

wc 75 ± 15

A 90-100  
A- 85-89  
B+ 80-84  
B 60-79  
B- 55-59  
C+ 50-54  
C 35-49

$c = 3 \times 10^8 \text{ m/sec}$   
 $1 \text{ nm} = 10^{-9} \text{ m}$   
 $h = 6.626 \times 10^{-34} \text{ J sec}$   
A  $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$

Chem 4190/6190  
Midterm Exam  
October 1, 2008

Name: \_\_\_\_\_

(Exam is closed book, but one 8.5 by 11 inch sheet of notes can be used.)

1. (5 pts) Light of wavelength 300 nm in air ( $n_D = \text{index of refraction} = 1$ ) has frequency (in hz)

$$\nu = c/\lambda = \frac{3 \times 10^8 \text{ m/sec}}{300 \times 10^{-9} \text{ m}} = 1 \times 10^{15}$$

- (a)  $1.0 \times 10^{-15}$  (b) 1000 (c)  $1.5 \times 10^{13}$  (d)  $1.0 \times 10^{15}$

2. (5 pts) In NMR, the frequency of "light" absorbed by nuclear spins is typically 60 Mhz. The corresponding photon energy, in eV, is

$$E = h\nu = (6.626 \times 10^{-34} \text{ J sec}) \times (60 \times 10^6 \text{ sec}^{-1})$$

- (a)  $2.38 \times 10^{-9}$  (b)  $2.48 \times 10^{-7}$  (c)  $2.48 \times 10^{-2}$  (d) 2.48

$$\frac{1.602 \times 10^{-19} \text{ J/eV}}{1} = 2.48 \times 10^{-7} \text{ eV}$$

3. (5 pts) The refractive index of 589 nm light in a liquid is 1.20. The speed of light in the the liquid (in m/sec) is

$$c = \frac{c_{vac}}{n} = \frac{3}{1.2} = 2.5 \times 10^8$$

- (a)  $2.10 \times 10^8$  (b)  $2.50 \times 10^8$  (c)  $3 \times 10^8$  (d)  $4.29 \times 10^8$

4. (5 pts) In a double beam experiment, the light emerging from the "sample" cell is only 1/5 the intensity of that emerging from the "reference" cell. What is the % Transmittance of the sample?

- (a) 5 (b) 20 (c) 50 (d) 500

5. (5 pts) What is the absorbance of the sample in the previous problem?

- (a) .05 (b) .20 (c) .70 (d) 1.61

$$A = -\log_{10} T = -\log_{10} (1/5) = 0.699$$

6. (5 pts) Suppose 5 ml of the sample in the previous two problems is diluted to 10 ml with a nonabsorbing liquid (the same solvent used in the reference cell). Also let  $A_0$  denote the absorbance of the undiluted sample. The transmittance of the diluted sample can be written

- (a)  $10^{-A_0/2}$  (b)  $10^{-A_0}$  (c) 0.1 (d) 0.4

$$T = 10^{-A} = 10^{-A_0/2}$$

7. (5 pts) Light of wavelength 91.2 nm is required to ionize a single hydrogen atom (promote an electron from ground level ( $j = 1$ ) to  $j = \infty$ ). This corresponds to what energy (in eV)?

- (a)  $2.18 \times 10^{-18}$  (b) .0014 (c) 13.6 (d)  $.18 \times 10^7$

A B  
1 → 1  
2 → 2  
3 → 3  
4 → 4  
5 → 5  
6 → 6  
7 → 7  
8 → 8  
9 → 9  
10 → 10  
11 → 11  
12 → 12  
13 → 13  
14 → 14

d  
b  
b  
b  
c  
c  
c

35 pts

8. (5 pts) A diffraction grating has 3000 blazes/mm and is illuminated at an angle of incidence of  $80^\circ$ . At an angle of reflection of  $30^\circ$ , the maximum wavelength of reflected light (in nm) is

$$n\lambda = d(\sin i + \sin r) = 500$$

$\uparrow$   
 $\frac{1 \times 10^6 \text{ nm/mm}}{3 \times 10^3 / \text{mm}}$

- (a) 250 (b) 500 (c) 604 (d) 1208

9. (5 pts) The angles of incidence and refraction of light passing through an air-crystal interface are  $45^\circ$  and  $28^\circ$ , respectively. What is the index of refraction,  $n_D$ , of the crystal (the refractive index of air is 1.00)?

$$\frac{\sin \theta_1}{\sin \theta_2} = \frac{n_2}{n_1} \Rightarrow \frac{\sin 45}{\sin 28} = \frac{n_2}{1} = 1.51$$

- (a) .66 (b) 1.00 (c) 1.23 (d) 1.51

10 (5 pts) Suppose the absorption maximum of a dye occurs at 250 nm in ethanol and at 270 nm in acetone (a less polar solvent). The electronic transition the absorption corresponds to is most likely to be?

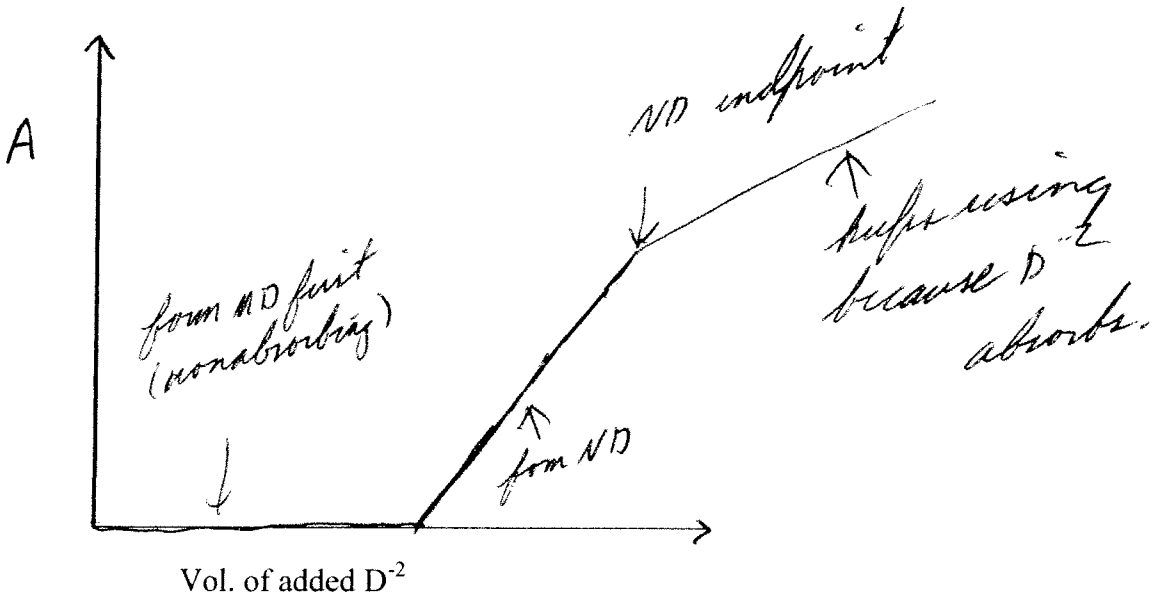
more polar  $\rightarrow$  shorter  $\lambda$   
(blue shift)

- (a)  $\sigma \rightarrow \sigma^*$  (b)  $\pi \rightarrow \pi^*$  (c)  $n \rightarrow \pi^*$  (d)  $\pi \rightarrow \sigma^*$

11. (15 pts) Consider the photometric titration of a mixture of two divalent metal ions:  $M^{+2}$ , and  $N^{+2}$ ; with dye  $D^{-2}$ . The equilibrium constants are given below



At a wavelength of 500 nm,  $D^{-2}$  and  $ND$  are strongly absorbing, but none of the other species are. Sketch the photometric titration curve of a mixture of  $M^{+2}$  and  $N^{+2}$  being titrated with  $D^{-2}$ .



b  
d  
c

30 pts

12. (17 pts) In preparing a 0.05 M NaCl solution (MW of NaCl = 58.44 gm/mole), mass  $m = 2.922 \pm 0.004$  gm of NaCl is diluted to volume  $V = 1.00 \pm 0.005$  liter in a volumetric flask. First of all write down a general expression for the uncertainty in concentration (in moles/liter),  $|\Delta c|$ , in terms of  $m$ ,  $V$ ,  $|\Delta m|$ , and  $|\Delta V|$ . Second, determine  $|\Delta c|$  given the above information. (You can ignore the buoyant mass correction).

$$\frac{|\Delta c|}{c} = \sqrt{\frac{|\Delta m|^2}{m^2} + \frac{|\Delta V|^2}{V^2}} = \sqrt{\left(\frac{0.004}{2.922}\right)^2 + \left(\frac{0.005}{1.0}\right)^2}$$

$$= \sqrt{\frac{1.67 \times 10^{-6}}{1.87 \times 10^{-6}} + \frac{2.50 \times 10^{-5}}{2.50 \times 10^{-5}}} = \sqrt{1.87 + 1} = 1.58 \times 10^{-3}$$

$$c = \frac{m}{VM} = \frac{2.922}{1.0 \times 58.44} = 5 \times 10^{-2} \frac{\text{moles}}{\text{liter}}$$

$$|\Delta c| = 2.59 \times 10^{-4} \frac{\text{moles}}{\text{liter}}$$

13. (10 pts) 4-Xylene ( $C_6H_4(CH_3)_2$ , MW = 106 gm/mole) absorbs strongly in the ultraviolet. A solution is prepared in which 0.1 ml of pure 4-Xylene liquid (density = 0.86 gm/ml) is diluted to 10 ml with cyclohexane. What is the concentration of 4-Xylene of the diluted sample in moles/liter?

$$\rho_{\text{pure liq}} = \frac{0.86 \text{ gm/ml}}{106 \text{ gm/mole}} = 8.11 \times 10^{-3} \frac{\text{moles}}{\text{ml}}$$

$$c = \frac{(8.11 \times 10^{-3} \frac{\text{moles}}{\text{ml}})(0.1 \text{ ml})}{(10 \text{ ml})} \left(10^3 \frac{\text{ml}}{\text{liter}}\right) = 0.0811 \frac{\text{moles}}{\text{liter}}$$

14. (8 pts) The Absorbance at 220 nm of the diluted 4-Xylene in the previous problem is 1.09 in a 1 mm pathlength cell. Assuming the "baseline" was measured using the same sample cell (in single beam mode) and contained cyclohexane only, what is the molar absorptivity of 4-Xylene (in liter/(mole cm))?

$$\epsilon = \frac{A}{c \ell} = \frac{1.09}{c (0.1 \text{ cm})} = \frac{10.9}{c} = 134 \frac{\text{L}}{\text{mole cm}}$$

from prev. problem)

35 pts