

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

Key

(Signature)

I. (22) **Least Squares.** Statistician Marge Inovera has collected some data (x_i, y_i) which she thinks should follow the relationship, $y = ax^3 + b/x$.

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.)

$$\text{Let } S = \sum \delta_i^2, \text{ where } \delta_i = y_{\text{calc}}(x_i) - y_i = ax_i^3 + \frac{b}{x_i} - y_i$$

$$\text{Obtain LS eqns from } \frac{\partial S}{\partial a} = \frac{\partial S}{\partial b} = 0.$$

$$\frac{\partial S}{\partial a} = 2 \sum \delta_i \left(\frac{\partial \delta_i}{\partial a} \right) = 2 \sum (ax_i^3 + \frac{b}{x_i} - y_i) x_i^3 = 0$$

$$\Leftrightarrow a \sum x_i^6 + b \sum x_i^2 = \sum x_i^3 y_i$$

$$\frac{\partial S}{\partial b} = 2 \sum \delta_i \left(\frac{\partial \delta_i}{\partial b} \right) = 2 \sum (ax_i^3 + \frac{b}{x_i} - y_i) \left(\frac{1}{x_i} \right) = 0$$

$$\Leftrightarrow a \sum x_i^2 + b \sum \frac{1}{x_i^2} = \sum \frac{y_i}{x_i}$$

$$\text{Matrix form: } \tilde{A} \vec{\beta} = \vec{z}; \quad \vec{\beta} = \begin{pmatrix} a \\ b \end{pmatrix}; \quad \vec{z} = \begin{pmatrix} \sum x_i^3 y_i \\ \sum y_i / x_i \end{pmatrix}$$

$$\tilde{A} = \begin{pmatrix} \sum x_i^6 & \sum x_i^2 \\ \sum x_i^2 & \sum \frac{1}{x_i^2} \end{pmatrix}; \quad \vec{\beta} = \tilde{A}^{-1} \vec{z}$$

B. In analyzing the wealth of data you collected in the lab this semester, you used KaleidaGraph to carry out both linear and nonlinear LS fits, both weighted and unweighted.

1. Give different specific examples (one of each) from your lab work, of (a) linear fitting other than fits to $y = a + bx$; (b) nonlinear fitting; and (c) weighted fitting (either linear or nonlinear).

Many possibilities here - 1pt each.

2. Even though KaleidaGraph can perform certain fits directly by menu selection, there is an important benefit to carrying out all fits using the "General" routine. Explain.

"General" (1) permits weighting, (2) gives parameter errors, and (3) gives "Chisq". From "Chisq", one can calculate $S_y^2 = \frac{\text{Chisq}}{n-p}$, where $n = \# \text{ data pts}$ + $p = \# \text{ parameters}$.

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, with max/min of 21/4. (no entry needed for groups of two; both partners will receive 25.)

II. (18) **Statistics and Probability.** Random numbers are drawn from the uniform distribution, which, in keeping with its name, is constant within the range over which it is defined. Consider the uniform distribution over the range $-1 \leq x \leq 1$.

A. Determine the normalization constant for this distribution.

$$P(x) = a; \quad \int_{-1}^1 P(x) dx = 1 = a \cdot 2 \rightarrow a = \frac{1}{2}$$

B. Determine the mean μ , median (x_{med}), and variance σ^2 for this distribution.

$$\mu \equiv \langle x \rangle = \int_{-1}^1 P(x) x dx = \frac{1}{2} \cdot \frac{x^2}{2} \Big|_{-1}^1 = 0$$

$$\frac{1}{2} = \int_{-1}^{x_{\text{med}}} P(x) dx = \int_{x_{\text{med}}}^1 P(x) dx \Rightarrow x_{\text{med}} = 0$$

$$\sigma^2 = \langle x^2 \rangle - \mu^2 = \langle x^2 \rangle = \int_{-1}^1 \frac{x^2}{2} dx = \frac{x^3}{6} \Big|_{-1}^1 = \frac{1}{3}$$

C. In Problem Set 3 we generated and histogrammed 1000 random deviates using the built-in random number generator in KaleidaGraph, which is defined over the range $0 \leq x \leq 1$. Suppose we did the same with our current uniform distribution ($-1 \leq x \leq 1$), binning the data into 10 equal-width bins. Briefly describe what the resulting histogram would look like.

Each bin should contain, on average, the same number of counts, or 100. Statistical fluctuations lead to about $\frac{2}{3}$ of the 10 bins containing between 90 + 110 counts.

D. We then generated and histogrammed averages of 12 such random deviates and fitted the resulting histogram data to a curve. Suppose for our current uniform distribution, we generated 1000 averages of 25 random deviates and carried out a similar fit. What functional form should we use for this fit? Be specific, including expected values for the mean and variance, if appropriate.

The histogram should now approximate the normal distribution - $P_G \propto \exp \left[-\frac{(x-\mu)^2}{2\sigma^2} \right]$ - with mean $\mu = 0$ and $\sigma^2 = \sigma_{\mu}^2 = \frac{\sigma^2}{25} = \frac{1}{75}$.

III. (40) Core Experiments. Do BOTH.

A. **Bomb Calorimetry.** O. G. Huiz uses bomb calorimetry to measure the heat of combustion of toluene $[C_7H_8(l), M = 92.15 \text{ g/mol}]$ and an unknown. The instrument is calibrated using benzoic acid ($q_{\text{specific}} = -26.413 \text{ kJ/g}$).

1. In one experiment at -25°C , 0.923 g of benzoic acid yields a temperature rise of 1.573 K. Then under the same conditions (same fill of water, T , etc.), 1.237 g of the unknown produces a temperature rise of 1.322 K. Calculate q_{specific} for the unknown.

$$q = q_{\text{spec}} \cdot m = C \cdot \Delta T, \text{ where } C \text{ is a calib. constant.}$$

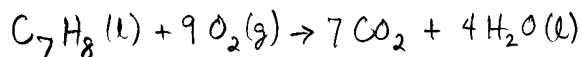
$$\begin{aligned} \hookrightarrow q_{\text{spec, unk}} &= q_{\text{spec, BA}} \cdot \frac{\Delta T_{\text{unk}}}{\Delta T_{\text{BA}}} \cdot \frac{m_{\text{BA}}}{m_{\text{unk}}} \\ &= -26.413 \frac{\text{kJ}}{\text{g}} \cdot \frac{1.322}{1.573} \cdot \frac{0.923}{1.237} = -16.56 \frac{\text{kJ}}{\text{g}} \end{aligned}$$

2. Under the same conditions, 0.694 g of toluene yields a temperature rise of 1.899 K. Calculate (a) the specific heat of combustion per gram of toluene, (b) ΔU_m of combustion, and (c) ΔH_m of combustion for toluene.

$$(a) q_{\text{spec, tol}} = -26.413 \frac{\text{kJ}}{\text{g}} \cdot \frac{1.899}{1.573} \cdot \frac{0.923}{0.694} = -42.41 \frac{\text{kJ}}{\text{g}}$$

$$(b) \Delta U_m = m \cdot q_{\text{spec}} = -3.908 \times 10^3 \frac{\text{kJ}}{\text{mol}}$$

$$(c) \Delta H_m = \Delta U_m + (\Delta n_g)RT$$



$$\hookrightarrow \Delta n_g = -2 \quad \Rightarrow \quad \Delta H_m = -3.913 \times 10^3 \frac{\text{kJ}}{\text{mol}}$$

3. In the determination of q_{specific} for the unknown (1, above), Huiz figures that the masses are uncertain by 0.003 g and the temperature changes are uncertain by 0.011 K. What is the uncertainty in his determined value of q_{specific} for the unknown?

$$\begin{aligned} \left(\frac{\Delta q_{\text{spec}}}{q_{\text{spec}}} \right)^2 &= \left(\frac{\Delta m_{\text{unk}}}{m_{\text{unk}}} \right)^2 + \left(\frac{\Delta m_{\text{BA}}}{m_{\text{BA}}} \right)^2 + \left(\frac{\Delta(\Delta T_{\text{unk}})}{\Delta T_{\text{unk}}} \right)^2 + \left(\frac{\Delta(\Delta T_{\text{BA}})}{\Delta T_{\text{BA}}} \right)^2 \\ &= \left(\frac{0.003}{1.237} \right)^2 + \left(\frac{0.003}{0.923} \right)^2 + \left(\frac{0.011}{1.322} \right)^2 + \left(\frac{0.011}{1.573} \right)^2 = 1.34_6 \times 10^{-4} \end{aligned}$$

Fundamental Constants, etc.

$$N_0 = 6.022137 \times 10^{23} / \text{mol}$$

$$R = 8.31451 \text{ J K}^{-1} \text{ mol}^{-1} = 0.0820578 \text{ L atm K}^{-1} \text{ mol}^{-1}$$

$$1 \text{ atm} = 1.0133 \times 10^5 \text{ Pa}$$

$$1 \text{ cal} = 4.184 \text{ J}$$

$$\begin{aligned} \hookrightarrow \Delta q_{\text{spec, unk}} &= 0.0116 \cdot q_{\text{spec, unk}} \\ &= 0.19 \frac{\text{kJ}}{\text{g}} \end{aligned}$$

B. **Inversion Kinetics.** T. T. Drinkwater 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 to the specific rotation $[\alpha]_D^t$. 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 T. T. 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.

$$r = -\frac{d[S]}{dt} = k[S][H^+] = -k_{\text{eff}}[S], \text{ with } k_{\text{eff}} = k[H^+]$$

$$\frac{d[S]}{dt} = -k_{\text{eff}}[S] \Rightarrow [S] = [S]_0 e^{-k_{\text{eff}}t}$$

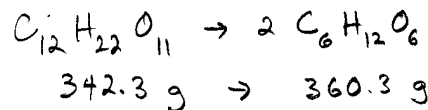
$$S \rightarrow G + F, \text{ so } [G] = [F] = [S]_0 (1 - e^{-k_{\text{eff}}t})$$

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_∞).

$$\alpha(t) = A e^{-k_{\text{eff}}t} + B \Rightarrow \alpha_0 = A + B + \alpha_\infty = B$$

$$\hookrightarrow \alpha(t) = \alpha_\infty + (\alpha_0 - \alpha_\infty) e^{-k_{\text{eff}}t}$$

3. Suppose that at 20°C $k = 0.0048 \text{ L mol}^{-1} \text{ min}^{-1}$. T. T. mixes 60.0 mL of sucrose solution (100.0 g/L) with 25.0 mL of 2.00 M HCl and starts measuring α using a 20.0-cm polarimeter cell. Calculate (a) his 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.



$$[S]_0 = 100.0 \frac{\text{g}}{\text{L}} \times \frac{60}{85} = 70.6 \frac{\text{g}}{\text{L}} = \frac{0.0706 \text{ g}}{\text{mL}}$$

$$70.6 \frac{\text{g}}{\text{L}} S \rightarrow \frac{360.3}{342.3} \times 70.6 \frac{\text{g}}{\text{L}} (G+F) = 37.2 \frac{\text{g}}{\text{L}} \text{ each}$$

$$\hookrightarrow (a) \alpha_0 = 0.0706 \times 2.00 \times 66.4^\circ = 9.37^\circ$$

$$\alpha_\infty = 0.0372 \times 2.00 \times (52.5^\circ - 88.5^\circ) = -2.68^\circ$$

$$(b) [H^+] = 2.00 \frac{\text{mol}}{\text{L}} \times \frac{25}{85} = 0.588 \frac{\text{mol}}{\text{L}} \Rightarrow k_{\text{eff}} = 0.00282 / \text{s}$$

$$0 = \alpha_\infty + (\alpha_0 - \alpha_\infty) e^{-k_{\text{eff}}t} \Rightarrow t = 533 \text{ min}$$

IV. (20) Elective Experiments. [DO 1 ONLY.]

A. Equilibrium and spectrophotometry. May B. Knott studies an equilibrium complexation reaction of form $I_2 + M \leftrightarrow I_2 \cdot M$ by spectrophotometry. She is able to ascertain that only the uncomplexed reagent I_2 (not M and not $I_2 \cdot M$) absorbs light at 540 nm. Consequently she elects to monitor the equilibrium at that wavelength, using absorption cells (cuvettes) having a path length of 1.000 cm. The experiments are done in CCl_4 solvent, which is inert with respect to the reaction and which also does not absorb light at 540 nm. The experiments are conducted at 22.0°C.

1. Give an expression for the equilibrium constant K_c for this reaction, in terms of the concentrations of reactants and products.

$$K_c = \frac{[I_2 \cdot M]}{[I_2][M]}$$

2. A cuvette containing just I_2 in CCl_4 at a concentration of 1.151×10^{-3} mol/L yields an absorbance A of 0.932 at $\lambda = 540$ nm. Calculate the transmittance T and the molar absorption coefficient ϵ for I_2 in CCl_4 at this wavelength.

$$T = \frac{I}{I_0} = 10^{-A} = 0.1169$$

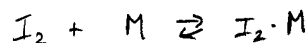
$$A = \epsilon c l \rightarrow \epsilon = \frac{A}{c l} = 809.7 \frac{L}{mol \cdot cm}$$

3. A solution is prepared by mixing 5.00 mL of the I_2/CCl_4 solution mentioned just above with 3.00 mL of a solution of M in CCl_4 having $[M] = 1.555 \times 10^{-3}$ mol/L. After equilibrium is established, a cuvette containing this mixture yields $A = 0.428$ at 540 nm. Calculate the concentrations of all three substances in this mixture and use these concentrations to evaluate K_c for the reaction. [Assume that volumes are additive for these dilute solutions.]

$$[I_2]_0 = 1.151 \times 10^{-3} \text{ mol/L} \times \frac{5}{8} = 7.194 \times 10^{-4} \frac{mol}{L}$$

$$[M]_0 = 1.555 \times 10^{-3} \text{ mol/L} \times \frac{3}{8} = 5.831 \times 10^{-4} \frac{mol}{L}$$

$$[I_2]_{eq} = \frac{A}{\epsilon \cdot l} = \frac{0.428}{809.7} \frac{mol}{L} = 5.286 \times 10^{-4} \frac{mol}{L}$$



$$([I_2]_0 - x) ([M]_0 - x) \quad x \Rightarrow x = 1.909 \times 10^{-4} \text{ mol/L}$$

$$\hookrightarrow [M]_{eq} = 3.923 \times 10^{-4} \frac{mol}{L} ; [I_2 \cdot M] = x$$

$$\hookrightarrow K_c = 920 \frac{L}{mol}$$

B. Liquid-vapor equilibrium. I. M. Al-Knowing collects equilibrium data for the chloroform/acetone system at 35.2°C and obtains the following results (where A \equiv acetone):

$x_{A,l}$	$x_{A,v}$	$P(\text{torr})$	$x_{A,l}$	$x_{A,v}$	$P(\text{torr})$
0.0000	0.0000	293	0.6034	0.6868	267
0.0821	0.0500	279.5	0.7090	0.8062	286
0.2003	0.1434	262	0.8147	0.8961	307
0.3365	0.3171	249	0.9397	0.9715	332
0.4188	0.4368	248	1.0000	1.0000	344.5
0.5061	0.5625	255			

1. From these data, answer the following questions:

- (a) What is the vapor pressure of pure acetone at 35.2°C? Of pure chloroform?

$$P_A^* = 344.5 \text{ torr} ; P_B^* = 293 \text{ torr}$$

- (b) For the solution having $x_{A,l} = 0.6034$, calculate P_A , P_B , $P_{A,id}$, $P_{B,id}$, γ_A , and γ_B (where "id" stands for ideal).

$$P_A = x_{A,v} \cdot P = 183.4 \text{ torr} ; P_B = 83.6 \text{ torr}$$

$$P_{A,id} = x_{A,l} \cdot P_A^* = 207.9 \text{ torr} ; P_{B,id} = 116.2 \text{ torr}$$

$$\gamma_A = P_A / P_{A,id} = 0.882 ; \gamma_B = 0.719$$

- (c) If this system behaved ideally, what would be the values of P and $x_{A,v}$ for this $x_{A,l}$?

$$P = P_{A,id} + P_{B,id} = 324 \text{ torr} ; x_{A,v} = \frac{P_{A,id}}{P_{id}} = 0.641$$

2. Assuming Al-Knowing used the same procedures you used in the lab, describe briefly how he determined the pressure P and compositions $x_{A,l}$ and $x_{A,v}$ for each solution he studied.

[Give brief description of lab procedures here.]

3. In analyzing his data, Al-Knowing smartly employed a special cubic polynomial to obtain a smooth representation of his measured dependence of $x_{A,v}$ on $x_{A,l}$. Give this equation and explain briefly why it is necessary to use this expression rather than a simple fit to $y = a + bx + cx^2 + dx^3$.

$$\text{We used } x_{A,v} = a x_{A,l} + b x_{A,l}^2 + (1-a-b) x_{A,l}^3$$

This form ensures that $x_{A,v} \rightarrow x_{A,l}$ at $x = 0 + 1$.