Name: KEY

Chemistry 61
Test 2
November 7, 2002

Instructions:

1. Write your name in the space above and on the backs of the other pages.
2. You may use as a reference both sides of an 8.5" x 11" piece of paper filled with information, and the packet of Problem Set 5 summaries. No other references are allowed.
3. Your exam booklet should have **ten** pages total, with questions on pages 2-9.
4. You will have two hours to work on this test. (Working time may be extended.)

Question (Possible Points)	Your Score
Question 1 (20)	
Question 2 (23)	
Question 3 (10)	
Question 4 (6)	
Question 5 (12)	
Question 6 (14)	
Question 7 (15)	
Total (100)	

1. Answer the following questions about two instruments in our department, the Buck Atomic Absorption Spectrometer and the Beckman Dispersive Infrared Spectrophotometer.

(a) (5 points) Which instrument has a set of four gratings and computer-controlled slit widths? Explain what this equipment allows us to do during a measurement.

Beckman Dispersive IR. Each grating has a different # of lines/mm ⇒ different D^{-1}. By choosing a grating with higher D^{-1}, we can widen slits (∴ increasing the # of photons hitting detector) w/o sacrificing resolution.

$\Delta\lambda_{eff} = w D^{-1}$

(b) (4 points) One of the gratings used in these instruments is blazed at 350 nm, and has 600 lines/mm. Calculate the blaze angle in first order.

$n\lambda = d(\sin i + \sin r) = 2d\sin\theta_B \quad (i = r)$

$\theta_B = \sin^{-1}\left(\frac{n\lambda}{2d}\right) = \sin^{-1}\left[\frac{(1)(350\,nm)}{2}\left(\frac{600}{mm}\right)\left(\frac{mm}{10^6\,nm}\right)\right] = 6.03°$

(c) (3 points) The grating in part (b) is 2.5 cm wide. Assuming that the optics in the monochromator collimate the source light to cover the entire width of the grating, calculate the smallest possible first-order resolution (in nm) provided by the grating at 350 nm.

$\frac{\lambda}{\Delta\lambda} = nN \Rightarrow \Delta\lambda = \frac{\lambda}{nN} = \frac{350\,nm}{(1)(2.5\,cm)\left(\frac{6000}{cm}\right)} = 2.3\times10^{-2}\,nm$

(d) (3 points) Briefly explain why the overall resolution of the monochromator containing the grating described in part (c) will be larger (that is, worse) than what you calculated in (c).

The exit slit width will surely let $\Delta\lambda > 2\times10^{-2}\,nm$ (@ 350nm) pass thru at once.

(Question 1 continues on the next page)

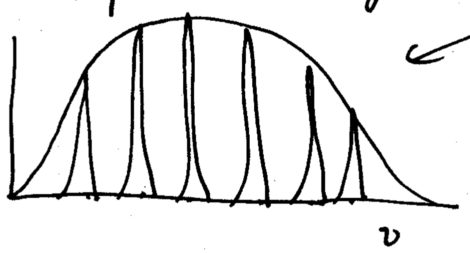
(e) (5 points) Which of the two instruments uses a double-beam approach, and why is this approach prudent for this instrument?

IR. ~~[crossed out]~~ Periodic monitoring of the background prudent because (i) $H_2O_{(g)}$ and $CO_{2(g)}$ absorb significantly in the mid-IR and (ii) their concentrations can fluctuate appreciably on the time scale of your experiment

2. Let's explore the common and useful helium-neon laser.

(a) (6 points) Under typical operating conditions, the He-Ne gain curve is reasonably monochromatic, with $\Delta\nu_{1/2}$ = 1500 MHz. However, it is possible to achieve a far higher degree of monochromaticity ($\Delta\nu_{1/2}$ = 0.5 MHz). Explain in terms of laser design and optics how one would achieve such a small bandwidth.

Having a cavity of fixed length supports standing waves (so-called "axial modes"), 6 of whose resonance freqs overlap the He-Ne gain curve. Each mode has $\Delta\nu_{1/2}$ = 0.5 MHz.



Inserting an étalon in the cavity selects out one of the modes.

(b) (5 points) Calculate the spread in wavelengths (in nm) to which a bandwidth of 0.5 MHz corresponds. (Remember that the most intense lasing transition in He-Ne is at 632.8 nm.)

$$\lambda = \frac{c}{\nu} \Rightarrow \left|\frac{d\lambda}{d\nu}\right| = \pm\left|-\frac{c}{\nu^2}\right| \Rightarrow \Delta\lambda = \pm\frac{c}{\nu^2}\Delta\nu$$

$$\frac{\lambda^2}{c^2} = \frac{1}{\nu^2} \quad\rightarrow\quad \Delta\lambda = \pm\frac{\lambda^2}{c}\Delta\nu$$

$$\Delta\lambda = \pm\frac{(632.8)^2 \times 10^{-18}\,\text{m}^2}{3\times10^8\,\text{m s}^{-1}}(0.5\times10^6\,\text{s}^{-1})\left(\frac{10^9\,\text{nm}}{\text{m}}\right) = \pm\, 7\times10^{-7}\,\text{nm}$$

(Question 2 continues on the next page)

(c) (5 points) Explain from fundamental ideas the pattern of He-Ne laser light you see displayed in this classroom.

we see 2D x sections of planar and cylindrical nodes present in transverse electromagnetic modes. This is the quantization of intensity present in the cylindrical laser cavity.

(d) (5 points) Would the laser beam on display be useful for the laser-induced fluorescence measurements described in Julia's and John's summaries? Explain why or why not in terms of your answer to part (c). (Note: A plausible case could be made for either answer; I will grade on the quality of your reasoning.)

everyone received full credit

(e) (2 points) The He-Ne laser on display is running continuously. Very briefly, what does this tell us quantum mechanically about the active medium?

4-level system

3. Two common detectors are the phototube and the photomultiplier tube (PMT)

(a) (5 points) Which of the two has the higher intrinsic gain? Explain your choice.

PMT, since it has several dynodes btwn the photocathode and the anode. The KE of any e⁻ hitting a dynode will supply the work function for several electrons at the surface of that dynode.

A phototube has nothing btwn photocathode and anode.
⇒ zero intrinsic gain

(b) (5 points) The current from which of the two devices can be amplified more accurately? Explain your choice.

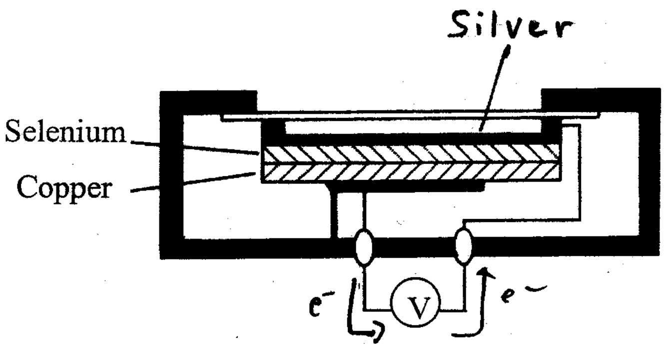
The lack of dynodes gives the phototube a higher impedence, which allows for more accurate measurement:

(one big vacuum gap)

(+) ·) (−)

$$\text{error in } i = -\frac{Z_{meter}}{Z_{int} + Z_{meter}}$$

4. Consider the following photovoltaic cell:



(a) (3 points) Briefly explain how this cell can detect light without being connected to a voltage source.

The free energy released in the spontaneous e⁻ xfer gives rise to a voltage

(b) (3 points) In the diagram above, label the direction of electron flow, and briefly justify your answer below.

$\mathcal{E}^\circ(Ag/Ag^+) > \mathcal{E}^\circ(Cu/Cu^{2+}) \Rightarrow e^-$ travel from Cu to Ag

5. A detailed analysis of noise in Beer's Law measurements facilitates the intelligent design of experiments.

(a) (4 points) Compute the relative uncertainty, s_C/C, in a measurement affected only by Case I noise. Assume that in the measurement, $A = 0.200$ and $k_1 = 0.00300$.

$$\frac{s_c}{C} = \pm\left|\frac{s_T}{T\ln T}\right| \qquad s_T = k_1 \qquad T = 10^{-A}$$

$$= \pm\left|\frac{0.00300}{(10^{-0.200})(\ln 10^{-0.200})}\right| = \pm 0.0103 \quad (\text{or } \pm 1.03\%)$$

(b) (8 points) Derive an equation that would allow us to calculate the value of T that would minimize s_C/C due to Case II noise. (Note that if your derivation fares well, you should obtain a transcendental equation which can only be solved numerically.)

$$\frac{s_c}{C} = \pm\left|\frac{s_T}{T\ln T}\right| = \pm\left|\frac{k_2\sqrt{T^2+T}}{T\ln T}\right|$$

Find T such that

$$\frac{d(s_c/c)}{dT} = 0 = \frac{(T\ln T)k_2(\tfrac{1}{2})(T^2+T)^{-1/2}(2T+1) + k_2\sqrt{T^2+T}\,(T(\tfrac{1}{T}) + \ln T))}{T^2(\ln T)^2}$$

$$0 = \frac{(T\ln T)(2T+1)}{2\sqrt{T^2+T}} + (1+\ln T)\sqrt{T^2+T}$$

$$0 = \frac{(T\ln T)(2T+1)}{T} + 2(1+\ln T)(T^2+T)$$

$$0 = (2T+1)\ln T + (2T+2)(1+\ln T)$$

$$0 = 2T\ln T + \ln T + 2T + 2 + 2T\ln T + 2\ln T$$

$$\boxed{0 = (4T+3)\ln T + 2T + 2}$$

6. (14 points) Inspired by the environmental chemistry research of Kris McNeill at the U, you seek to device a method for the precise determination of unmetabolized and partially metabolized pharmaceutics. You have the choice of monitoring the concentration of an α,β-unsaturated ketone either by its electronic transition at ~300 nm, or by its C=O stretch at ~1600 cm^{-1}.
   (i) Propose an appropriate source, wavelength selector, and detector for both the UV and IR experiments. (Note that FTIR is not an option.)
   (ii) Discuss in detail the sources of random error (noise) in either the UV or the IR experiment.

-1 per error in part (i)

-2 no mention of Johnson (but do mention dark current)

-3 no mention of Case III

7. (15 points total) Circle the best answer to each of the following five questions. Your answers need not be justified, and no partial credit will be awarded.

A. Which of the following statements about wavelength selectors is true?

(a) Prisms, which use refraction to separate wavelengths of light, have reciprocal linear dispersions that are independent of wavelength.

3 chose this (b) Using spectroscopy to identify a substance often requires smaller effective bandwidths ($\Delta\lambda_{eff}$) than using spectroscopy to quantify the concentration of that substance.

(c) The bandpass of a pair of absorbance filters is typically narrower than the bandpass of an interference filter.

(d) The equation $D^{-1} = \frac{d}{nF}$ provides an accurate estimate of the reciprocal linear dispersion of a grating regardless of the angle the incident light ray makes to the normal to the plane of the grating.

(e) Statements (a), (b), (c), and (d) are all false.

B. Which of the following statements about lasers is false?

(a) One of the mirrors in a laser cavity is designed to have a reflectance of less than 100 %.

(b) In the He-Ne laser, stimulated emission in the visible region occurs from electronically excited He atoms.

4 (c) A substance at thermal equilibrium is capable of lasing.

(d) Higher-order transverse electromagnetic modes (TEM's) excite a greater fraction of the active medium than TEM_{00}.

(e) Unlike a dye laser, a Nd^{3+}:YAG-pumped optical parametric oscillator is capable of producing tunable light in the mid-infrared.

C. Which of the following detectors measure changes in temperature by changes in resistance?

(a) A silicon diode.

6 (b) A bolometer.

(c) A pyroelectric detector.

(d) A thermocouple.

(e) None of the above.

(Question 7 continues on the next page)

D. Which of the following statements about spectroscopy instrumentation is true?

(a) A colorimeter can quantify the percent transmittance of a sample.
(b) A diode array spectrometer requires neither an entrance or exit slit.
(c) A photometer uses either a grating or a prism as part of its wavelength selector.
(c) Double-beam absorption spectrophotometers require a separate detector for each beam.
2 (e) Statements (a), (b), (c), and (d) are all false.

E. Which of the following statements about laser applications is false?

(a) Detection of NO by laser ionization is more sensitive than detection of NO by laser-induced fluorescence..
(b) Lasers can be used to probe the presence of both radical and cationic intermediates.
2 (c) In the high-resolution study of NiF, the researchers used a dye laser pumped by a doubled Nd:YAG laser.
(d) The stability of argon ion laser intensity is essential for growing needles of *para*-hexaphenyl on mica.
(e) Fluorescence lifetime can be used to probe the composition of potentially contaminated water samples in the environment.

Possibly Useful Information

Standard Reduction Potentials at 25 °C[a]
A. Acidic Aqueous Solution

Half-Reaction	E°, Volts
$F_2(g) + 2e^- \longrightarrow 2F^-$	2.87
$H_2O_2(aq) + 2H^+ + 2e^- \longrightarrow 2H_2O(l)$	1.76
$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O(l)$	1.51
$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O(l)$	1.36
$Cl_2(g) + 2e^- \longrightarrow 2Cl^-$	1.36
$O_2(g) + 4H^+ + 4e^- \longrightarrow 2H_2O(l)$	1.23
$Br_2(l) + 2e^- \longrightarrow 2Br^-$	1.07
$NO_3^- + 4H^+ + 3e^- \longrightarrow NO(g) + 2H_2O(l)$	0.96
$Ag^+ + e^- \longrightarrow Ag(s)$	0.80
$Fe^{3+} + e^- \longrightarrow Fe^{2+}$	0.77
$O_2(g) + 2H^+ + 2e^- \longrightarrow H_2O_2(aq)$	0.70
$I_2(s) + 2e^- \longrightarrow 2I^-$	0.54
$Cu^+ + e^- \longrightarrow Cu(s)$	0.52
$Cu^{2+} + 2e^- \longrightarrow Cu(s)$	0.34
$Cu^{2+} + e^- \longrightarrow Cu^+$	0.16
$2H^+ + 2e^- \longrightarrow H_2(g)$	0.00
$Fe^{3+} + 3e^- \longrightarrow Fe(s)$	−0.04
$Cr^{3+} + e^- \longrightarrow Cr^{2+}$	−0.42
$Fe^{2+} + 2e^- \longrightarrow Fe(s)$	−0.44
$Cr^{3+} + 3e^- \longrightarrow Cr(s)$	−0.74
$Zn^{2+} + 2e^- \longrightarrow Zn(s)$	−0.76
$Cr^{2+} + 2e^- \longrightarrow Cr(s)$	−0.90
$Al^{3+} + 3e^- \longrightarrow Al(s)$	−1.67
$Mg^{2+} + 2e^- \longrightarrow Mg(s)$	−2.36
$Na^+ + e^- \longrightarrow Na(s)$[b]	−2.71
$Ca^{2+} + 2e^- \longrightarrow Ca(s)$	−2.84
$Sr^{2+} + 2e^- \longrightarrow Sr(s)$	−2.89
$Ba^{2+} + 2e^- \longrightarrow Ba(s)$	−2.92
$Cs^+ + e^- \longrightarrow Cs(s)$	−2.92
$Rb^+ + e^- \longrightarrow Rb(s)$	−2.93
$K^+ + e^- \longrightarrow K(s)$	−2.93
$Li^+ + e^- \longrightarrow Li(s)$	−3.05