

# Chemistry 524--Final Exam--Keiderling

May 6, 2009 – 3-8 pm -- 4440 SES

Please answer all questions **in the answer book** provided. Calculators, rulers, pens and pencils are permitted. **No open books or extra sheets allowed.** If you need a specific fundamental constant, conversion factor or definition ask for it; but everything needed should be in the exam, unless I made an error!

**Strategy** – there are lots of small questions, if you do not know one, skip ahead, leave a space in your answer book, it may come to you later and you will not waste time. You do not need to answer everything to get a good grade.

There is some possibly helpful information at the end of the exam. GOOD LUCK!

*In the second half of the course we surveyed a number of different optical spectroscopic techniques and for each we reviewed the technologies used for building the spectrometers used and the kinds of analytical applications they were put to. The beginning of this Final exam (questions 1 – 7) is organized like the end of the course. All answers should be very short and to the point, but should be best is in a few sentences. Unless it is clearly indicated to choose between them, all parts should be answered:*

**1. [7] Atomic spectroscopy** is very valuable but got a short attention in our lecture but was a large component of in the text. It comes in several flavors: Atomic Absorption (AA), atomic emission (AE), resonance fluorescence, and I am sure several others.

a. AA is the most commonly used of these. Give 1 – 2 good reasons why.

**Answer only one (1) of b or c:**

b. Explain how AA creates high selectivity among analytes (elements) while using relatively modest resolution optical components?

c. AE detection is sometimes enhanced in resolution by use of an echelle grating spectrograph. Explain how this might work to separate more emission lines.

**2. [9] Molecular spectra** are in general broader and, if they were resolved, much more complex than atomic spectra

a. Explain the broadening seen in molecular spectra

**Answer only one (1) of b or c:**

b. Explain why fluorescence and absorption between the ground and excited states (for example,  $S_0 \leftrightarrow S_1$ ) are not observed at the same frequency (wavelength).

c. If there is a large gap in frequency between the absorption and fluorescence maxima, give an explanation related to molecular structure.

**3. [33] Absorbance spectroscopy** in the uv-vis region underlies the most commonly used analytical techniques

a. Common scanning spectrometers, like our Varian 300, have a double beam design, while multichannel spectrometers, like the HP diode array one (used in freshman lab) are single beam. Explain why there is a difference.

**Answer only two (2) of b or c or d:**

b. Explain why the detector is placed after the monochromator in the scanning instrument yet before the monochromator in the diode array spectrometer?

c. Some absorbance spectrometers use double monochromators, explain typical reasons.

d. UV-vis spectrometers sometimes have dual gratings, explain why.

**Answer only one (1) of e or f:**

e. Explain what is the most commonly used detector for uv-vis spectrometers and why.

f. Cooling often can help improve S/N in uv-vis detectors. Why is this not commonly used in commercial absorbance instruments?

**Answer each one of g, h and i:**

g. Sometimes, usually top of the line, absorbance spectrometers are extended to the near IR region. Explain why this might be a convenient engineering solution for near IR, and itemize and explain the kinds of optical modifications needed to accomplish this extension.

h. If two analytes are present in solution and have absorbance broad bands that partially overlap, explain how their concentrations can be best determined using absorbance spectra.

i. Relate the intensity measured at the detector in an absorbance spectrometer to the concentration. Writing an equation is insufficient, deriving it or explaining the relationship would help.

**Answer only one (1) of j or k:**

j. Why are most organic analytes not colored, thus studied in the UV?

k. Why are transition metal complexes characterized by weak (low molar absorbance,  $\epsilon$ ) bands in the visible and near IR?

**4. [35] Molecular luminescence** is the counterpart to absorbance and consists of fluorescence and phosphorescence (and other less analytically relevant methods)

a. Common fluorimeters have two monochromators, but these are normally not double monochromators. Explain their use.

b. Sometimes polarizers are inserted to the excitation and emission beams, explain their use.

c. Many fluorimeters have two detectors, one for emission signal, and another placed at some point in the light path before the sample. Explain its use.

d. Explain the difference between fluorescence and excitation spectroscopy. Be sure to note the differences in how each monochromator is used.

**Answer only one (1) of e or f:**

- e. Explain how you might discriminate between fluorescence and phosphorescence.
- f. Lifetime has a useful analytical role in measuring and discriminating between fluorescence signals. Explain one way to determine lifetimes experimentally, what components would you add to the spectrometer and how would you interpret the signal from the detector?

**Answer only one (2) of g or h or i or j:**

- g. What is intersystem crossing and how could you change a molecular environment to promote it?
- h. Explain conditions or experimental design changes you might use to enhance phosphorescence intensity.
- i. Kasha's rule suggests most fluorescence is from the lowest lying excited singlet state (typically designated  $S_1$ ). Explain why it is often true.
- j. What is quenching and give an example of using it to determine fluorophore properties?

**Answer k:**

- k. Fluorescence is often said to be ideal for low concentrations. Derive conditions under which it is linear in concentration.

**5. [37] IR absorbance spectra** are primarily used to monitor molecular vibrations

- a. Modern FTIRs dominate the market, why are they favored over dispersive (monochromator based) instruments?
- b. For near IR one needs good S/N and broad spectral coverage to get band shapes, why are dispersive instruments still used (actually FTIR is also used)?
- c. Explain how ATR sampling works and what advantage it has over transmission IR sampling.

**Answer only one (1) of d or e:**

- d. Explain why IR sampling is such a major issue, i.e. why do you not just use standard cuvettes?
- e. Why do IR experiments require high concentrations?

**Answer only two (2) of f or g or h:**

- f. FTIRs usually include a DTGS detector, explain what this is and how it works.
- g. If I also have a MCT detector, which is more sensitive, explain why some experiments are better done with the DTGS?
- h. Explain why I must cool my MCT detectors and why I must move the mirror more rapidly to get better S/N, when using an MCT.

**Answer only one (1) of i or j:**

- i. The Jacquinot advantage has to do with throughput, explain how it is better than with a monochromator.
- j. Give an example where dispersive IR is favored over FTIR and explain why.

**6. Raman spectroscopy** also is focused primarily on vibrational spectra.

- How do selection rules in general change between IR and Raman and why does that make the spectra different if  $\Delta v = \pm 1$  for both?
- Explain the difference between Stokes and anti-Stokes Raman spectra, where you find these transitions and why Stokes is usually more intense.

**Answer only one (1) of c or d:**

- What is Resonance Raman spectra and how is it different from ordinary Raman? Give an analytical applications of Resonance Raman?
- What is SERS, how does it work? Give an example of how is it used for analytical purposes?

**Answer only one (1) of e or f:**

- Why is it difficult to use Raman for absolute concentration determination even though the scattering signal is linear with concentration?
- Why are sample cells and solvents less of a problem in Raman than IR if both detect vibrational transitions?

**Answer both g and h:**

- Why is linear polarization valuable (relative between excitation and scattered beams) for Raman spectra of isotropic systems (e.g. solutions) but not for IR?
- Your professor is biased and feels that FT-Raman spectrometers will fade from use in the coming decade. Is he right or wrong, justify argument for either side (there is no uniquely correct answer!).

**7. Circular dichroism** is measured as a modulation absorption spectroscopy.

**Answer only one (1) of a or b:**

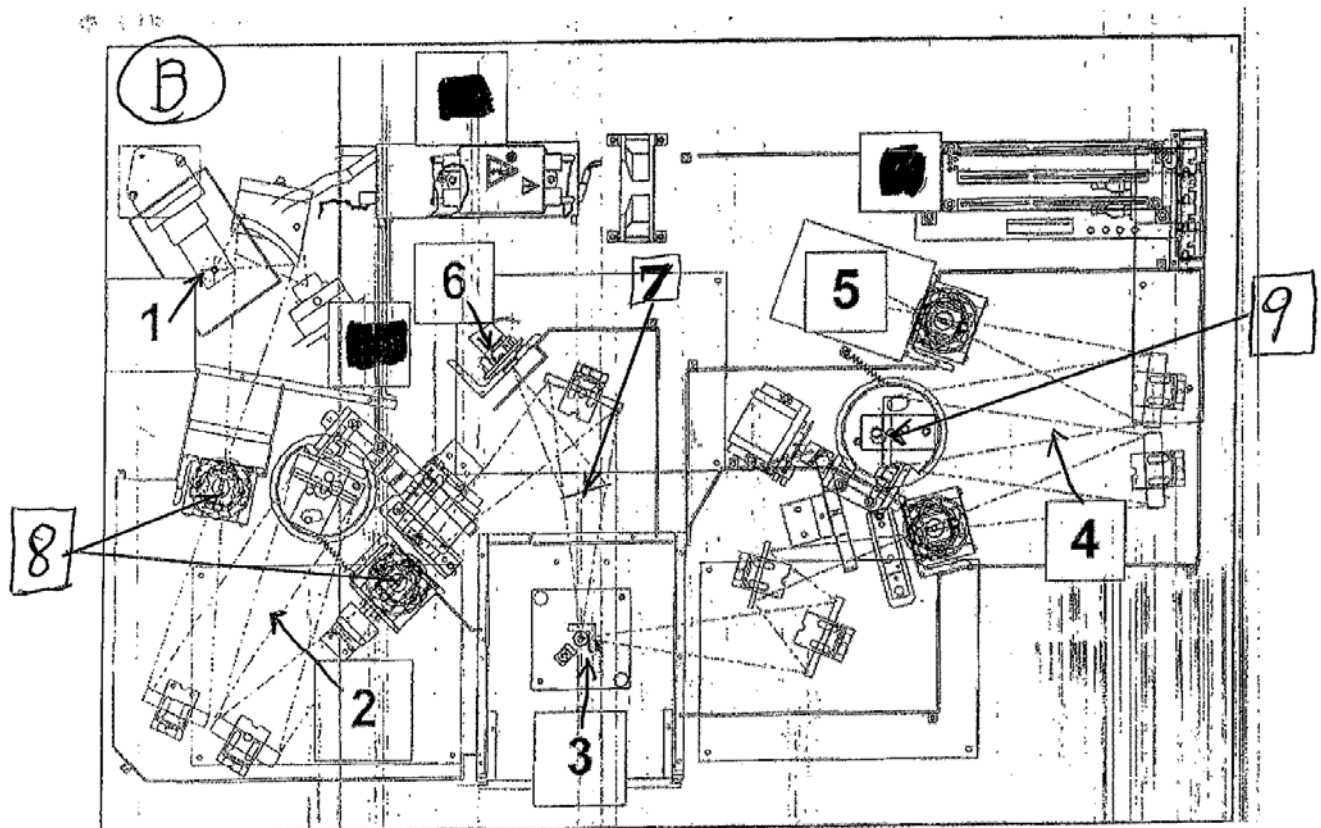
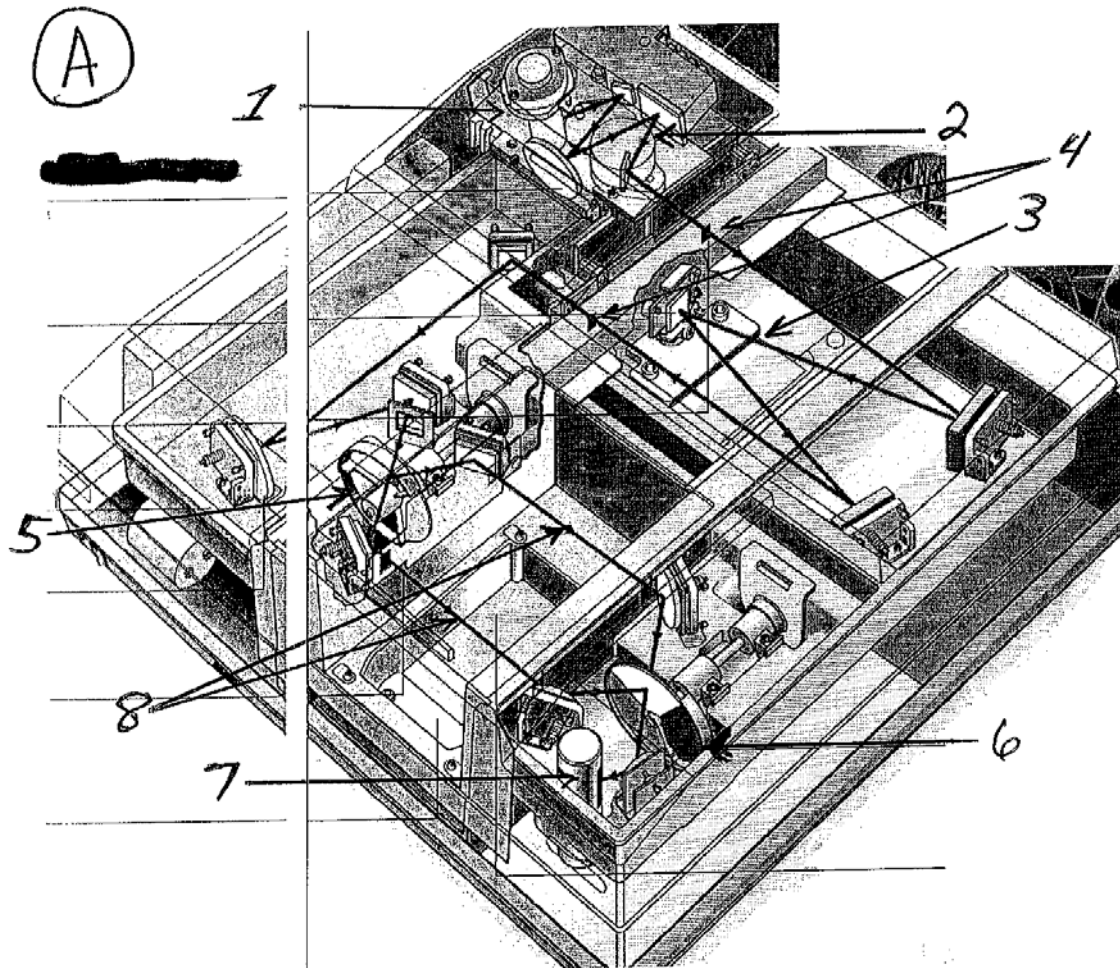
- Why is CD expressed in ellipticity units?
- What kinds of samples can be measured with CD and what can be learned?

**Answer only one (1) of c or d:**

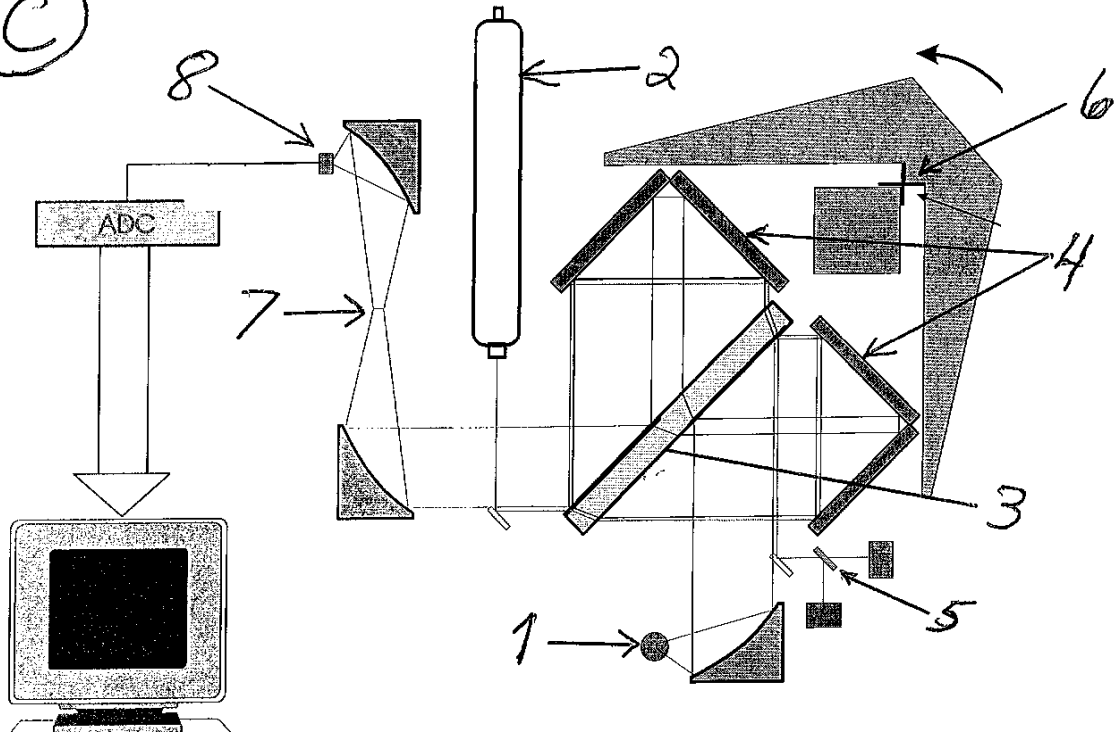
- What is being modulated in the CD instrument and why is the signal proportional to  $\Delta A$ ?
- Why are double monochromators used if CD is absorbance?

**8. [60]** For the **six (6) attached instrument diagrams (A,B,C,D,a,b) do A and D and choose between B and a and between C and b [i.e. do four (4) total]**. Enumerate their possible function and design of each labeled (by #) part. You may make a table with the numbers coding the objects in the diagram and for each identified item propose specifically which type of component (e.g. "source: quartz-halogen or W-I lamp" or "detector: PMT") is being used (note: for optical components, just put what it is and purpose, e.g. lens, focus beam on slit). For the source and detector, briefly justify the choice. **Finally state the purpose of the instrument shown and why you think that.**

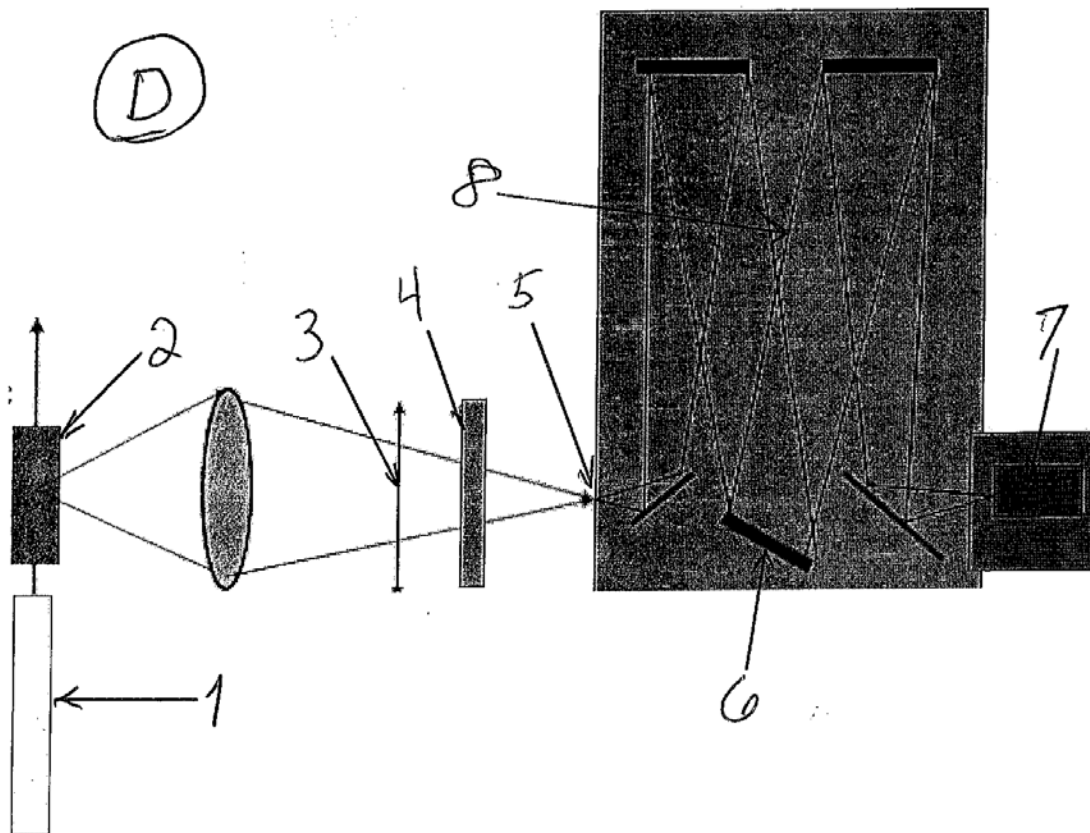
9. **[8]** For only two (2) of the following, very briefly explain the physical source of this type of noise and/or how it varies with experimental parameters (e.g. temperature, light level, etc.) and propose a common solution to reduce its impact on measurement.
- Shot noise
  - Flicker noise
  - 1/f noise
  - dark noise
  - Johnson noise
10. **[10]** Choose two (2) of the following for short discussion answers.
- Distinguish between real and ideal blanks for determining detection limits by detailing what is missing from one or the other.
  - Describe how stray radiation can lead to deviations from Beer's law and how photometric inaccuracy could result from improper choice of slit width.
  - Explain how the S/N varies in an absorption experiment for increasing absorbance when the measurement is initially shot noise limited. Be sure to be realistic, in terms of changing conditions with increasing absorbance.
  - Explain why S/N for fluorescence increases (or comes to a constant value) with photon flux under all conditions, while absorbance spectra have a maximum S/N with increasing absorbance.
11. **[5]** Choose one: Explain how a lock-in amplifier or a boxcar averager works and how it leads to S/N enhancement. Be very clear as to any experimental constraints that are required to make use of such an instrument.
12. **[8]** We described a number of simple circuits in class, **for two (2) of the following**, sketch a minimal circuit diagram and relate the output to the input signal:
- Op Amp inverting amplifier
  - Cathode follower (op amp)
  - Low pass filter
  - Band pass (tank) filter
13. **[12]** My FTIR came with two sources, 3 beam splitters and 3 detectors and works in the near IR, mid IR and far IR. Describe the changes needed in these components between spectral regions and what types of components are used in each (e.g. type detector etc.).

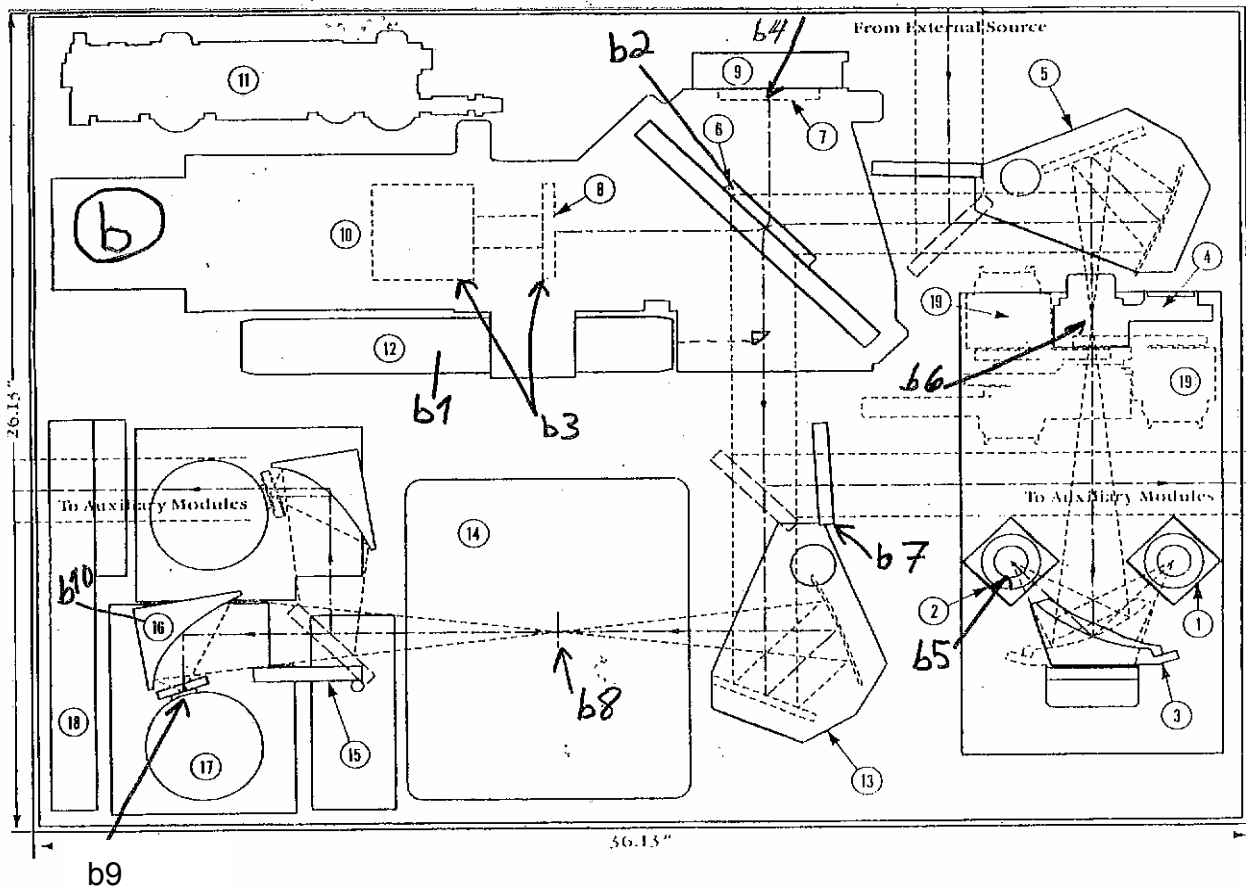
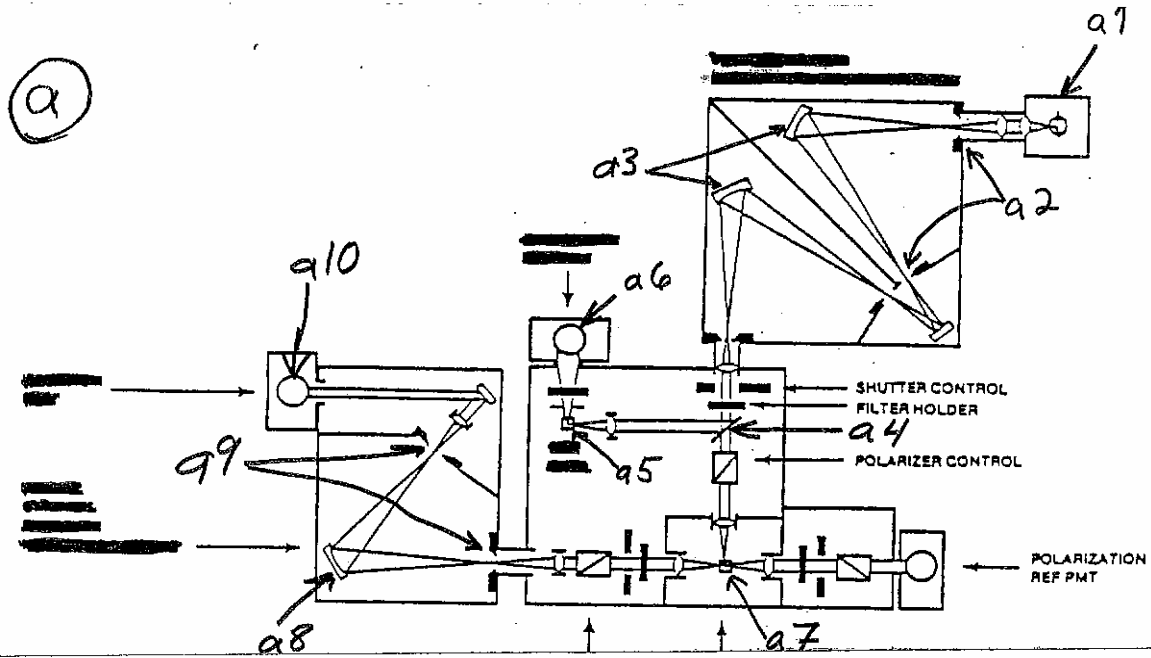


(C)



(D)





For drawing b: answer for labels "b#" and NOT for numbers (#) in a circle