CHEM 133 Exam 3
May 10, 2016
KEY

Equations and constants that you may find useful:

$0ºC = 273$ 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:

```
                1
             1     1
          1     2     1
       1     3     3     1
     1     4     6     4     1
   1     5    10    10     5     1
 1     6    15    20    15     6     1
```

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)

SHORT ANSWER SECTION: (Each question worth 4 points)

1. In inductively coupled plasma-atomic emission spectroscopy (ICP-AES), spectral interference from molecular species is usually less than in flame atomic absorption (AA) spectroscopy because:
    a) ICP atomization is more complete
    b) AA doesn't use a monochromator
    c) atoms and molecules have different masses
    d) emission bands are narrower than absorption bands

BONUS. (3 pts) A proton NMR is obtained on CH_3CDCl_2 (where D = ^2H, an I = 1 nucleus). The presence of D instead of ^1H will:
    a) have no effect on the NMR spectrum
    b) cause a large change in the chemical shift of the CH_3 protons
    c) cause a change in the splitting observed by CH_3 protons
    d) cause a large increase in the intensity of the CH_3 protons

2. In NMR, knowledge of spin-lattice relaxation is important because it affects:
a) the rate at which sample can be irradiated without causing saturation
b) the frequency where nuclei absorb
c) the number and type of splitting nuclei undergo
d) the ability of other nuclei to absorb light

3. Give the name or describe an ionization method that can be applied as part of a detector for GC-MS. Method = __*Electron impact (EI), or Chemical ionization (CI)*_____

4. Aromatic hydrogens (hydrogens on benzene rings) in NMR absorb at downfield (lower magnetic frequencies or higher ppm values) primarily because:
a) the benzene ring is an electron withdrawing region leading to deshielding
b) the high electron density leads to a high degree of shielding
c) electron circulation induced in the benzene ring leads to an increased magnetic field at protons
d) all ringed compounds fix the orientation so protons get the full magnetic field

5. Alkyl amines are what make tuna fish smell bad. These compounds are weak bases and are volatile as molecules but non-volatile in the ion form. To reduce the smell from alkyl amines, one should prepare tuna fish under:
a) acidic conditions   b) basic conditions   c) pH has no effect.

6. Two compounds are being separated by reversed phase HPLC using a mobile phase of 60% methanol and 40% water and a C8 stationary phase. The separation is not good because of insufficient retention. To increase retention, the chemist should:
a) increase the percent methanol
b) increase the percent water
c) go with a C4 stationary phase (similar polarity but less volume)
d) use a faster flow rate

7. Name or describe one source of band broadening. Source of band broadening: _1) Eddy diffusion/multi-path term, 2) longitudinal diffusion, 3) mass transport limitations___

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

1. A soil sample (4.00 g) is digested and analyzed for Cd by atomic absorption analysis. The digestion results in 25.0 mL of extract. Because there is concern of matrix effects, standard addition is used. A portion of the extract is analyzed directly by AA and gives an absorbance of 0.211. Another 10.0 mL portion of the extract is spiked with 50.0 μg of Cd (ignore any added volume from Cd spiking) and gives an absorbance of 0.539.
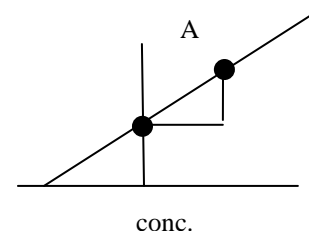a) Calculate the Cd concentration in the (unspiked) extract (in μg/mL). (10 pts)
To calculate the conc., we calculate the x-intercept (see plot).
The spiked conc. = 50 μg/10 mL = 5.00 μg/mL
The slope = $\Delta A/\Delta C$ = (0.539 – 0.211)/(5.00 – 0) = 0.0656 mL/μg
Slope also = (A_{sample} – 0)/[0 – (-C_{sample})] = 0.0656 mL/μg
*C_{sample} = A_{sample}/m = 0.211/0.0656 = **3.22 μg/mL***

b) Calculate the Cd concentration in the soil in ppm (by mass). (4 pts)
*ppm Cd = (3.22 μg/mL)(25 mL)/4.00 g = 20.1 μg/g = **20.1 ppm***

c) A Cd standard prepared in dilute nitric acid to a concentration of 1.00 µg/mL is analyzed and gives an absorbance of 0.191. Was the standard addition justified? (4 pts)
Standard addition is justified if the slope is "significantly" different. A one point calibration can be performed on the above standard. The slope is 0.191/1.00 = 0.191 which is almost 3 times greater. **Standard addition is justified.**

2. Sketch an NMR ^{1}H spectrum for methyl isopropyl ketone ($CH_3COCH(CH_3)_2$).
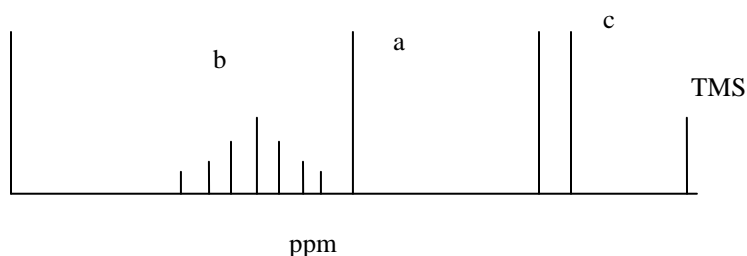(15 points) Indicate: a   b   c
a) the number of groups of equivalent nuclei. *3*
b) the relative position (higher vs. lower field) of the different groups of equivalent nuclei. *c is furthest upfield. a and b will be close but H is electron donating so b is downfield relative to a.*
c) the splitting pattern (number of peaks) for each group of equivalent nuclei. *(see below)*

ppm

2 - BONUS) if the CH proton and the left CH_3 protons are located 0.32 ppm apart, will their peaks overlap on a 200 MHz spectrometer? Assume a 10 Hz coupling constant for splitting if needed. Show work. (3 pts)
$\Delta v = (0.32$ ppm$/10^6)(200$ MHz$)(10^6$ Hz/MHz$) = 64$ Hz. The distance from the center of the septet (CH peak) to the smallest peak on the right is 3(10 Hz) = 30 Hz so there is no overlap.

3. A scientist is trying to produce 2-chloroacetophenone ($C_6H_5C(O)CH_2Cl$) but is worried that chlorination occurred on the benzene ring instead (producing $ClC_6H_4C(O)CH_3$ – e.g. 4'chloroacetophenone – instead). Atomic weights: ^{1}H – 1.008 amu, ^{12}C – 12.000 amu, ^{16}O – 15.995 amu, and ^{35}Cl – 34.969 amu.
a) Given that ketones tend to fragment between the α carbon and the carbonyl carbon, indicate two fragment peaks (give the mass to charge ratio and structure) that would be indicative of 2-chloroacetophenone. (6 pts)

Fragment	Mass	Equivalent for Ring Cl comp.	Mass
$C_6H_5C(O)^+$	105	$ClC_6H_4C(O)^+$	139
$C_6H_5^+$	77	$ClC_6H_4^+$	111
$OCCH_2Cl^+$	77	$OCCH_3^+$	43
CH_2Cl^+	49	CH_3^+	15

b) What two related fragments would be expected from $ClC_6H_4C(O)CH_3$ instead? (4 pts)

(see right part of table above)

3

4. 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)

*M+1/M – all from C. Two Cs means 2(1.08)/100 = **2.16/100** (or 0.0216)*
M+2/M – from Cl and Br (either 1 ^{37}Cl or 1 ^{81}Br – since or we add numbers)
*M+2/M = 32/100 + 97/100 = **129/100** = 1.29*
M+4/M – requires both a 1 ^{37}Cl and 1 ^{81}Br (must multiply numbers)
*M+4/M = [(32)(97)/100]/100 = **31/100** = 0.31*

5. Two columns, a non-polar DB-1 column and a moderately polar DB-17 column, were tested to separate methyl stearate – MS or $CH_3O_2C(CH_2)_{16}CH_3$ from methyl oleate – MO or $CH_3O_2C(CH_2)_7CH=CH(CH_2)_7CH_3$ (cis form) using GC in two trial chromatograms with retention times and peak widths listed below. The columns had similar dimensions (length, diameter and film thickness) and were run using the same temperature program.

Peak	DB-1 Retention Time (min)	DB-1 Peak width at base (min)	DB-17 Retention Time (min)	DB-17 Peak width at base (min)
CH_4 (unretained)	1.71	-	1.83	-
MO	8.53	0.185	10.31	0.213
MS	8.79	0.190	8.84	0.186

a) Determine the retention factor (k) for MO on the DB-1 column. (4 pts)
*k = (8.53 – 1.71)/1.71 = **3.99***

b) Determine the plate number (N) for each column using MS. (6 pts)
*DB-1: N = 16(8.79/.19)^2 = **34,200** DB-17 N = (8.84/.186)^2 = **36,100***

c) Calculate relative retention (α) for MO and MS for each column. For which column is this better? (6 pts)
*α = k(MS)/k(MO) = (8.79 – 1.71)/(8.53 – 1.71) = **1.038** (DB-1)*
*α = k(MO)/k(MS) = (10.31 – 1.83)/(8.84 – 1.83) = **1.210** (DB-1)*

d) Based on their separations, which compound (MS or MO) is more polar? Explain your answer. (4 pts)
***MO** – it is more retained on the more polar column.*