CHEM 133 FINAL EXAM
May 19, 2016

Name ________________________

Equations and constants that you may find useful:

Equation for voltage across resistor in RC circuit as a function of time for a step change of ΔV_{in} at time t = 0:

$V_R = \Delta V_{in} e^{-t/RC}$

Standard deviation:

$$S = \sqrt{\frac{\sum (x_i - \bar{x})^2}{n-1}}$$

Digitization equation for n bit digitizer: decimal # = $(V_{meas} - V_{min}) \cdot 2^n / V_{range}$

Noise Equations: 1) Thermal noise: $V_{noise}(rms) = (4kTRB)^{1/2}$

2) Shot Noise: $I_{noise}(rms) = (2eIB)^{1/2}$

k = Boltzmann's constant = 1.38×10^{-23} V^2 s Ω^{-1} K^{-1}, T = temperature (K), R = resistance, B = bandwidth, I = current, and e = elementary charge = 1.60×10^{-19} C. C = coulombs

F = Faraday's constant = 96,500 C/mol e

Units: 1 A = 1 C/s; 1 J = 1 C·V; 1 W = 1 V·A , A = amps, V = volts, W = watts, J = joules

Nernst Equation:

$$E = E^o - \frac{RT}{nF}\ln Q = E^o - \frac{2.303RT}{nF}\log Q = E^o - \frac{0.05916}{n}\log Q \text{ (T = 298 K)}$$

R = Universal Gas Constant = 8.314 J mol^{-1} K^{-1}; F = Faraday's constant = 96,500 C/mol e^-; n = moles e^-

h = Planck's constant = 6.626×10^{-34} J·s, speed of light in a vacuum = c = 2.998×10^8 m/s

Dispersion of a grating monochromator:

constructive interference occurs for: $n\lambda = d(\sin\theta - \cos\phi)$

angular dispersion: $\frac{\Delta\phi}{\Delta\lambda} = \frac{n}{d\cos\phi}$ linear dispersion: $\frac{\Delta y}{\Delta\lambda} = \frac{F\Delta\phi}{\Delta\lambda}$

where n = order, θ = entrance angle from normal ϕ = exit angle from normal, F = focal length, and d = groove spacing

Boltzmann Distribution: $N^*/N_o = (g^*/g_o)e^{-E/kT}$ with Boltzman Constant = k = 1.38×10^{-23} J/K

0ºC = 273 K; Planck's constant h = 6.626×10^{-34} J·s

Boltzmann Distribution: $N^*/N_o = (g^*/g_o)e^{-E/kT}$ with Boltzman Constant = k = 1.38×10^{-23} J/K

NMR frequency equation: $\nu = (\gamma/\pi)B_o$ (ν = frequency and B_o = magnetic field at the nucleus)

Pascal's triangle:

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                1
            1       1
        1       2       1
    1       3       3       1
1       4       6       4       1
1    5      10      10     5      1
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Chromatography Equations: retention factor = k = $(t_r - t_m)/t_m$
$\alpha = k_y/k_x$ for components x and y (eluting in that order)
N = plate number = $16(t_r/w)^2$ (w = width at base)
Resolution optimization equation: k_2 = retention factor of second eluting compound

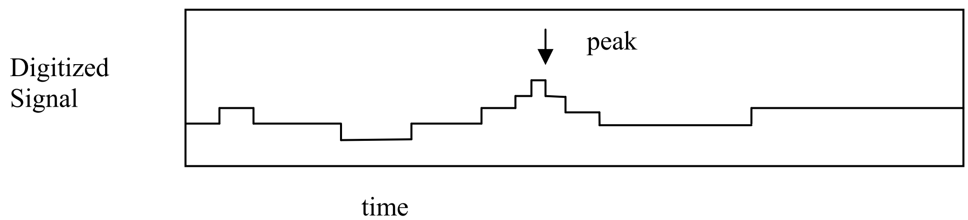
$$R_S = \frac{1}{4}\sqrt{N}\left(\frac{\alpha - 1}{\alpha}\right)\left(\frac{k_2}{1+k_2}\right)$$

SHORT ANSWER SECTION: (Each question worth 3 points)

1. Which electrical device is used to store charge?
   a) diode b) capacitor c) resistor d) operational amplifier

2. Which of the following **analog** electronics parts is most commonly used for signal processing?
a) transducer
b) Excel based moving average
c) analog to digital convertor
d) RC filter

3. A portion of a signal is collected from a GC detector and digitized (through an analog to digital converter). A peak comes out where marked. What is a clear problem with the digitization?



a) sampling at too high of a frequency
b) input voltage exceeding input range
c) not enough bits in digitizer
d) it is missing the Minecraft people

4. Besides absorption of light, list one other way in which a molecule in the ground state can be excited. Other way = ______________________________

5. Which of the following monochromator components causes dispersion of light?
a) collimating optics b) grating c) focusing optics d) exit slit

6. The most common atomization method used with atomic emission spectrometers is:
a) inductively coupled plasma
b) electrospray
c) flame
d) graphite furnace

7. In NMR in order to increase sensitivity, we want to decrease:
a) the % of active nuclei
b) the ratio of excited to ground state nuclei
c) the number of scans
d) the magnetic field

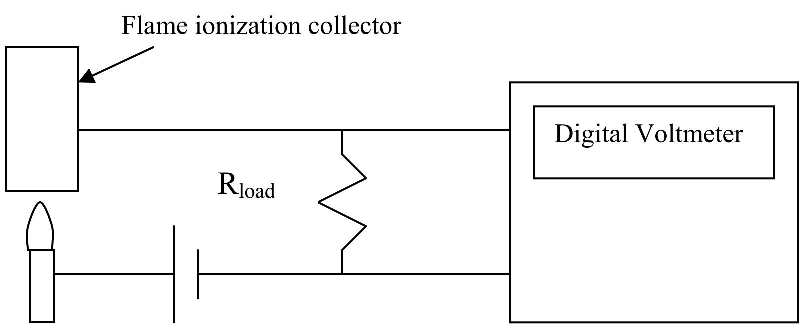
8. List (give name or describe how it works) a type of mass analyzer in a mass spectrometer.
Mass analyzer = ______________________________

9. In a liquid – liquid extraction performed using hexane and water buffered to a pH of 6.0, which of the following components is expected to have the highest concentration in the hexane phase.
a) C_6H_5OH (phenol, pK_a of -OH = 10.00)
b) $C_6H_5CO_2H$ (benzoic acid, pK_a of $-CO_2H$ = 4.20)
c) $C_6H_5CH_2NH_2$ (benzylamine, pK_a of $-NH_3^+$ conjugate acid = 9.35)
d) $HOC_6H_4CO_2H$ (salicylic acid, pK_{a1} of $-CO_2H$ = 2.97 and pK_{a1} of -OH = 13.7)

10. In capillary GC, which band broadening term is minimal
a) A (multiple pathways term)
b) B (longitudinal diffusion term)
c) C (mass transport term)
d) u (the flow velocity)

SECTION II. PROBLEM SECTION. Show work – use the back side if needed

1. The following circuit is used to measure the current from a flame ionization detector (FID). The flame ionization collector collects positively charged ions. The load resistor is 6,810 kΩ. (15 pts)



a) The digital voltmeter (DVM) reads 0.0571 V when a methane flux of 1.00×10^{-9} mol/s goes to the detector, what current is being produced by the FID? Assume no current goes to the digital voltmeter.

b) If the DVM has non-infinite internal resistance, will the true current be greater or less than the measured current? Explain your answer.

c) If the noise level (the standard deviation in the voltage readings when no hydrocarbon goes to the detector) is 0.0008 V, what is the minimum detectable flux of methane (the flux level capable of giving a signal of 3x the noise)?
Assume there is no DVM error and the FID response is linear with methane flux.

2. A chemist is testing an electrode for measuring Cd^{2+} in solution by using the following cell: $Cd(s)|Cd^{2+}(aq, 1.0\ M)||KCl(aq, 1.0\ M)|AgCl(s)|Ag(s)$. Given the E° for the following reactions, calculate the cell potential (remember in the cell notation that the left half is for oxidation). (8 pts)

Standard reduction potentials: $Cd^{2+}(aq) + 2e^- \leftrightarrow Cd(s)$ E° = -0.380 V

$AgCl(s) + e^- \leftrightarrow Ag(s) + Cl^-(aq)$ E° = 0.222 V

3. Atomic emission spectrometers for inductively coupled plasmas (ICPs) often use polychromators (dispersion of light to an array of detection elements) instead of standard grating monochromators. (12 pts)

a) What component of a monochromator is not present with a polychromator?

b) What is the advantage to using a polychromator (as opposed to a scanning monochromators) for atomic emission spectroscopy?

c) These polychromators typically are designed for high resolution measurements. Why is this desirable for atomic emission spectrometry?

4. 1,2-dichloropropane ($CH_3CH(Cl)CH_2Cl$) is analyzed by ^1H NMR. It is observed to have a jumbled multiplet (unclear number of split peaks) at 4.1 ppm, and simpler peaks at 3.6 and 1.6 ppm. (10 pts)

a) Indicate which protons are giving the signals at each peak.

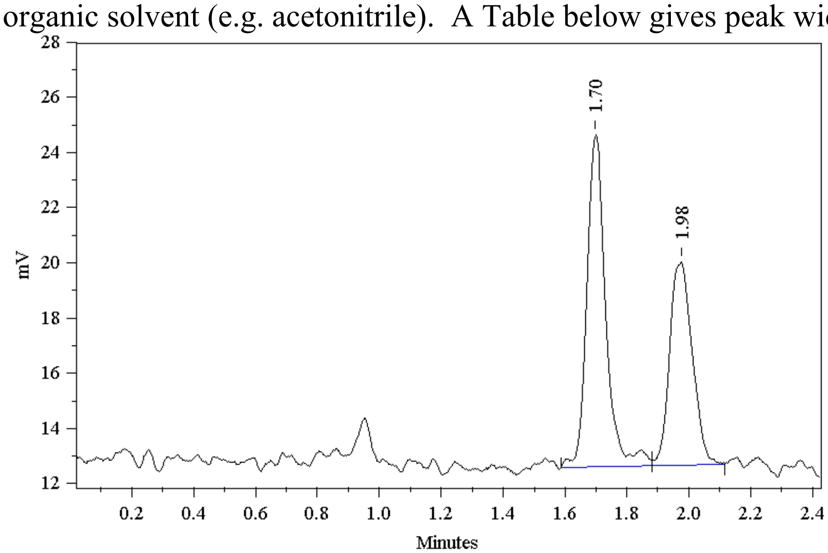
b) Predict the splitting pattern (e.g. triplet) observed at 3.6 and 1.6 ppm.

5. Upon analysis by mass spectrometry 1,1-bromo-chloro-ethane ($CHBrClCH_3$) gives a most common isotope peak of 142. Given information for less common isotopes below, give ratios of peak intensities for **M+1/M** (e.g. ratio of intensity of 143 peak to 142 peak), **M+2/M** and **M+4/M** ratios. The most common isotopes are: ^{12}C, ^{35}Cl, and ^{79}Br

Isotope/Element	C	Cl	Br
M	100	100	100
M+1	1.08	none	none
M+2	none	32	97

You can ignore the contribution of 2 ^{13}Cs to any ratios. (9 pts)

6. The chromatogram below shows the separation of glucose (1.70 min) from levoglucosan (1-6-anhydro-β-glucose) (1.98 min). The chromatogram was obtained with a 150 mm length C18 column using 90% water, 10% acetonitrile at a flow rate of 1.0 mL/min. Note: that water is the most polar solvent for this column, and it is not possible to use the column with less than 10% organic solvent (e.g. acetonitrile). A Table below gives peak widths and areas. (16 pts)



Name	Ret. Time (min)	Conc. (mg/L)	Peak Height (mV)	Width at base (min)
Unretained	0.95	-	-	-
glucose	1.70	1.0	12.05	0.115
levoglucosan	1.98	1.0	7.36	0.133

a) Choosing one peak, calculate the plate number (N) and plate height (H, in mm) of the column.

b) Determine retention factor (k) of glucose and the resolution (R_S) between glucose and levoglucosan.

c) If a chemist was planning on using this column to analyze samples that had five to ten sugars present (in addition to glucose and levoglucosan) under current conditions, is it likely that all the sugars would be well resolved? Assume the other sugars have similar polarity. Explain your answer.

Bonus) For the situation in c), could any changes be made to improve the analysis? would it require a different column or just different solvents? (3 pts)