1. **Least Squares.** Statistician Marge Inovera has collected some data \((x_i, y_i)\) which she thinks should follow the relationship, \(y = ax^2 + bx\).

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.)

Let \(d = \sum S_i^2\) where \(S_i = y_i - \hat{y}_i = \frac{a}{x_i} + bx_i^2 - y_i\), then the 2 least-squares equations are obtained by setting \(\frac{\partial d}{\partial a} = 0\) and \(\frac{\partial d}{\partial b} = 0\).

\[
\frac{\partial d}{\partial a} = 2 \sum x_i \frac{\partial S_i}{\partial a} = 2 \sum \left( \frac{a}{x_i} + bx_i^2 - y_i \right) x_i = 0
\]

\[
\frac{\partial d}{\partial b} = 2 \sum x_i \frac{\partial S_i}{\partial b} = 2 \sum \frac{a}{x_i} x_i^2 = 0
\]

\[
A \beta = \bar{y}
\]

\[
A = \begin{pmatrix} \sum \frac{1}{x_i^2} & N \\ N & \sum x_i^4 \end{pmatrix}, \quad \beta = \begin{pmatrix} a \\ b \end{pmatrix}, \quad \bar{y} = \begin{pmatrix} \sum y_i / x_i \\ \sum x_i y_i \end{pmatrix}
\]

**Matrix Form:**

\[
A \beta = \bar{y}
\]

\[
\Rightarrow \beta = A^{-1} \bar{y}
\]

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.)

\[
s_y^2 = \frac{\sum S_i^2}{N-2} = \frac{1}{N-2} \sum \left( \frac{a}{x_i} + bx_i^2 - y_i \right)^2
\]

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

A. (25) This problem is a continuation of Problem I on the first page.

1. For a 2x2 matrix \(A = \begin{pmatrix} a & b \\ c & d \end{pmatrix}\), the inverse \(A^{-1} = D^{-1} \begin{pmatrix} d & -b \\ -c & a \end{pmatrix}\), where \(D\) is the determinant, \(D = ad - bc\). Give expressions for the estimated variances \((s_{a^2}^2\) and \(s_{b^2}^2\)) in the parameters from the least-squares fit of data to \(y = ax^2 + bx^2\). (Your answers should be in terms of the quantities obtained in your solution to Problem I, including \(s_y^2\)).

\[
V_a = \frac{s_y^2}{s_{a^2}^2}, \quad V_b = \frac{s_y^2}{s_{b^2}^2}
\]

\[
D = \left( \sum \frac{1}{x_i^2} \right) \left( \sum x_i^4 \right) - N^2
\]

\[
s_{a^2}^2 = \frac{s_y^2}{D} \sum x_i^4, \quad s_{b^2}^2 = \frac{s_y^2}{D} \sum \frac{1}{x_i^2}
\]

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 \(\sigma_i\) = 1, what should the weights be in this transformed fit?

(a) Define \(Y_i \equiv X_i^2 \cdot Y_i + X_i \equiv X_i^4\)

in terms of \(X_i\) and \(Y_i\).

(b) \(W_{Y_i} \equiv \frac{1}{S_{Y_i}^2}, \quad W_{X_i} \equiv \frac{1}{S_{X_i}^2} = \frac{2}{S_{Y_i}^2} \cdot s_{Y_i}^2 = X_i^4 \cdot s_{Y_i}^2
\]

\[
S_{Y_i}^2 = X_i^4, \quad (\text{since} \ S_{Y_i}^2 = \sigma^2 = 1)
\]

\[
W_{Y_i} = \frac{1}{X_i^4}
\]

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 (Recall KG exercises, Prob. Set 2.)
B. (20)

1. A desired physical quantity $z$ can be expressed as a ratio of two intermediate quantities $x$ and $y$, viz. $z = \frac{x}{y}$. Suppose that $x$ and $y$ are in turn obtained from measured quantities $t$, $u$, and $v$, according to $x = tu^2v$ and $y = tuv$.

(a) Express the relative uncertainty in $z$ in terms of the relative uncertainties in $t$, $u$, and $v$.

$$z = \frac{x}{y} = \frac{tu^2v}{tuv} = uv^2$$

$$\left(\frac{\Delta z}{z}\right)^2 = \left(\frac{\Delta x}{x}\right)^2 + \left(\frac{\Delta y}{y}\right)^2 = \left(\frac{\Delta tu^2v}{tu^2v}\right)^2 + \left(\frac{\Delta tuv}{tuv}\right)^2$$

$$\therefore \Delta z^2 = \left(\frac{\Delta t}{t}\right)^2 + \left(\frac{\Delta u}{u}\right)^2 + \left(\frac{\Delta v}{v}\right)^2$$

(b) What is the percent uncertainty in $z$ for percent uncertainties of 3.0%, 5.0%, and 2.0% in $t$, $u$, and $v$, respectively.

$$\left(\frac{\Delta z}{z}\right)^2 = \left(0.03\right)^2 + \left(0.05\right)^2 + \left(0.02\right)^2 = 0.06$$

$$\therefore \frac{\Delta z}{z} = 0.26$$

(c) Suppose you discover a systematic error of +2.0% in $v$. What is the corresponding percent systematic error in $z$?

$$\Delta z = \left(\frac{\Delta v}{v}\right)z = \left(0.02\right)z = 0.02z$$

$$\therefore \Delta z = 0.02z$$

2. Give answers to the appropriate number of significant figures (follow normal rules here!):

(a) $9.0 \times 4.0 = 1.3 \times 10^2$
(b) $7.1113 - 2.0000 = 5.1113$
(c) $\ln(3.1) = 1.13$
(d) $529 + 200 = 729$
(e) $25.79 \div 2.00 = 5.57$

C. (15) J.B. Thoro measures a quantity $y$ 250 times and obtains an estimated mean $\bar{y} = 46.23$ and an estimated variance $s^2 = 19.7442$. What error limits should Thoro quote for 90% confidence in his mean? (See integral table below, last page.) Using this confidence limit, state his average and its uncertainty to the proper number of significant figures.

$$s^2 = 19.7442 \Rightarrow s_y = \sqrt{s^2} = \sqrt{19.7442} = 0.07898 \Rightarrow s_y = 0.281$$

From the table, using linear interpolation, 80% corresponds to $t = 1.283$. This is the # of sigmas to quote, so $\Delta \bar{y} = 0.36$

$$\bar{y} = 46.23 \pm 0.36 \ (80\% \ confidence).$$

D. (30) J. Walker studies the temperature dependence of a certain first-order reaction and obtains $k = 2.87(9) \times 10^{-4} \text{s}^{-1}$ [i.e., $(2.87 \pm 0.09) \times 10^{-4} \text{s}^{-1}$] at 22.0°C and $11.49(44) \times 10^{-4} \text{s}^{-1}$ at 35.0°C.

1. Neglecting any uncertainty in the temperatures, calculate the activation energy $E_a$ and its uncertainty for this reaction in kJ/mol, and report your answer with the correct number of significant figures.

$$k = Ae^{-\frac{E_a}{RT}} \Rightarrow \ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$T_1 = 395.15 \text{ K}; \ T_2 = 308.15 \text{ K}; \ k_1 = 11.49 \times 10^{-4} \text{ s}^{-1}; \ k_2 = 2.87 \times 10^{-4} \text{ s}^{-1}$$

$$G(E_a) = 80.69 \text{ J/mol}$$

$$E_a = \frac{R \ln\left(\frac{k_2}{k_1}\right)}{\frac{1}{T_1} - \frac{1}{T_2}} \Rightarrow E_a = \frac{80.69}{\left(\frac{1}{395.15} - \frac{1}{308.15}\right)}$$

$$\therefore E_a = 80.7 \pm 2.9 \text{ kJ/mol}$$

2. Now suppose that in addition both temperatures are uncertain by 0.8 K and repeat the uncertainty calculation.

$$\text{Now } f = f(T_1, T_2) \text{ is also uncertain, so}$$

$$\left(\frac{\Delta E_a}{E_a}\right)^2 = \left(\frac{\Delta T_1}{T_1}\right)^2 + \left(\frac{\Delta T_2}{T_2}\right)^2$$

$$\therefore \Delta E_a = \sqrt{(0.8)^2 \frac{1}{T_1} + (0.8)^2 \frac{1}{T_2}}$$

$$\therefore \Delta E_a = 0.007602$$

$$G\left(\frac{\Delta E_a}{E_a}\right)^2 = 0.03568^2 + 0.007602 = 0.0088782 \Rightarrow \frac{\Delta E_a}{E_a} = 0.0942$$

$$\therefore S_{E_a} = 7.602 \text{ kJ/mol} \Rightarrow E_a = 80.7 \pm 7.6 \text{ kJ/mol} \ (80\% \ confidence).$$
III. (30) Short Answers to Tall Questions.

A. In several of the experiments in the laboratory, you used a vacuum system, and in each case the
system was equipped with a cold trap. What is the purpose of this device? More specifically, (a)
What does it do? (b) How does it accomplish this? (c) Why is it included in the system?

(a) It collects condensable vapors.
(b) At the very low T of liquid H2, most substances have a vanishingly
small vapor pressure, and they deposit on the glass walls as solids.
(c) It keeps the trapped substances out of the pump, protecting it.
It also keeps pump oil vapors, etc. out of the system.

B. A pycnometer is weighed in air on an analytical balance, yielding 39.601 g. It is then filled with
water at 20.0°C (ρ = 0.998206 g/mL) and reweighed, yielding 138.111 g. Finally, it is filled with an
unknown alcohol and weighed, yielding 114.578 g. Calculate the density of the unknown alcohol
(a) neglecting the buoyancy of air, and (b) taking the buoyancy of air into account. (The density of
air may be taken as 1.19 mg/mL, and the effect of buoyancy on the balance weights may be neglected.)

(a) \[ m_{\text{H}_2\text{O}} \text{(app)} = 138.111 - 39.601 g = 98.509 g \] \[ \Rightarrow \rho = \frac{m_{\text{H}_2\text{O}}}{V_{\text{app}}} = \frac{98.509}{98.687} = 0.998206 \text{ g/mL} \]

(b) \[ m_{\text{H}_2\text{O}} \text{(app)} = 114.578 - 39.601 g = 74.977 g \]
\[ \Rightarrow \rho = \frac{m_{\text{H}_2\text{O}}}{V_{\text{app}}} = \frac{74.977}{74.807} = 0.998206 \text{ g/mL} \]

C. In analyzing our vapor pressure data for water, we assumed that \( \Delta H_{\text{m,vap}} \) was independent of
temperature. Over an extended T range, this becomes a poor approximation. Suppose we include the
T-dependence in \( \Delta H_{\text{m,vap}} \) by treating \( \Delta C_P = C_{P,m,d} - C_{P,m,l} \) as independent of T.

1. Obtain an expression for \( \Delta H_{\text{m,vap}}(T) \) in terms of \( \Delta C_P \) and \( \Delta H_{\text{m,vap}} \) at the triple point.

\[ \Delta H_{\text{m,vap}}(T) = \Delta H_{\text{m,vap}}(273.16 K) \times [1 + \frac{C_P}{R}(T-273.16 K)] \]

2. Use this expression to obtain a version of the integrated Clausius-Clapeyron equation that could
be used to analyze vapor pressure data to obtain \( \Delta C_P \) and \( \Delta H_{\text{m,vap}} \) at 273.16 K.

IV. (40) Experiments. [DO 2 ONLY — 20 points each.]

A. Equilibrium and spectroscopy. May B. Knott studies an equilibrium complexation reaction of
form \( I_2 + M \leftrightarrow I_2 M \) by spectrophotometry. She is able to ascertain that only the uncomplexed
reactant \( I_2 \) (not M and not \( I_2 M \)) absorbs light at 500 nm. Consequently she elects to monitor the
equilibrium at that wavelength, using absorption cells (cuvettes) having a path length of 1.00 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 500 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.

\[ K_c = \frac{[I_2 M]}{[I_2][M]} \text{ (at equilibrium)} \]

2. A cuvette containing just \( I_2 \) in CCl\(_4\) at a concentration of \( 8.50 \times 10^{-4} \text{ mol/L} \) yields a
transmittance \( T = 0.026 \) at \( \lambda = 500 \text{ nm} \). Calculate the absorbance \( A \) and the molar
absorption coefficient \( e \) for \( I_2 \) in CCl\(_4\).

\[ T = \frac{I}{I_0} = 10^{-A} \Rightarrow A = -\log_{10} T = -\frac{0.026}{10} = 0.0026 \]

\[ e = \frac{A}{cL} = \frac{A}{8.50 \times 10^{-4} \text{ mol/L} \times 1.00 \text{ cm}} = \frac{0.0026}{759.9} \text{ cm}^{-1} \]

3. A solution is prepared having initial concentrations \( [I_2]_0 = 9.75 \times 10^{-4} \text{ mol/L} \) and \( [M]_0 = 1.755 \times 10^{-3} \text{ mol/L} \). After equilibrium is established, a cuvette containing this mixture yields \( T = 0.682 \). Calculate the concentrations of all three substances in this mixture and use these
concentrations to evaluate \( K_c \) for the reaction.

\[ I_2 + M \leftrightarrow I_2 M \]

at equil.: \( [I_2]_0-x \times [M]_0-x \times x \)

\[ [I_2]_{eq} = \frac{A}{eL} = -\log_{10}(0.682) = \frac{0.682}{eL} = 2.187 \times 10^{-4} \text{ mol/L} \]

\[ [I_2]_0-x \times x = \frac{[I_2]_{eq} + [I_2]_0}{2} \]

\[ [M]_{eq} = [M]_0-x = \frac{9.987 \times 10^{-4} \text{ mol/L}}{2} \]

\[ K_c = 3.462 \times 10^3 \text{ L/mol} \]
B. Les Cool considers using freezing point depression to study aqueous solutions of weak and strong acids. To check out his procedures he first uses acetic acid, for which \( K_a = 1.75 \times 10^{-5} \) mol/kg. (This \( K_a \) is improperly called \( K_n \) in the lab text.)

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

\[
\begin{align*}
\text{HAc} + \text{H}_2\text{O} &\rightleftharpoons \text{H}_3\text{O}^+ + \text{Ac}^- \\
\text{m}(1-x) &\rightarrow \text{m}^' \\
K_a &= \frac{\alpha \text{m}(\text{H}_2\text{O}) \alpha \text{m}(\text{Ac}^-)}{\text{m}(\text{HAc})} \\
&= \frac{\alpha^2 \text{m}^2}{\text{m}(1-x)} = \frac{\alpha^2 \text{m}}{1-x} \\
m &= 0.200 \text{ m} \Rightarrow \alpha = 0.00931 \Rightarrow m^' = m(1+x) \\
s' = m' \text{ m}^' \Rightarrow \alpha T = K_f \text{ m}^' = 0.374 K
\end{align*}
\]

2. Based on your experience with this apparatus, do you think Les can succeed in determining \( K_a \) for an acid as weak as acetic acid or weaker? Explain.

3. Calculate the freezing-point depression expected for 0.250 \( m \) HCl (a) taking activity coefficients to be 1.00, and (b) taking into account the predictions of the Debye-Hückel theory. (See table of \( \sigma \) and \( n \) values given below.)

(a) \( \Delta T = \nu \text{ m}_1 K_f = 2 \times 0.250 \text{ m} \times 1.855 \frac{K}{m} = 0.928 K \)

(b) \( \Delta T = \nu \text{ m}_1 K_f g_1 \)

\[ g_1 = 1 - 0.38 \text{ m}^{1/2} ; \quad K_a \approx \text{ m}^{1/2} = 0.5 \]

\[ \sigma = 0.5376 \Rightarrow g_1 \approx 0.898 \]

\[ \Delta T = 0.833 K \]

---

C. Bomb Calorimetry. Stryangelove uses bomb calorimetry to measure the heat of combustion of an unknown substance. The instrument is calibrated using benzoic acid (\( Q_{\text{specific}} = -26.413 \text{ kJ/g} \) at 25.0°C and Fe fuse wire (\( Q_{\text{specific}} = -6.68 \text{ kJ/g} \)), and for each run is filled with 2.000 kg of water (\( c_p = 4.1796 \text{ J K}^{-1} \text{ g}^{-1} \) at 25.0°C).

1. In one experiment at -25°C, 0.923 g of benzoic acid yields a temperature rise of 2.584 K. When the bomb is opened, Stryangelove finds that 34 mg of Fe fuse wire has been consumed. Calculate (a) the total combustion heat for the benzoic acid and Fe; and (b) from this the heat capacity \( C_p \) of the calorimeter.

(a) \( Q_{\text{benzoic}} = \text{Q}_{\text{fuel}} \cdot \text{m}_{\text{fuel}} \cdot \text{c}_{\text{water}} \) \( \Delta T = -24.379 \text{ kJ} \) \( \sum \text{total} = -24.61 \text{ kJ} \)

(b) \( Q_{\text{Fe}} = \text{c}_{\text{water}} \cdot \text{m}_{\text{Fe}} \cdot \Delta T = 4.1796 \text{ kJ/kg} \cdot 0.00034 \text{ kg} \cdot 2.584 \text{ K} = 21.60 \text{ kJ} \)

2. Benzoic acid (\( M = 122.13 \text{ g/mol} \)) in \( \text{C}_6\text{H}_5\text{COOH} \). Write a balanced equation for the complete combustion of 1.00 mol of benzoic acid in oxygen.

\[ \text{C}_6\text{H}_5\text{COOH} \text{(s)} + 15.02 \text{O}_2 \text{(g)} \rightarrow 7 \text{CO}_2 \text{(g)} + 3 \text{H}_2\text{O} \text{(l)} \]

3. Calculate \( \Delta U \) (\( \Delta G \)) in SGN and \( \Delta H \) for the complete combustion of 1 mol of benzoic acid in oxygen at 25.0°C.

\[ \Delta U = M \cdot \text{Q}_{\text{fuel}} = -3225.8 \text{ kJ} \]

\[ \Delta H = \Delta U + n \cdot (n \cdot \text{RT}) \]

\[ n = \text{mol}_{\text{gas}} = (7 - 15) = -8 \text{ mol} \]

\[ \Delta H = \Delta U - \frac{1}{2} \text{ RT} \]

\[ \Delta H = -3227.0 \text{ kJ} \]

---

Table 4.3: Error Function \( f(m) = e^x + x \) and Ordinate Values of \( f(x) \) at \( x = 0 \)

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<th>( f(x) )</th>
<th>( x = 0 )</th>
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</table>

Fundamental Constants and Conversion Factors

\( N_A = 6.022137 	imes 10^{23} \text{ mol}^{-1} \)

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

1 atm = 1.01325 \times 10^5 \text{ Pa}

1 cal = 4.184 J