Chemistry 236 — Hour Exam
November 28, 2001 — Tellinghuisen

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

(Signature)

I. (25) Least Squares. Statistician Marge Inovera has collected some data (x_i,y_i) which she thinks should follow the relationship, $y = a/x + b\,x$.

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. Suppose the fit has been carried out and the values of a and b determined. Give an equation Marge can use to compute the estimated variance in y, s_y^2. (Be specific.)

Before beginning Part II, please enter here the names of your lab partners and the number of peer points you wish to award to each. The total must sum to 25.

II. (30-40) Error Propagation, Confidence Limits, etc. Do 2 and **ONLY 2** of the following three problems. [Note: They are not all equal in point value.]

A. (15) This problem is a continuation of Problem I on the first page.

1. For a 2×2 matrix $\mathbf{A} = \begin{pmatrix} p & q \\ r & s \end{pmatrix}$, the inverse $\mathbf{A}^{-1} = D^{-1} \begin{pmatrix} s & -q \\ -r & p \end{pmatrix}$, where D is the determinant, D = ps – qr. Give expressions for the estimated variances (s_a^2 and s_b^2) in the parameters from the least-squares fit of data to $y = a/x + b\,x$. (Your answers should be in terms of the quantities obtained in your solution to Problem I, including s_y^2).

2. Describe a way you could transform the (x_i, y_i) data into a form that would permit you to fit to the straight-line relationship, $Y = a + b\,X$. Specifically, (a) How would you define X_i and Y_i in terms of x_i and y_i? (b) Assuming the original y_i values have constant uncertainty $\sigma_y = 1$, what should the weights be in this transformed fit?

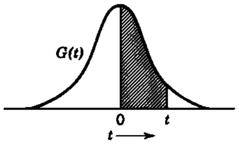
3. Suppose you actually carry out both fits, with a data set consisting of 100 points. Should the results be (a) noticeably different, (b) roughly the same, or (c) identical within the limits of the numerical precision of the computation.

B. (25) Erroneous Beer? Beer's law is often used to relate unknown concentrations of absorbing substances to the transmittance $T = I/I_0$ of light through a sample. For present purposes, this relation can be expressed as $T = \exp[-\alpha \ell C]$, where C is the unknown concentration, ℓ is the path length, and α is the absorption coefficient. I and I_0 both have percent standard deviations of 1.0%, and $T = 0.50$, with negligible uncertainty in α and ℓ. Determine (1) the percent standard deviation and the standard deviation in T, and (2) the percent standard deviation in C. [Hints: (a) 1.0% standard deviation in x means that $\sigma_x/x = 0.010$; (b) You do not need to know C in order to calculate its relative error.]

C. (15) Confidence Game. A certain quantity to be measured experimentally is known to have a true value of 74.1, and for the instrument to be employed in the experiment the inherent scatter of measurements about their mean is Gaussian, with a standard deviation of 2.3. Use the accompanying table to answer the following questions.

1. In a single measurement of this quantity with this instrument, what is the probability of obtaining a value ≤ 72.9?
2. In a single measurement, what is the probability of obtaining a value which differs from 74.1 by 1.2 or more?
3. If an average of 25 measurements is taken, what is the probability that this average will differ from 74.1 by 1.2 or more?

Table 4-4. Error Function $\frac{1}{2}\,\mathrm{erf}\,(t)$ from 0 to t and Ordinate Values $G(t) = (1/\sqrt{2\pi})\, e^{-t^2/2}$



t	$\frac{1}{2}$ erf (t) Area	$G(t)$ Ordinate	t	$\frac{1}{2}$ erf (t) Area	$G(t)$ Ordinate
0	0	0.3989	2.0	0.4773	0.0540
0.1	0.0398	0.3970	2.1	0.4821	0.0440
0.2	0.0793	0.3910	2.2	0.4861	0.0355
0.3	0.1179	0.3814	2.3	0.4893	0.0283
0.4	0.1554	0.3683	2.4	0.4918	0.0224
0.5	0.1915	0.3521	2.5	0.4938	0.0175
0.6	0.2258	0.3332	2.6	0.4953	0.0136
0.7	0.2580	0.3123	2.7	0.4965	0.0104
0.8	0.2881	0.2897	2.8	0.4974	0.0079
0.9	0.3159	0.2661	2.9	0.4981	0.0060
1.0	0.3413	0.2420	3.0	0.4987	0.0044
1.1	0.3643	0.2179	3.1	0.4990	0.0033
1.2	0.3849	0.1942	3.2	0.4993	0.0024
1.3	0.4032	0.1714	3.3	0.4995	0.0017
1.4	0.4192	0.1497	3.4	0.4997	0.0012
1.5	0.4332	0.1295	3.5	0.4998	0.0009
1.6	0.4452	0.1109	3.6	0.4998	0.0006
1.7	0.4554	0.0941	3.8	0.4999	0.0003
1.8	0.4641	0.0790	4.0	0.5000	0.0001
1.9	0.4713	0.0656	4.4	0.5000	0.0000

Fundamental Constants, etc.

$N_0 = 6.022137\times10^{23}$/mol
$R = 8.31451$ J K^{-1} mol^{-1} = 0.0820578 L atm K^{-1} mol^{-1}
1 atm = 1.0133×10^{5} Pa
1 cal = 4.184 J

III. (20) Everyone's Best Friend: KaleidaGraph

A. On several occasions you fitted data to a polynomial in the independent variable. Using *a*, *b*, *c*, *d*, etc. for the adjustable parameters, and *x* for the independent variable, write exactly what you would enter in the Define Fit box of KG for a fit to a 5th-order polynomial with a constant term.

B. In Problem Set 3, you used the random number generator to produce 1000 random numbers in the range 0-1 and then binned the results into 10 equal-width bins.

1. Describe briefly the appearance of the resulting histogram.
2. How would the results differ if you had generated and binned 10^5 random numbers?

C. The fit functions you employed to analyze the bomb calorimetry data were fairly complex. Explain briefly what they were fitting to: (1) at short time, (2) at long time, and (3) at times just after ignition of the bomb.

D. It is possible to analyze the vapor pressure data (liquid/gas region) from the Triple Point experiment by means of the standard straight-line relation, $y = a + bx$. However, it is preferable to analyze them in a different way.

1. What are y, a, b, and x in such a straight-line analysis?
2. Give an alternative form for analyzing the data, write the fit function exactly as you would enter it in the Define Fit box, and explain briefly why this approach is preferable.

IV. (60) Experiments. Do only TWO of the following three problems.

A. Inversion Kinetics. Honey Sweetwater studies the acid-catalyzed inversion of sucrose in water, using polarimetry to measure the changing rotation of polarized light from a sodium discharge lamp. The angle of rotation α is proportional to the optical path length, the concentration of solute, and the specific rotation $[\alpha]_{\lambda}^{T}$. The latter is given in units degrees decimeter^{-1} c^{-1}, where the concentration c is in g/mL. Values (in these units) for sucrose, glucose, and fructose, for measurements at the sodium wavelength and 20˚C, are +66.4, +52.5, and –88.5, respectively.

1. Help Honey derive an expression for the kinetics of inversion, which is pseudo-first order. (Start by giving the rate law.) Taking the initial concentration of sucrose to be $[S]_0$, express the concentrations of all three reagents in terms of $[S]_0$, k_{eff}, and the time t; and define k_{eff} clearly.

2. Obtain an expression for $\alpha(t)$, in terms of k_{eff}, the time t, and the rotations at $t = 0$ (α_0) and at $t = \infty$ (α_∞).

3. Honey wants to carry out a run with $[S]_0 = 80.0$ g/L and [HCl] = 1.50 M; and she will initiate the run by mixing 40.0 mL of sucrose solution with 40.0 mL of acid, under the assumption that volumes are additive. If her stock solutions have [S] = 200.0 g/L and [HCl] = 4.00 M, describe precisely how she will prepare the two 40.0-mL solutions.

4. Suppose that at 20˚C $k = 0.039$ L mol^{-1} min^{-1}. For the experiment described just above, Honey uses a 20.0-cm polarimeter cell. Calculate (a) her expected initial and infinite-time rotations (α_0 and α_∞) and (b) the time it will take for the reaction mixture to reach the inversion point. [Note: There is a 5.3 % "mass gain" in the reaction, considering just the three sugars.]

B. Deep Freeze. Les Cool considers using freezing point depression to study aqueous solutions of weak and strong acids. To check out his procedures he first uses sulfurous acid, for which the first ionization constant is $K_a = 0.012$ mol/kg. (K_{a2} is so small that dissociation of HSO_3^- is negligible.)

1. Calculate the fraction dissociated α for a 0.200 m° solution of sulfurous acid. Then calculate the freezing-point depression for this solution. ($K_f = 1.855$ K kg/mol; assume activity coefficients are all 1.00.)

2. Next Les considers a 1.00 % HCl (*aq*) solution. [$M = 36.47$ for HCl, 18.015 for H_2O.]
   - (a) Calculate the freezing-point depression expected for this solution if the activity coefficients are all 1.00.
   - (b) Les measures a depression of 0.989 K. Calculate the practical osmotic coefficient φ, the solvent activity a_A, and the activity coefficient γ_A.

C. Expanding Thermals. A pycnometer is fitted with a capillary extension (*i.e.*, like those used in our lab) having an internal diameter of 1.00 mm. In the initial calibration with water, I. B. Allwette measures the capillary height to be 33.7 mm above the zero level.

1. Calculate the volume of water in the capillary extension.

2. The pycnometer apparent mass (empty) is 22.379 g; filled with water to capillary height 33.7 mm, the apparent mass is 48.112 g. At the temperature of the height measurement, the density of water is 0.998011 g/mL. The density of air is 1.19 mg/mL. Calculate the volume V_0 (*i.e.*, the volume to the zero mark on the capillary) (a) neglecting the buoyancy of air, and (b) taking it into account. [Neglect the buoyancy effect on the balance weights.]

3. An unknown liquid is measured next, giving an apparent mass (pycnometer + sample) of 56.777 g and a capillary height of 19.3 mm. Calculate it's density.

4. Allwette obtained these data in the makeup lab. In the first shot at this experiment, he took the pycnometer w/ water out of the water bath and let it stand on the bench for 10 minutes, during which time the capillary rose 4.3 mm. Which of the following properties of the calibration water changed during this 10-minute period: mass, density, temperature, volume?

5. Also in his first attempt, Allwette obtained dilatometric data for an unknown alcohol in four temperature ranges: 9-13˚C, 21-25˚C, 29-32˚C, and 37-40˚C. In each case there were five measurements spanning essentially the entire scale of the capillary extension. Allwette then analyzed his data by fitting all 20 points simultaneously to the exponential polynomial suggested in the course Class Pak, $V = V_r \exp[a\,(T-T_r) + b\,(T-T_r)^2]$, with $T_r = 25.0$˚C. What is wrong with his procedure?