CHEM 133 Final Exam
May 18, 2017
167 Points

Name _____

h = Planck's constant = 6.626 x 10^{-34} J·s, speed of light in a vacuum = c = 2.998 x 10^8 m/s
Boltzman Constant = k = 1.38 x 10^{-23} J/K, Avogadro's number = N$_A$ = 6.02 x 10^{23} items/mol
F = Faraday's constant = 96,500 C/mol e$^-$
Pascal's triangle:

```
           1
        1     1
     1     2     1
  1     3     3     1
1     4     6     4     1
```

SHORT ANSWER SECTION: (Each question worth 4 points)

1. Method A has a limit of detection of 20 µg while method B has a limit of detection of 300 ng
(nanograms). Which of the following is the best statement in comparing method A to method B?
a) method B is more accurate   b) method B is more precise
c) method B is more sensitive   d) method A has a greater range of response

2. A fluoride selective electrode has a useful output range of 0.6 to 2.1 V and is being recorded
by a digitizer with an input voltage range of 0 to 1 V. Noise is not a major issue. What type of
analog signal processing is needed?
a) RC high pass filter   b) RC low pass filter   c) a voltage divider   d) a voltage amplifier

3. If the reference electrode is acting as the cathode and the analyte electrode as the anode, the cell
voltage = (where E$_{ref}$ and E$_{analyte}$ refer to the reference and analyte electrode potentials, respectively):
a) E$_{ref}$ b) E$_{analyte}$ c) E$_{analyte}$ − E$_{ref}$ d) E$_{ref}$ − E$_{analyte}$
(assume E$_{cell}$ > 0)

4. Which of the following monochromator components is designed to disperse light?
a) collimating optics   b) grating   c) focusing optics   d) exit slit

5. In NMR, the light transducer is:
a) an antenna to pick up radio frequency waves   b) the magnet shims
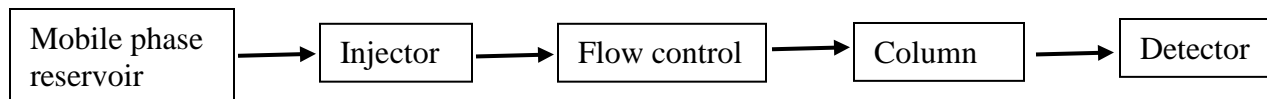c) the Fourier Tranformer   d) the permanent magnet

6. List a main component (one of 3) of a mass spectrometer and a specific example of this
component (e.g. if this question were asking about UV-visible spectrometers you could say <u>lamp</u>
and <u>deuterium lamp</u>). Main component _____ Specific Example: _____

7. It is desired to remove free fatty acids from biodiesel. These compounds are only weakly soluble in
water if in their molecular form, but can be dissolved if fatty acids exist as ions. A way to remove these
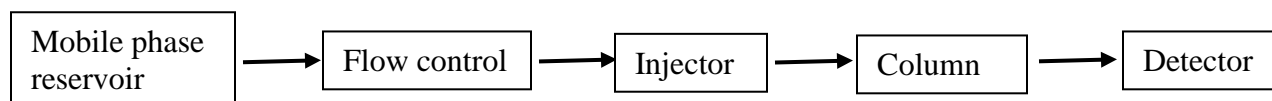from biodiesel is to wash the biodiesel with water containing:
a) an acidic buffer   b) a basic buffer   c) dissolved NaCl

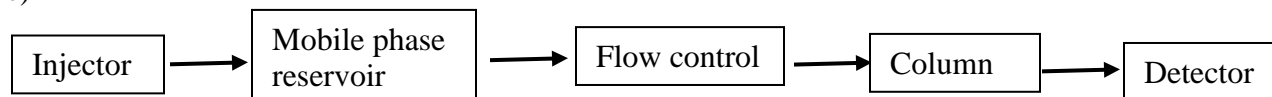8. Which of the following chromatograph block diagrams has components in the correct order?
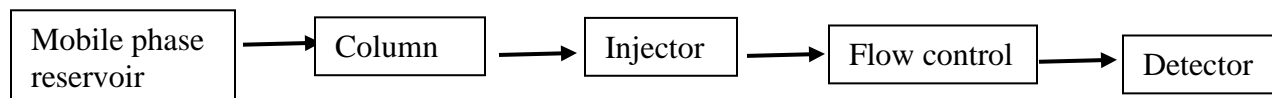
a)

| Mobile phase reservoir | → | Injector | → | Flow control | → | Column | → | Detector |

b)

| Mobile phase reservoir | → | Flow control | → | Injector | → | Column | → | Detector |

c)

| Injector | → | Mobile phase reservoir | → | Flow control | → | Column | → | Detector |

d)

| Mobile phase reservoir | → | Column | → | Injector | → | Flow control | → | Detector |

9. GC is desired to separate two compounds. In looking up compound properties, a scientist finds both compounds have the same boiling point temperature but different polarities (e.g. octanol – water partition coefficients). He will expect the resulting chromatogram:
a) to show slower elution of the compound with polarity similar to the stationary phase
b) to show faster elution of the compound with polarity similar to the stationary phase
c) to always give overlapping peaks
d) to give unexpected results because he was supposed to look up the melting point temperature

10. A separation is performed using normal phase HPLC with a mobile phase of 90% hexane/10% 2-propanol and a 150 mm x 4.6 mm silica column. Because solute peaks are found to elute quickly and overlap, it is desired to increase retention. This can be accomplished by:
a) using 95% hexane/5% 2-propanol   b) using a 150 mm x 8.0 mm column
c) using 75% hexane/25% 2-propanol   d) it is impossible to increase retention in this case

11. The primary reason going to smaller diameter open tubular columns and thinner stationary phase films in GC results in smaller H values under the same linear velocities is:
a) the flow rate will be lower   b) molecular diffusion is decreased
c) mass transport to and within the stationary phase is faster
d) the variations in paths around the smaller particles is greater

12. In GC analysis, broad or tailing peaks often occur and give poor performance. If it is expected that this is from column overload, an approach in reducing this is to:
a) concentrate the samples before injection   b) make sure splitless injection is being used
c) decrease the fraction being injected by split injection
d) use a smaller diameter column

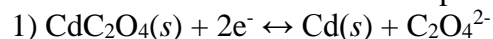SECTION II. PROBLEM SECTION. Show work – use the back side if needed

1. A student is building a tube heater by wrapping heating wire around a tube. The heating wire has 0.60 Ω/m. See the figure below.
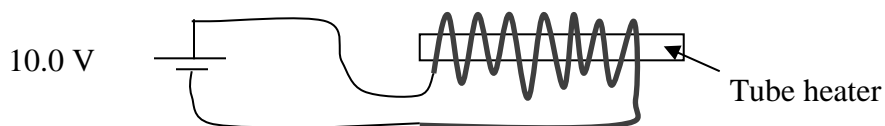
10.0 V   Tube heater

a) Assuming the heating wire is the only source of resistance in the circuit, what is the current needed in the heating wire if it is desired to to provide 35 W to the tube heater? (6 pts)

b) What length of wire would be needed to produce the desired 35 W of heat? (6 pts)

2. A researcher is developing an electrode to measure oxalate ($C_2O_4^{2-}$) in water. She needs to determine the standard reduction potential ($E°$) for the reduction reaction:
1) $CdC_2O_4(s) + 2e^- \leftrightarrow Cd(s) + C_2O_4^{2-}$
Given that $E°$ for 2) $Cd^{2+} + 2e^- \leftrightarrow Cd(s)$ is -0.402 V
and K_{sp} for 3) $CdC_2O_4(s) \leftrightarrow Cd^{2+} + C_2O_4^{2-}$ is 8.72 x 10^{-5}, calculate the reduction potential for the first reaction. Note: standard conditions include 25°C. (12 pts)

3. Some infrared detectors measure temperature increases (e.g. due to infrared light hitting a thermistor). If the minimum temperature increase detectable by a thermistor corresponds to a heat flux of 1.0 x 10^{-6} J (over a 1 s period), calculate the minimum number of photons needed for detection for infrared radiation with a wavenumber of 800 cm^{-1}. (10 pts)

4. In flame atomic absorption spectroscopy a number of processes can decrease the atomization efficiency. (10 pts)
a) Give an example of one process that decreases atomization efficiency

b) Give a method to reduce the effect of this process

5. Alkyne protons (see figure below) are influenced by electron circulation in the two pi bonds resulting in an induced magnetic field as shown below. Explain how you would expect this to affect the chemical shift (e.g. upfield or downfield) of the $HC\equiv$ protons (compared to protons with the same electron density from the HC bond). (6 pts)
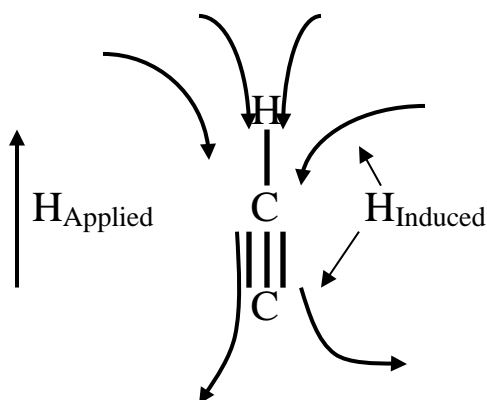
6. A compound is analyzed by GC-MS (using electron impact ionization) and is suspected to be dichlorobenzene ($C_6H_4Cl_2$). Given information below,

Element/Isotope	Mass (amu)	Abundance (relative to main isotope)
^1H	1.01	100
^{12}C	12.00	100
^{35}Cl	34.97	100
^{37}Cl	36.97	32.0

a) predict the mass to charge ratio of three mass peaks associated with the parent ion (main peak plus isotope peaks only from different Cl isotopes). Assume no multiple charges. (6 pts)

6 – cont. b) Calculate the expected ratio of the abundances of the two isotope peaks in a) relative to the main isotope peak. (10 pts)

6 – cont c) The sensitivity of the mass spectrometer can be changed by changing the amount of time the quadrupole spends on specific m/z ion (e.g. by changing the mass range scanned). If the mass spectrometer spent 5.0 ms (milliseconds) on each m/z during the scan and the signal to noise of the main isotope peak was 73, what time is needed to obtain a signal to noise ratio of 10 for the smallest isotope peak? (5 point bonus)

7. A sulfated maltose molecule is prepared and isolated. It is believed that the compound consists of three sulfate groups in which $-OSO_3H$ replaces -OH. It is analyzed by negative ion electrospray ionization (ESI) – mass spectrometry. The formula for (unsulfated) maltose is $C_{12}H_{22}O_{11}$. If it is known that sulfated maltose loses one, two or three H^+s, predict the m/z value for the three peaks corresponding to these H^+ losses. (12 pts)

Isotope	Mass (Da)
^1H	1.0078
^{12}C	12.0000
^{16}O	15.9949
^{32}S	31.9721

8. Two columns, a non-polar DB-1 column and a moderately polar DB-225 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-225 Retention Time (min)	DB-225 Peak width at base (min)
CH₄ (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. (5 pts)

b) Determine the plate number (N) for the DB-225 column using MO. (5 pts)

c) Based on their separations, which compound (MS or MO) is more polar? Explain your answer. (5 pts)

d) Calculate the resolution on the DB-1 column. Are the peaks baseline resolved? (6 pts)

e) **Select a column**, which when optimized for a fast separation, should allow better analysis of biodiesel assuming MO and MS are the main biodiesel constituents of interest. Assume that both columns could be run hotter or cooler than the test conditions used above and that there will be no change in α value with change in temperature. Explain your choice (you may want to perform calculations to justify your selection). Also, **indicate what change in conditions** you would use to optimize the separation. (6 pts)

9. **Additional Problem 3.1** The table below shows the retention times and peak widths for 3 compounds separated by reversed-phase HPLC using a 250 mm length x 4.6 mm inside diameter column with an eluent of 45% acetonitrile, 55% water and a flow rate of 1.00 mL/min:

Compound	Retention time (min.)	Peak Width at half height (min.)	pK$_a$
unretained	1.58	NA	NA
phenol	4.72	0.21	9.98
2-nitrophenol	5.68	0.25	8.39
2-methylphenol	5.91	0.26	10.09

Note: $w_b = 1.70 * w_{1/2}$

a) Based on the elution order, which compound is most polar? Explain. (4 pts)

b) Suggest a change in mobile phase without changing pH to increase retention. (4 pts)

c) If the pH of the eluent is increased to 8.0 (from an assumed pH of ~7 in the first eluent) and the composition remains 45% acetonitrile, 55% aqueous buffer, what will happen to each retention time? (6 pts)