CHEM 322 **Name**__________________________________
Exam 1 **Spring 2010**

Due by 5:00 PM Friday, February 5
NO LATE PAPERS ACCEPTED!

Complete these problems on separate paper and staple it to these sheets when you are finished. Please put your name or initials on each sheet as well. Clearly mark your answers. YOU MUST SHOW YOUR WORK TO RECEIVE CREDIT.

Instructions

- This is **NOT** an open-book, open-note take exam. You MAY NOT consult any human or nonhuman resource besides Dr. Lamp as you complete the exam. This exam MUST be completed INDIVIDUALLY and in your own words. Group work or plagiarism will result in a zero for the exam.
- You will be allowed to ask Dr. Lamp a maximum of two (2) questions regarding the exam. Additional questions may be asked at a 3-point penalty per question. If you are working on the exam in the evening, you may try to reach Dr. Lamp on his cell phone at 660-341-0067 before 10:00 PM.
- Before opening the exam, prepare for it like you would for a traditional, in-class exam. Review concepts and examples from the text, as well as those discussed in class. This preparation will help to maximize your effort on the exam and allow you to complete it more efficiently.

Time Restriction

You may spend no more than two (2) hours working on this exam. This must be in one continuous block of time. You are on your honor to adhere to this restriction and record the time spent in the chart below.

Date	Time Began	Time Finished	Total Time
Total Time Spent on the Exam			

Pledge

I pledge on my honor that I have completed the exam in accordance with the above instructions and that I have not provided or received unethical assistance. I realize that failure to comply with these instructions will result in a score of zero on the exam.

____ ________________
Signature Date

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Warm-up (2 points each)

1. The _____ rectifier ____________________________ in a power supply converts the incoming AC voltage to an oscillating voltage of either all positive or all negative sign.

2. One can reduce __flicker___________________________ noise by increasing the frequency at which the signal is sampled.

3. __Loading__________________________ of a power supply can cause a decrease in the output voltage of the power supply itself.

4. Digital filtering using ______Fourier Transforms__________ can help to remove the contributions of specific frequencies to time-dependent signals.

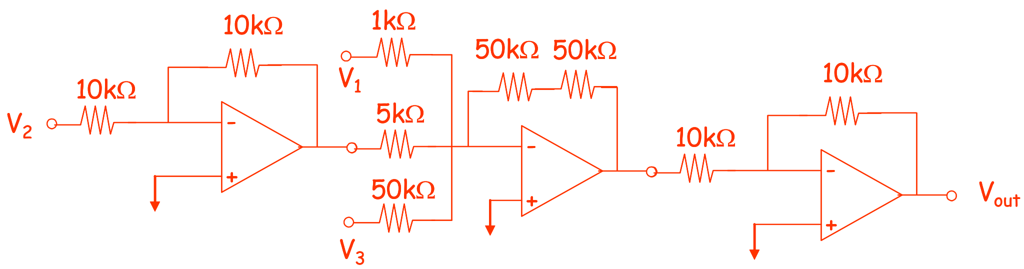
Answer in a sentence or two, or with a calculation. Complete five of the following. Clearly indicate which problem is not to be graded. (10 points each)

5. You have a box that contains 50 op-amps and five each of the following resistors: 1, 2, 5, 10, 20, 50 kΩ. Design an op-amp circuit to do the following calculation:

$$V_o = 20(5V_1 - V_2) + 2V_3$$

(You may not need all of the components in your box.). Qualitatively describe the function of each op-amp in your circuit.

There are several options that will do the trick. You need to be sure that your circuit performs the function $V_o = 100V_1 - 20V_2 + 2\,V_3$ and that the sign of the output is correct. The circuit below is an example:



The first opamp in the circuit inverts the sign of V_2. The second opamp sums V_1, $-V_2$, and V_3 with the appropriate ratios, while the third opamp gets the correct sign for the result.

6. For a spectrophotometric analysis, the following calibration curve was obtained:

$$\text{Signal} = (0.467\ \text{units/ppm}) \times \text{concentration} + 0.024\ \text{units}$$

a. If five blank readings gave 0.022, 0.027, 0.021, 0.025, 0.022 units, what is the detection limit for this measurement?

b. Does working near the detection limit have a greater influence on the accuracy or the precision of a measurement? Briefly explain.

a. The detection limit is the concentration that corresponds to a signal that is equal to the blank plus three times the standard deviation of the blank. For this data, s_{blank} = 0.00251 units. That means that the signal at the detection limit is 0.024 +3(0.00251) = 0.315 units. To convert this to concentration units, rearrange the calibration curve.

c = (0.315 – 0.024) units/(0.467 units/ppm) = 0.0148 ppm = **0.015 ppm**

b. Working near the detection limit has the greatest effect on the precision of the measurement. In only random noise contributes, taking several measurements will still result in a reasonably accurate average. However, the large variability in each measurement will result in poor reproducibility and decreased confidence in the results.

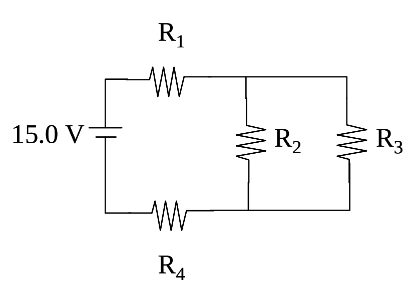
7. White noise corresponds to extraneous signals whose intensity does not depend on frequency. Two of the types of noise we've discussed can be classified as white noise. Name and briefly describe the physical phenomena that give rise to these two types of noise. How do we minimize their contribution to a measured signal?

Shot noise and thermal noise are both independent of frequency. Shot noise is a result of quantized motion of e^- across boundaries in semiconductors and is proportional to the size of the signal. Thermal noise is due to random thermal motion of electrons in conductors (resistors) and is related to temperature and resistance. Decreasing the bandwidth of the measurement can minimize contributions from both sources. Decreasing the magnitude of the signal being measured can also diminish shot noise. Lowering the temperature of the measurement can decrease thermal noise.

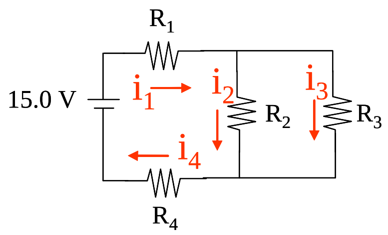
8. In electronics lab 2 (the op amp lab), we used reverse-biased diode to produce a small current. Describe the properties of the diode that lend itself to this application. What considerations must be made to ensure that only a very small current is produced?

Diodes are good conductors when forward biased, but poor conductors when reverse biased. By reverse-biasing the diode, we allow only a very small leakage current to pass, as opposed to a much larger current that would result if the diode were forward biased. We must be careful not to apply too large of a reverse bias potential, or we risk causing the diode to operate under breakdown conditions, producing a very large current.

9. Consider the following circuit. If the current through R_1 is 10.94 μA and the current through R_2 is 4.69 μA, what is the value of R_3? What is the power that is dissipated by R_1? What is the potential drop across R_4?

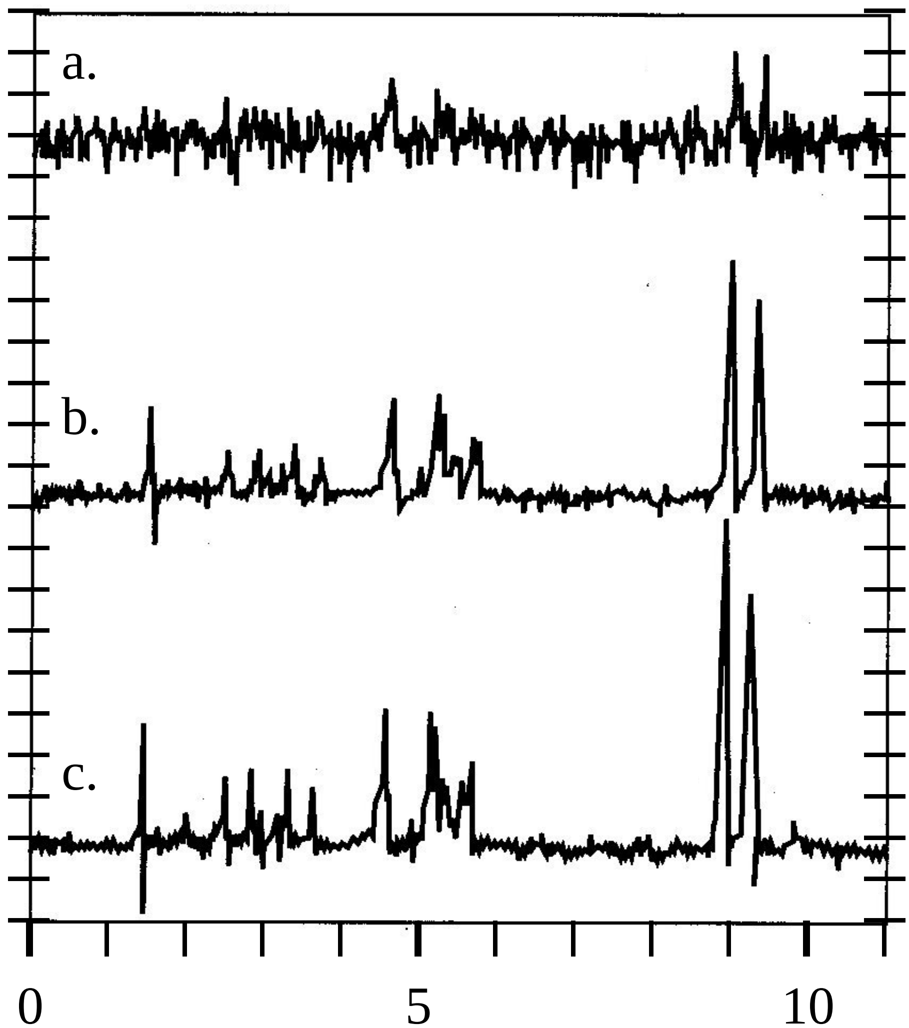


R_1 = 200 kΩ
R_2= 400 kΩ
R_3 = ?
R_4 = 1 MΩ



V_1 = 10.94 μA(200kΩ) = 2.188 V = 2.19 V
V_4 = 10.94 μA(1MΩ) = 10.94 V
So, the potential dropp across R_2 and R_3 in series is:
V_{eq} = 15.0 V – 10.94 V – 2.19 V = 1.87 V
$i_2 = V_{eq}/R_2$ = 1.87V/400kΩ = 4.66 μA
i_3 = (10.94 - 4.66) μA = 6.28 μA
$R_3 = V_{eq}/i_3$ = 1.87 V/6.28 μA = 299 kΩ
$P = I^2R = (10.94 \times 10^{-6}A)^2(200 \times 10^3\Omega)$ = 2.39 μW

10. Estimate the S/N ratio in data sets **a** and **c** below. Be sure to briefly describe the procedure you used to estimate the S/N. If data set **a** is the result of four scans, how many scans must have been averaged to produce set **c**?



Data Set	Size of largest peak (S)	Size of noise (N) Peak to peak	S/N
a	~2	~1	**2**
c	~8	~0.5	**16**

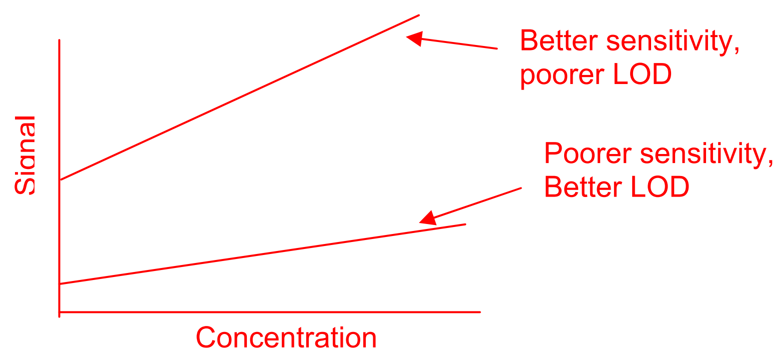
On going from set a to c, S/N improved by a factor of 16/2 = 8. Therefore the number of scans must have increased by a factor of 8^2 = 64. So, 4 x 64 or 256 scans must have been taken to obtain scan c.

A little more involved. Complete three of the following. Be clear and concise. Clearly indicate which problem is not to be graded. (14 points each)

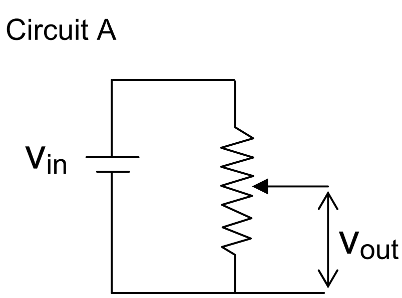
11. Why is the limit of quantitation larger than the limit of detection for a measurement? When comparing two measurements, is it true that the one with the greatest sensitivity will have the lowest LOD? Explain your reasoning.

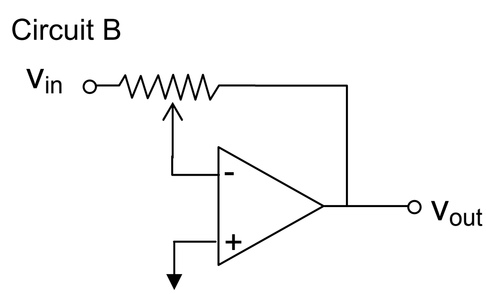
At the limit of detection, the analytical signal is barely distinguishable from the background. As a result, the precision of a measurement taken at the LOD is very poor. In order for the precision to improve, it is necessary to keep the analytical concentration (and signal) larger than the LOD, therefore, the LOQ is typically larger than the LOD (~10x).

Sensitivity and LOD are influenced by very different phenomena. LOD is influenced most significantly by instrument variations (noise) and instability of sample and matrix. Sensitivity corresponds to the instrument response to a change in analyte concentration. It is certainly possible for an instrument to be very sensitive (have a calibration curve with a steep slope) but have a very poor detection limit (as a result of instrument noise or sample instability). Therefore, you should NOT assume that sensitivity and low LOD go hand in hand.

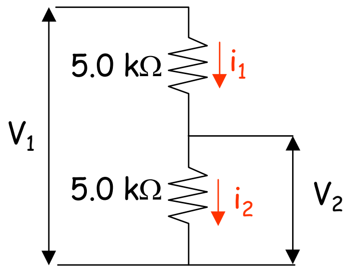


12. Consider the two circuits below. Both circuits produce similar output. How is v_{out} related to v_{in} for each circuit? What are the benefits of using circuit B compared to circuit A?





For the circuit on the left:

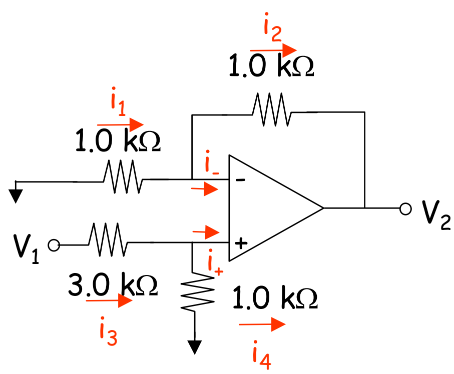


Since there is only one path from V_1 to ground, the current through the first resistor must be the same as the current through the second ($i_1 = i_2 = I$) so:

$i = V_1/10k\Omega = V_2/5k\Omega$

OR $\mathbf{V_2 = V_1/2}$

For the circuit on the right:



For the inverting input:

$$\frac{0 - v_-}{1.0\ k\Omega} = \frac{v_- - V_2}{1.0\ k\Omega} \quad \text{rearrange} \rightarrow \quad v_- = \frac{V_2}{2}$$

For the non-inverting input:

$$\frac{V_1 - v_+}{3.0\ k\Omega} = \frac{v_+ - 0}{1.0\ k\Omega} \quad \text{rearrange} \rightarrow \quad v_+ = \frac{V_1}{4}$$

Setting $v_+ = v_-$ leads to $\mathbf{V_2 = V_1/2}$ (the same result as in the first circuit!)

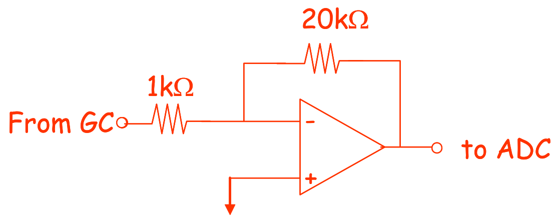
Since the current path through the circuit is through the opamp, the opamp circuit will be able to supply some current to the load (because of low output impedance) without loading the voltage source V_1 (because of high input impedance). The resistor-only circuit cannot supply current without loading the source.

13. You have been assigned the task of interfacing a liquid chromatograph to a computer-based data acquisition system. You have an 8-bit ADC with a ±10 V range to accomplish this task.

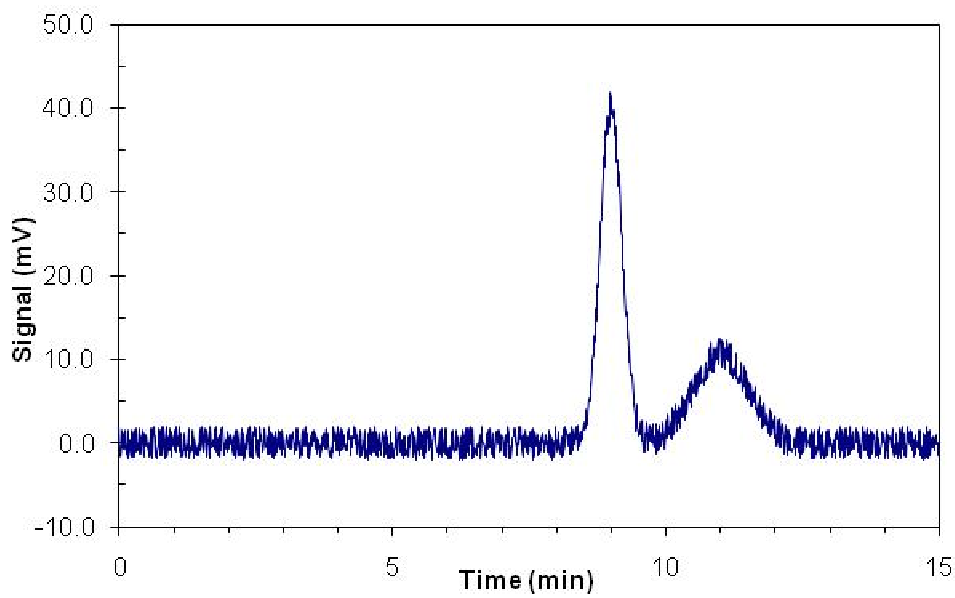
a. Because of the design of your LC detector, the maximum output voltage of the detector is 500 mV, with chromatographic peaks typically being a few tens of mV in size. Clearly describe the potential problems using your ADC system to monitor this signal.
b. Design an op-amp circuit to help address the primary problems you discussed in part a.

a. For this ADC, we have a total of 20V split into 2^8 or 256 bits. Therefore the size of the least significant bit, and ultimately the resolution, is 20V/256 or about 78 mV. Ultimately, this means that, on its own, the ADC cannot distinguish between signals that differ by less than 78 mV. Since our peaks are only a few mV in size, this poses a significant problem. Many of our peaks might be buried in the noise!

b. One possible solution is to amplify the signal before it reaches the ADC. A simple voltage follower circuit can accomplish this. Note that since the ADC has a ±10 V range, the sign of the output of the amplifier will not be an issue. Here is a circuit that would do the trick by providing a factor of 20 amplification. This effectively decreases the size of the LSB to about 4 mV, less than the size of a typical peak.



14. Below is an example chromatogram for the system described above. Each run consumes your sample and takes about 15 minutes to complete. The data below is an example of the results of one of your separations. You are unhappy with the signal to noise ratio of your data. Estimate the S/N ratio for the first peak and describe two approaches that are appropriate to this experiment that you might take to improve S/N for **this application**. Note any potential problems with these approaches. You **do not** need to have a solution to problem 13 to complete this problem.



The magnitude of the signal at the peak is ~40 mV. The average p-p noise, estimated away from the peak, is ~5 mV, giving a S/N of about 8.

For a chromatographic experiment, signal averaging is impractical because of the run-to-run variability in the measurement and the time necessary for a run. Therefore other options must be chosen. You should **discuss** how the method works and its limitations. Here are a few reasonable choices:

- Boxcar Averaging: Works on a single dataset, but you need to be careful so that you have enough data that when the boxcar is run, the result is still representative of the real data.
- Polynomial Smoothing: Same concerns as with boxcar averaging.
- Fourier Filtering: Math intensive, important not to filter out useful frequencies.

Possibly Useful Information

$\frac{dQ}{dt} = I = C\frac{dV}{dt}$	$P = IV = I^2R$
$V = IR$	$v_o = A(v_+ - v_-)$
$v_{rms} = \sqrt{4kTR\Delta f}$	001 + 001 = 010
$i_{rms} = \sqrt{2Ie\Delta f}$	Just because you're paranoid doesn't mean people aren't out to get you!
When all else fails, plug in the power cord.	$S_m = \overline{S}_{bl} + ks_{bl}$