperature of the solution
(C) the ionic strength of the solution
(D) the presence in the solution of an ion common to the insoluble salt

3. Why is it easier to analyze a mixture of atomic species by absorption spectroscopy than it is to analyze a mixture of molecular species?

(A) Atomic species do not have side reactions.

(B) Molecular species do not absorb light.

(C) Molecules are larger, therefore more difficult to analyze.

(D) Atomic spectra have narrower lines that are easier to resolve than the features of molecular spectra.

4. A tap water sample is to be analyzed for nickel at the ppm level. Which method would yield accurate results with the least amount of sample preparation?

(A) UV–visible spectrometry

(B) fluorescence spectroscopy

(C) ion exchange chromatography with UV detection

(D) atomic absorption spectrometry

5. The chromium on the surface of a piece of automobile trim was dissolved with hydrochloric acid and diluted to 100.0 mL. A 25.00 mL aliquot of the resulting solution was buffered to pH 5, and 50.00 mL of 0.00862 M EDTA was added. Titration of the excess EDTA required 9.62 mL of 0.01247 M Zn^{2+}. Calculate the mass of chromium on the piece of trim.

Molar Mass, M	
Cr	51.996 g·mol^{-1}

(A) 0.0162 g (B) 0.0224 g

(C) 0.0624 g (D) 0.0647 g

6. A solution of CuL_4^+ has a transmittance of 19.8% at 475 nm in a 2.00 cm cell. The molar absorptivity for the complex at this wavelength is 8.97×10^4 L·mol^{-1}·cm^{-1}. What is the concentration of CuL_4^+ in the solution?

(A) 1.10×10^{-6} M (B) 1.96×10^{-6} M

(C) 5.92×10^{-6} M (D) 7.84×10^{-6} M

7. A 0.0100 M solution of $AgNO_3$ has a concentration of Ag^+ ion equivalent to

Molar Masses, M	
Ag	108. g·mol^{-1}
$AgNO_3$	170. g·mol^{-1}

(A) 1080 ppb (B) 1080 ppm

(C) 1700 ppm (D) 10.0 ppm

8. A solution is formed from 25.0 mL of 0.0500 M Ni^{2+} and 25.0 mL of a 0.0200 M EDTA and buffered to a pH of 8.5. Calculate the concentration of free Ni^{2+} in the solution.

Formation constant for $Ni(EDTA)^{2-}$
$\log K_f = 18.62$

(A) 1.00×10^{-3} M (B) 1.50×10^{-2} M

(C) 2.50×10^{-2} M (D) 6.70×10^{-2} M

9. A sample containing Ca^{2+} is titrated with EDTA using Eriochrome Black T as an indicator. The titration solution is buffered to a pH of 10. Which color change will indicate the endpoint of the titration (H_3In = Eriochrome Black T).

Colors of Species	
($CaIn^-$)	wine red
(H_2In^-)	red
(HIn^{2-})	blue
(In^{3-})	orange

Data for Species
K_f $Ca(EDTA)^{2-} = 5.0 \times 10^{10}$
K_f $CaIn^- = 2.5 \times 10^5$
$pK_2(H_3In) = 6.3$
$pK_3(H_3In) = 11.6$

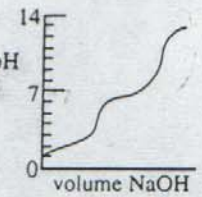
(A) orange → wine red (B) wine red → blue

(C) wine red → orange (D) blue → wine red

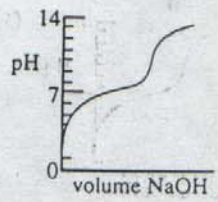
10. Which titration curve most closely approximates that expected for the complete titration of a solution of aqueous sodium hydrogen sulfate, $NaHSO_4$, with aqueous NaOH?

Dissociation constant for HSO_4^-
$K_a = 1.26 \times 10^{-2}$

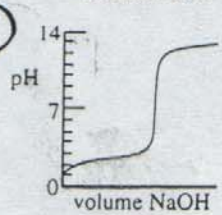
(A)



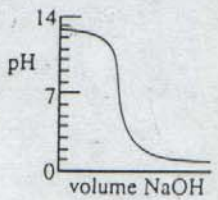
(B)



(C)



(D)



11. How many moles of NaOH must you add to 0.500 mol of benzoic acid to make 1.00 L of a pH 4.50 buffer?

Dissociation constant for C_6H_5COOH
$K_a = 6.28 \times 10^{-5}$

(A) 1.000 (B) 0.333 (C) 0.250 (D) 0.170

12. The isothermal gas chromatographic separation of a mixture of three compounds produced retention times of 0.95 min, 1.15 min, and 8.40 min. The best means to shorten the analysis time without sacrifice of resolution would be to use

(A) a longer chromatographic column.

(B) a column operated at a higher isothermal temperature.

(C) temperature programming of the column.

(D) increased flow rate of the mobile phase in the column.

13. Which compound is expected to have the greatest retention time in a reversed-phase HPLC column?

(A) sodium acetate, CH_3COONa

(B) phenol, C_6H_5OH

(C) butanoic acid, $CH_3CH_2CH_2COOH$

(D) n-dodecane, $CH_3(CH_2)_{10}CH_3$

14. The intensity of the molecular fluorescence of a compound is related to all of these parameters ***except***

(A) the power of the excitation radiation.

(B) the fluorescence quantum efficiency of the fluorescing molecule.

(C) the molar mass of the compound.

(D) the absorptivity of the compound.

Problems

4. A known mixture of compounds **A and B** gave the following peak areas when separated on a GC column: 4.80 cm^2 and 5.40 cm^2, respectively . The concentrations of each component in the known mixture was exactly the same: 230 µg/mL of A and 230 µg/mL of B. An unknown sample containing A was spiked with B by mixing 1.20 mg of B into a 10 mL sample containing A, and diluting to 25 mL. A sample of the resulting mixture was injected onto the GC column, and this resulted in a peak for A that had an area of 3.30 cm^2 and for B, 2.20 cm^2. Find the concentration of unknown A compound in the original sample? (7)

Internal Standard Method. → $F = \frac{A_A}{[A]} \cdot \frac{[B]}{A_B} = \frac{4.80}{5.40} = 0.889$

$\frac{A_x}{[x]} = F \frac{A_y}{[y]}$; F = ratio of sensitivities = $\frac{4.80}{5.40} = 0.88$

(since conc. was same for A + B in std soln)

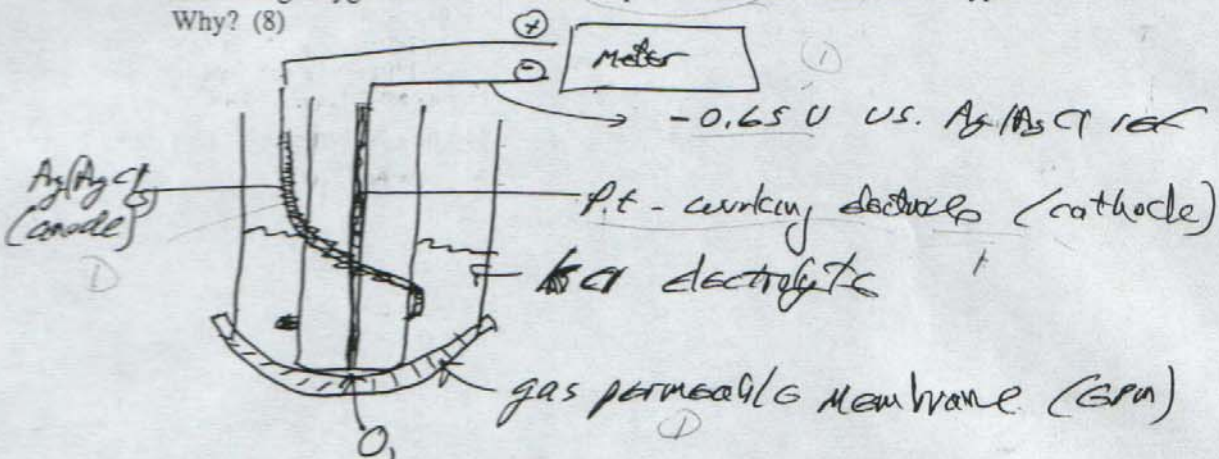
$[Y] = [B] = \frac{1.20\ mg}{25\ mL} = 48\ ug/mL$ (2)

$\therefore \frac{A_B}{[A]} = F \frac{A_B}{[B]} = \frac{3.30}{[A]} = 0.889 \frac{2.20}{48\ ug/mL}$

$[A] = 81.0\ ug/mL$; freezer sample was diluted from 10 mL → 25 mL (3)

$\therefore [A]_{sample} = \frac{25}{} \times 81.0\ ug/mL = 202.5\ ug/mL$ or 203 ug/mL

5. Sketch the design of a Clark Style oxygen sensor that is used to measure the partial pressure of oxygen in blood samples and explain the role of each component. Is measuring oxygen with device an amperometric or voltammetric type measurement? Why? (8)



- Amperometric device (2)
- O_2 diffuses from sample through GPM; gets reduced at surface of Pt working electrode ($O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$)
- Current flows in circuit in proportion to O_2 level.
- GPM prevents other species in sample from reaching Pt to be reduced; increases selectivity. (1)

6. Pointing to various terms in the Van Deemter equation, explain why the optimal linear velocity of mobile phase used to achieve the largest number of theoretical plates in gas chromatography (with packed column), will generally be much greater the velocity required to achieve the largest number of theoretical plates in a liquid chromatography experiment with a packed. (8)

$H = A + \frac{B}{u} + Cu$ (4)

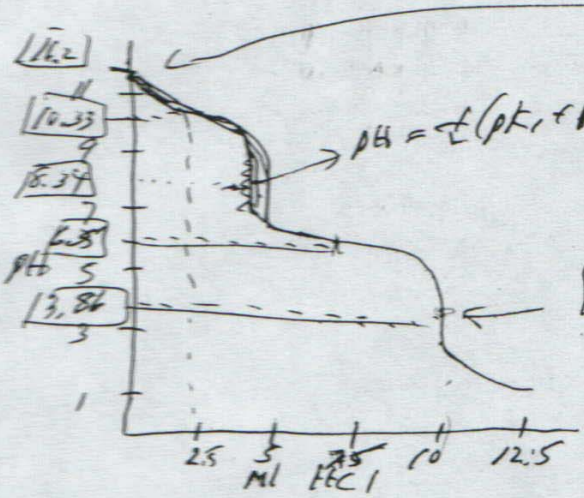
- In GC; $B_{GC} >>> B_{LC}$, ∴ must operate column with higher linear velocity of mobile phase (u) to decrease $\frac{B}{u}$ term. Lower $\frac{B}{u}$ low, so H is low and since $H = \frac{L}{N}$, small H gives larger N. (2)
- In LC; since $B_{LC} << B_{GC}$; you can afford to slow flow rate to decrease Cu term without $\frac{B}{u}$ term becoming too large. This yields lower H and therefore larger N at lower flow rate. (2)

7. Carbonic acid, H_2CO_3 has two pKa values, 6.35 and 10.33. Sketch the titration curve you would expect to see if a 50 mL solution of 0.05 M of Na_2CO_3 is titrated with a 0.50 M HCl. Make sure you label your axes (pH on y axis, mL HCl on x axis) and try to draw the titration curve starting pH, endpoint pH values, etc. to a close approximation to the true curve you would anticipate obtaining (assume activities equal concentrations).. (7)

$pK_2 = 2.14 \times 10^{-10}$; K_b for $CO_3^{-2} = 4.67 \times 10^{-5}$ M

∴ $CO_3^{-2} + H_2O \rightleftharpoons HCO_3^- + OH^-$ $\quad K_b = 4.67 \times 10^{-5} = \frac{x^2}{0.05 - x}$; $x \simeq 1.53 \times 10^{-3} \simeq [OH^-]$

$pH = 11.2$



$pH = \frac{1}{2}(pK_1 + pK_2)$

$V_e^1 = 5$ ml

$V_e^2 = 10$ ml (2)

$[H_2CO_3] = 0.042$ M

$K_{a_1} = 4.47 \times 10^{-7} = \frac{x^2}{.042 - x}$

$x \simeq 1.37 \times 10^{-4}$

$x \simeq [H^+]$

$pH = 3.86$

Bonus Questions:

When using release of low levels of nitric oxide (NO) to prevent clots from forming on the surface of intravascular sensors, what types of cells within the blood stream are inhibited by the presence of a local increase in the NO level (2). What is the name for an organic adduct structure between NO and secondary amines that can be embedded in polymers to create polymers that continuosly release NO for extended time periods (2).

1) Platelets (2)

2) diazeniumdiolates (2)