Chemistry 237 — First Exam
March 4, 2010 — Tellinghuisen

Honor Code Pledge: I have neither given nor received aid on this exam. _____

(Signature)

I. (30) **Least Squares**. Statistician Marge Inovera has collected some data (x_i, y_i) which she thinks should follow the relationship, $y = a\,x + b\,\exp(3x^2)$.

A. Help Marge with her analysis by obtaining the least-squares equations for an unweighted fit of data to this equation. Then express these using matrix notation. (Note: It is NOT necessary to solve these equations. Assume, as we have always done, that x is error-free.)

B. Alternatively, Marge could modify the fit relation to permit use of a straight-line fitting routine. If she chooses to fit to the form $Y = a + b\,X$, how should she define Y and X in terms of y and x?

C. In the latter analysis, how should the data be weighted?

D. A quantity is measured 29 times, yielding 12.3456 for its mean and $S = 0.7114$ for its sum of squared residuals. What is the approximate uncertainty of measurement (s_y) for this quantity? If you repeated the experiment but did 290 measurements, what (approximately) would you expect for S and s_y?

II. (16) **Conjugated Dye Absorption.** One of the conjugated dyes we studied in the laboratory has a molar mass of 454.4 g/mol.

A. A stock solution is prepared by dissolving 5.3±0.2 mg of dye in 25.0 mL of methanol. Calculate the concentration of this solution and its uncertainty, and report the results correctly.

B. 3.00 mL of this solution is placed in a second 25.0-mL volumetric flask, which is then filled to the mark with methanol. When placed in a 2.00-mm cuvette, this solution yields a peak absorbance of 3.45. Assuming this measurement is valid, what would you expect for the peak absorbance of a 3rd sample, prepared by placing 2.00 mL of the 2nd solution in a 25.0-mL vol flask and filling to the mark, if this sample is measured in a 1.000-cm cuvette.

C. A conjugated dye like those we studied has 5 C atoms in its chromophoric chain and shows peak absorbance at 535 nm. From the simple theory, where do you expect the peak to occur for the dye having 9 C atoms in its chromophoric chain? (Treat wavelengths as vacuum.)

III. (30) **Atomic Term Notation.** Consider the $_5$B atom.

A. Give the ground configuration, the ground term, and the ground state.

B. The first excited configuration of B is obtained by promoting a 2*s* electron to 2*p*. Give this configuration.

C. Using what we found in class for the ground configuration of $_6$C, work out all the terms of this excited configuration. [Hint: Use the C results for L_{12} and S_{12} and then couple on the 2s electron.]

D. Compute the total degeneracy of this excited configuration from the standpoint of the available orbitals. Then confirm that you get the same results by considering (1) the S and L degereracies of all terms, and (2) the summed J degeneracies.

E. Give all the eigenvalues for $\hat{S}^2$, $\hat{S}_z$, $\hat{L}^2$, $\hat{L}_z$, $\hat{J}^2$, and $\hat{J}_z$, operating on the states of a ^{3}D term.

IV. (12) **Significance**.

A. Consider the following two cases: (1) In 1948 Babcock and Herzberg analyzed an electronic absorption transition in O_2 and obtained for the ground-state rotational constant, B_0'' = 1.437770(15) cm^{-1}, whereas in 1968 McKnight and Gordy used microwave spectroscopy to obtain B_0'' = 1.437681(1) cm^{-1}. (2) In 1976 Tellinghuisen, *et al.* estimated the dissociation energy of the ground state of XeCl to be 255(10) cm^{-1}, whereas later analysis by Sur, *et al.* yielded D_e = 281(10) cm^{-1}.

Which of these two cases constitutes the greater cause for "concern," and why?

B. This question concerns the KaleidaGraph output shown to the right, for an unweighted least-squares fit.

(a) Report each result and its error with the proper number of significant figures.

(b) Are any of the fit parameters statistically insignificant? Explain.

y = a*exp(b*(x-20) + c*(x-20...		
	Value	Error
a	28.513702	0.0002869884
b	0.0010948899	6.41379e-06
c	-1.909398e-06	5.418037e-06
Chisq	3.6412854e-06	NA
R	0.99989437	NA

V. (12) **Spectroscopic Fundamentals.** A particular atom has four energy levels, labeled 1-4 in order of increasing energy. A transition between levels 1 and 3 occurs at 246 nm, while one between levels 2 and 4 falls at 410 nm (both measured in vacuum). Level 4 is 11430 cm^{-1} above level 3. Calculate the wavenumber and wavelength (vacuum) of a transition between levels 1 and 2.

Fundamental Constants

$N_A = 6.022\,142\,0\times10^{23}$/mol	$c = 2.997\,924\,58\times10^{8}$ m/s	$h = 6.626\,068\,8\times10^{-34}$ J s
$e = 1.602\,176\,462\times10^{-19}$ C	$m_e = 9.109\,381\,9\times10^{-31}$ kg	$m_p = 1.672\,621\,6\times10^{-27}$ kg