

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

KEY

(Signature)

I. ²⁰ ~~(22)~~ Least Squares. Statistician Marge Inovera has collected some data (x_i, y_i) which she thinks should follow the relationship, $y = ax + b/x^2$.

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.)

$$\text{Define } \delta = \sum \delta_i^2 \text{ where } \delta_i = y_{\text{calc}}(x_i) - y_i = ax_i + \frac{b}{x_i^2} - y_i$$

$$\text{Then set } \frac{\partial \delta}{\partial a} = \frac{\partial \delta}{\partial b} = 0 \Rightarrow 2 \text{ eqns in 2 unknowns.}$$

$$0 = \frac{\partial \delta}{\partial a} = 2 \sum \delta_i \frac{\partial \delta_i}{\partial a} = 2 \sum (ax_i + \frac{b}{x_i^2} - y_i)x_i = 2 [a \sum x_i^2 + b \sum \frac{1}{x_i} - \sum x_i y_i]$$

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

$$\frac{\partial \delta}{\partial b} = 2 \sum \delta_i \frac{\partial \delta_i}{\partial b} = 2 \sum (ax_i + \frac{b}{x_i^2} - y_i) \frac{1}{x_i^2} = 2 [a \sum \frac{1}{x_i} + b \sum \frac{1}{x_i^3} - \sum \frac{y_i}{x_i^2}]$$

$$\hookrightarrow a \sum \frac{1}{x_i} + b \sum \frac{1}{x_i^3} = \sum \frac{y_i}{x_i^2}$$

$$\vec{A} \vec{\beta} = \vec{z} \quad \text{w/} \quad \vec{A} = \begin{pmatrix} \sum x_i^2 & \sum \frac{1}{x_i} \\ \sum \frac{1}{x_i} & \sum \frac{1}{x_i^3} \end{pmatrix}; \quad \vec{\beta} = \begin{pmatrix} a \\ b \end{pmatrix}$$

$$\vec{z} = \begin{pmatrix} \sum x_i y_i \\ \sum \frac{y_i}{x_i^2} \end{pmatrix}$$

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.)

$$s_y^2 = \frac{\delta}{\nu} = \frac{\delta}{N-2} = \frac{\sum [ax_i + \frac{b}{x_i} - y_i]^2}{N-2}$$

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 18/7 for groups of 3, 13/6 for groups of 4.

II. Error Propagation, Confidence Limits, etc. Do 2 and ONLY 2 of the following. [Note: They are not all equal in point value.]

A. ¹⁵ ~~(18)~~ This problem is a continuation of Problem I on the first page.

1. For a 2×2 matrix $A = \begin{pmatrix} p & q \\ r & s \end{pmatrix}$, the inverse $A^{-1} = D^{-1} \begin{pmatrix} s & -q \\ -r & p \end{pmatrix}$, 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 $y = ax + b/x^2$. (Your answers should be in terms of the quantities obtained in your solution to Problem I, including s_y^2 .)

$$s_a^2 = V_{11} + s_b^2 = V_{22}, \text{ where } \underline{V} = s_y^2 \underline{A}^{-1}$$

$$\hookrightarrow s_a^2 = \frac{s_y^2}{D} s = \frac{s_y^2}{D} \cdot \sum \frac{1}{x_i^4}$$

$$s_b^2 = \frac{s_y^2}{D} \cdot p = \frac{s_y^2}{D} \cdot \sum x_i^2$$

$$D = (\sum x_i^2)(\sum \frac{1}{x_i^3}) - (\sum \frac{1}{x_i})^2$$

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, $Y = a + bX$. 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?

$$y = ax + \frac{b}{x^2} \Rightarrow Y = a + bX$$

$$\text{Let } Y = y/x. \text{ Then } X = \frac{1}{x^3} \Rightarrow Y_i = \frac{y_i}{x_i}; X_i = \frac{1}{x_i^3}$$

$$W_i \propto \frac{1}{s_{y_i}^2} \quad s_{Y_i}^2 = \left(\frac{\partial Y_i}{\partial y_i} \right)^2 s_{y_i}^2 = \frac{1}{x_i^2} \cdot 1$$

$$\hookrightarrow W_i \propto x_i^2$$

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.

(c) Identical

B. (20) Sampling Statistics.

1. A physical quantity x is measured N times. Give expressions for its average \bar{x} , its estimated variance s_x^2 , and its estimated variance in the mean $s_{\bar{x}}^2$.

$$\bar{x} = \frac{\sum x_i}{N} ; s_x^2 = \frac{\sum \delta_i^2}{N-1} = \frac{\sum (x_i - \bar{x})^2}{N-1}$$

$$s_{\bar{x}}^2 = \frac{s_x^2}{N}$$

2. Jones measures x 16 times and obtains $\bar{x} = 35$, $s_x^2 = 1$ (units unimportant). If she now makes one more measurement, the probability that she observes a value larger than 36 or smaller than 34 is about

- (a) 0.50 (b) 0.68 (c) 0.32 (d) 0.95 (e) 0.05 (f) >0.99 (g) <0.01

3. Now Jones repeats the entire experiment (16 measurements). The probability that she obtains an \bar{x} value larger than 36 or smaller than 34 is about

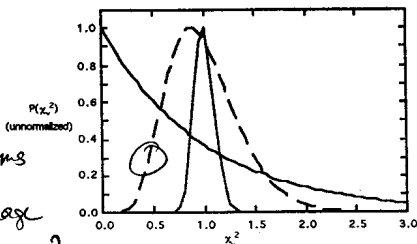
- (a) 0.50 (b) 0.68 (c) 0.32 (d) 0.95 (e) 0.05 (f) >0.99 (g) <0.01

4. Smith does the same experiment using the same equipment and procedures, but makes 100 measurements. Estimate his standard deviation in the mean and compare it with Jones's value for the same quantity.

$$s_{\bar{x}} (\text{Smith}) = \frac{s_x}{\sqrt{N}} \approx \frac{1}{10} = 0.10 \leftarrow \text{factor 2.5 smaller}$$

$$s_{\bar{x}} (\text{Jones}) = \frac{s_x}{\sqrt{16}} \approx \frac{1}{4} = 0.25$$

5. Prof. Stern makes his entire class of 1111 students repeat this experiment, with each student making 16 measurements. He then prepares a histogram of their estimates of s_x^2 . This histogram should resemble which of the curves in the accompanying figure. Explain your choice briefly.



Since $s_x^2 \sim 1$, its histograms as χ^2 , or χ^2 has an average of 1. χ^2 also has variance $\frac{2}{\nu}$, hence stand. dev. = $\sqrt{\frac{2}{\nu}} = \sqrt{\frac{2}{15}}$ here. $\sqrt{\frac{2}{15}} = 0.37$, so the middle curve is correct.

C. (12) Error Propagation.

1. Cheatham and Howe carry out measurements of the vapor pressure of water from -20°C to 20°C and estimate from their analysis of the data, $\Delta H_{\text{vap}} = 40.738 \pm 0.107 \text{ kJ/mol}$ and $\Delta H_{\text{sub}} = 47.597 \pm 0.072 \text{ kJ/mol}$. Calculate from these data ΔH_{fus} and its uncertainty, and give your result with the correct number of significant figures.

$$\Delta H_{\text{fus}} = \Delta H_{\text{sub}} - \Delta H_{\text{vap}} = (47.597 - 40.738) \frac{\text{kJ}}{\text{mol}} = 6.859 \frac{\text{kJ}}{\text{mol}}$$

$$s_{\Delta H_{\text{fus}}}^2 = s_{\Delta H_{\text{sub}}}^2 + s_{\Delta H_{\text{vap}}}^2 = (0.072)^2 + (0.107)^2 = 0.01663$$

$$s_{\Delta H_{\text{fus}}} = 0.129 \frac{\text{kJ}}{\text{mol}} \Rightarrow \Delta H_{\text{fus}} = 6.859(129) \text{ or } 6.86(13) \frac{\text{kJ}}{\text{mol}}$$

2. Morely Smartt does very careful vapor pressure measurements on water and obtains $\Delta H_{\text{vap}} = 44.000 \pm 0.003 \text{ kJ/mol}$, while Bud Wizer breezes through and obtains $43.0 \pm 0.9 \text{ kJ/mol}$. The literature value reads 44.012 kJ/mol . Which of the two determinations — Smartt's or Wizer's — is the greater cause for "concern"? Explain.

Smartt's is more accurate and also much more precise. But therein lies the problem. His value disagrees with literature by 4 σ — a very improbable outcome for a correct study. Therefore, either Smartt or literature must be wrong. Wizer is within $\sim 1.1 \sigma$ of lit., which is reasonable.

D. (15) A priori and a posteriori errors. In Problem Set 2 you fitted the 12 points in the data set PROBI.DAT to a straight line through the origin, $y = ax$, obtaining the following results:

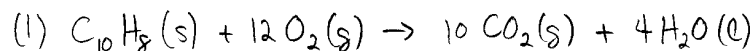
- unweighted: $\sigma_a = 0.02883656$, $\chi^2 = 23.782247$.
- weighted, $\sigma_{y_i} = 1.0$: $\sigma_a = 0.01961161$, $\chi^2 = 23.782247$.
- weighted, $\sigma_{y_i} = 1.5$: $\sigma_a = 0.0294174$, $\chi^2 = 10.5699$.

Give a quantitative explanation of these differences.

unwtd uses a posteriori assessment: $\chi^2 = s_y^2 A^{-1}$, while wtd uses a priori: $\chi^2 = A^{-1}$. $\chi^2(1) = \chi^2(2)$, because $s_{y_i} = 1$ is assumed in unwtd. fits. χ^2 is $\sum (\delta_i / \delta_i)^2$, which is therefore the same in 1 + 2, but smaller by a factor $(1.5)^2$ in 3. $\sigma_a(1) = \sigma_a(2) \times s_y = \sigma_a(2) \times \left(\frac{\chi^2}{\nu}\right)^{1/2} = \sigma_a(2) \times (23.782247/11)^{1/2}$. $\sigma_a(3) = 1.5 \times \sigma_a(2)$, since $\sigma_a \propto \sigma_{y_i}$

III. (60) Short Answers to Tall Questions. [Do FOUR Of SIX.]

- A. One of the compounds you studied in bomb calorimetry was naphthalene ($C_{10}H_8$). (1) Give a balanced equation for the complete combustion of naphthalene in the bomb calorimeter, being sure to identify the states (s, l, g) of all reactants and products. (2) Then obtain an equation relating ΔU° for this reaction at temperature T to ΔH° at the same T . (3) Which of these did you measure in this experiment?



$$(2) \Delta H = \Delta U + \Delta(PV) = \Delta U + \Delta(nRT) \\ \approx \Delta U + \Delta n_g RT$$

$$\text{so } \Delta H^\circ \approx \Delta U^\circ + \Delta n_g RT \quad \text{where } \Delta n_g = \sum_g(\text{prod.}) - \sum_g(\text{react.}) \\ = 10 - 12 = -2 \\ \hookrightarrow \Delta H^\circ \approx \Delta U^\circ - 2 RT$$

- (3) Bomb calorimetry is constant V , in fact involves a "pseudo-isolated" system. ΔU° is the directly determined quantity.

- B. The density of ethanol in the range 20-90°C can be represented as $\rho = 0.76302 \exp(bx + cx^2 + dx^3)$, where ρ is in g/mL and $x = \theta(^\circ\text{C}) - 50^\circ\text{C}$. (1) Obtain from this an expression for the thermal expansivity α for ethanol in this temperature range. (2) The coefficients b , c , and d , are -0.00118 , -2.262×10^{-6} , and -1.3639×10^{-8} , respectively. Calculate ρ and α at $\theta = 30.0^\circ\text{C}$.

$$(1) \alpha \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = - \frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_P = - \left(\frac{\partial \ln \rho}{\partial T} \right)_P$$

$$\ln \rho = \ln(0.76302) + bx + cx^2 + dx^3$$

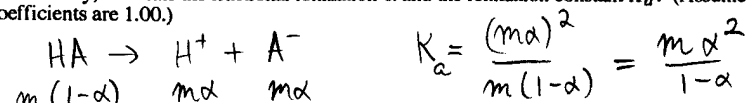
$$\text{Since } P \text{ was constant throughout, } \left(\frac{\partial \ln \rho}{\partial T} \right)_P = \frac{d \ln \rho}{dT}$$

$$\frac{d \ln \rho}{dT} = \frac{d \ln \rho}{dx} \cdot \frac{dx}{dT} \quad \text{but } x = \theta - 50^\circ\text{C} = T - 323 \text{ K} \\ \text{so } \frac{dx}{dT} = 1$$

$$\hookrightarrow \alpha = -(b + 2cx + 3dx^2)$$

$$(2) \rho = 0.78062 \frac{\text{g}}{\text{cm}^3} \quad ; \quad \alpha = 0.001106 \text{ K}^{-1}$$

- C. Les Cool carries out freezing-point depression experiments on a weak acid HA in water, obtaining a freezing point of -0.423°C for a molality of 0.2053 mol/kg. Using $K_f = 1.855 \text{ K/m}^\circ$ and showing all work clearly, calculate the fractional ionization α and the ionization constant K_a . (Assume all activity coefficients are 1.00.)



total molality @ equilibrium is $m(1+\alpha) \equiv m'$

$$\Delta T_f = K_f \cdot m' \Rightarrow m' = 0.2280 m^\circ$$

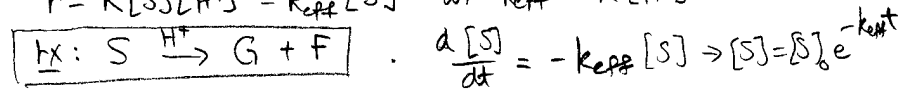
$$\alpha = \frac{m'}{m} - 1 = \frac{0.2280}{0.2053} - 1 = 0.1107$$

$$\hookrightarrow K_a = 2.83 \times 10^{-3}$$

- D. Inversion Kinetics. Honey Sweetwater studies the acid-catalyzed inversion of sucrose, 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 $^{-1}$ cm^{-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. 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 .

$$r = k[S][H^+] \equiv k_{\text{eff}}[S] \quad \text{w/ } k_{\text{eff}} = k[H^+]$$



$$[G] + [F] \text{ given by } [S]_0 (1 - e^{-k_{\text{eff}}t})$$

2. Honey does her experiments at 20°C , using solutions that contain 75.0 g sucrose per liter, in a polarimeter that has a path length of 25.0 cm. Calculate the rotation α expected in her experiments (a) at the start (α_0), and (b) after the inversion has proceeded to completion (α_∞).

$$(a) \alpha_0 = [\alpha]_{\lambda, S}^T \cdot l \cdot c = 66.4^\circ \cdot 2.5 \times 0.075 = 12.45^\circ$$

$$(b) \alpha_\infty \approx \frac{75.0}{2 \times 1000} \times 2.5 \times \left[[\alpha]_{\lambda, G}^T + [\alpha]_{\lambda, F}^T \right] = -3.4^\circ \quad (-3.38^\circ)$$

3. Obtain an expression for $\alpha(t)$, in terms of k_{eff} , the time t , α_0 , and α_∞ .

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

$$\alpha(0) = A + B \equiv \alpha_0 \quad ; \quad \alpha_\infty = A \Rightarrow B = \alpha_0 - \alpha_\infty$$

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

E. Equilibrium and spectrophotometry. Justin Tyme studies an equilibrium complexation reaction of form $I_2 + M \leftrightarrow I_2 \cdot M$ by spectrophotometry at a wavelength of 350 nm, where only the complex $I_2 \cdot M$ absorbs light. He uses absorption cells (cuvettes) having a path length of 1.000 cm and does the experiments at 22.0°C in CCl_4 solvent, which is inert with respect to the reaction and does not absorb light at 350 nm.

Suppose that ϵ_{350} is known to be $8.95 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$. Tyme mixes 1.00 mL of 0.330 M M with 3.00 mL of 0.00136 M I_2 and measures an absorbance of 0.4566. ($M = \text{mol/L}$) Calculate (1) the transmittance, I/I_0 ; (2) the concentration of $I_2 \cdot M$; (3) the concentrations of M and I_2 at equilibrium; and (4) the equilibrium constant K_c .

$$(1) T = I/I_0 = 10^{-A} = 0.3495$$

$$(2) A = \epsilon \cdot c \cdot \ell \Rightarrow [I_2 \cdot M] = \frac{0.4566}{8.95 \times 10^3 \frac{\text{mol}}{\text{L}}} = 5.102 \times 10^{-5} \text{ M}$$

$$(3) I_2 + M \rightleftharpoons I_2 \cdot M \quad [M]_0 = \frac{1}{4} \cdot 0.330 \text{ M} = 0.0825 \text{ M}$$

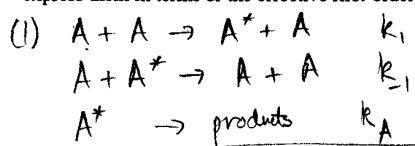
$$[I_2]_0 = \frac{3}{4} \cdot 0.00136 \text{ M} = 0.00102 \text{ M}$$

$$\hookrightarrow [I_2]_{\text{eq}} = [I_2]_0 - [I_2 \cdot M] = 9.69 \times 10^{-4} \text{ M}$$

$$[M]_{\text{eq}} = [M]_0 - [I_2 \cdot M] = 0.08245 \text{ M}$$

$$(4) K_c = \frac{[I_2 \cdot M]}{[I_2][M]} = 0.639$$

F. Gas-Phase Decomposition. Although many gas-phase thermal decomposition processes display first-order kinetics, they are actually bimolecular in nature. (1) Give chemical equations for the bimolecular excitation of A to A^* , the bimolecular deactivation of A^* to A, and the unimolecular decay of A^* to products; and then use the steady-state approximation to obtain an expression for $d[A^*]/dt$ that can yield the observed first-order kinetics. (2) Define the characteristic times $t_{1/3}$ and $t_{1/2}$, and express them in terms of the effective first-order rate constant k .



$$\text{Steady-state: } \frac{d[A^*]}{dt} = 0$$

$$= k_1 [A]^2 - k_{-1} [A][A^*] - k_A [A^*]$$

$$(2) \frac{[A]}{[A]_0} = \frac{1}{2} = e^{-k \cdot t_{1/2}} \Rightarrow t_{1/2} = \frac{\ln 2}{k}$$

$$\hookrightarrow [A^*] = \frac{k_1 [A]^2}{k_A + k_{-1} [A]}$$

$$\text{For } t_{1/3}, \text{ either } \frac{[A]}{[A]_0} = \frac{1}{3} \text{ or } \frac{2}{3}$$

$$\hookrightarrow t_{1/3} = \frac{\ln 3}{k} \text{ or } \frac{\ln 1.5}{k}$$

$$r = k_A [A^*]. \text{ At large } [A],$$

$$k_{-1} [A] \gg k_A, \text{ +}$$

$$r \approx \frac{k_1 k_A [A]}{k_{-1}}$$

Fundamental Constants, etc.

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

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

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

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