

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

KEY

(Signature)

- I. (30) **Least Squares.** Obtain the least-squares equations for an unweighted fit of data to the relationship,  $y = a/x + bx^2$ . Express these using matrix notation. (Note: It is NOT necessary to solve these equations. Assume, as usual, that  $x$  is error-free.)

$$\text{Let } d = \sum \delta_i^2 \quad \text{with } \delta_i = y_{\text{calc}}(x_i) - y_i = \frac{a}{x_i} + bx_i^2 - y_i$$

$$\text{Eqs.} = \frac{\partial d}{\partial a} = \frac{\partial d}{\partial b} = 0 \quad \frac{\partial \delta_i}{\partial a} = \frac{1}{x_i} \quad ; \quad \frac{\partial \delta_i}{\partial b} = x_i^2$$

$$\frac{\partial d}{\partial a} = 2 \sum \delta_i \frac{\partial \delta_i}{\partial a} = 2 \sum \left( \frac{a}{x_i} + bx_i^2 - y_i \right) \frac{1}{x_i} = 0$$

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

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

$$\hookrightarrow \boxed{a \sum x_i + b \sum x_i^4 = \sum x_i^2 y_i}$$

$$\underset{\sim}{A} \underset{\sim}{\beta} = \underset{\sim}{z} \quad \underset{\sim}{A} = \begin{pmatrix} \sum \frac{1}{x_i^2} & \sum x_i \\ \sum x_i & \sum x_i^4 \end{pmatrix} ; \quad \underset{\sim}{\beta} = \begin{pmatrix} a \\ b \end{pmatrix} \quad \underset{\sim}{z} = \begin{pmatrix} \sum \frac{y_i}{x_i} \\ \sum x_i^2 y_i \end{pmatrix}$$

- II. **Error Propagation and Confidence Limits.** Do 3 and ONLY 3 of the following. [Note: They are not all equal in point value.]

- A. (15) The density of steel is about  $7.85 \text{ g/cm}^3$ . Calculate the density and its uncertainty for a spherical steel ball of mass  $10.000(5)$  (i.e.,  $\pm 0.005$ ) g and radius  $0.6725(15)$  cm. ( $V = \frac{4}{3} \pi r^3$ .) Report your answer with the correct number of significant figures.

$$\rho = \frac{m}{V} = \frac{m}{\frac{4}{3} \pi r^3} = 7.849365 \frac{\text{g}}{\text{cm}^3}$$

$$\left( \frac{s_\rho}{\rho} \right)^2 = \left( \frac{s_m}{m} \right)^2 + 3^2 \left( \frac{s_r}{r} \right)^2 = \left( \frac{0.005}{10} \right)^2 + 9 \left( \frac{0.0015}{0.6725} \right)^2 = 4.5026 \times 10^{-5}$$

$$\frac{s_\rho}{\rho} = 6.71 \times 10^{-3} \rightarrow s_\rho = \rho \cdot 6.71 \times 10^{-3} = 0.0527$$

$$\hookrightarrow \rho = 7.849(53) \text{ or } 7.85(5) \frac{\text{g}}{\text{cm}^3}$$

- B. (30) J. Walker studies the temperature dependence of a certain first-order reaction and obtains  $k = 3.78(9) \times 10^{-4} \text{ s}^{-1}$  [i.e.,  $(3.78 \pm 0.09) \times 10^{-4} \text{ s}^{-1}$ ] at  $22.0^\circ\text{C}$  and  $11.49(44) \times 10^{-4} \text{ s}^{-1}$  at  $35.0^\circ\text{C}$ . 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. (Neglect uncertainties in T.)

$$k = A e^{-E_a/RT} \rightarrow k_2/k_1 = e^{-E_a/RT_2 + E_a/RT_1} = e^{\frac{E_a}{R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]}$$

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right] \rightarrow \boxed{E_a = 64.6706 \frac{\text{kJ}}{\text{mol}}}$$

$$E_a = c \left[ \ln k_2 - \ln k_1 \right] \quad \text{w/ } c = R \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]^{-1}$$

$$S_{E_a}^2 = c^2 \left[ \left( \frac{S_{k_2}}{k_2} \right)^2 + \left( \frac{S_{k_1}}{k_1} \right)^2 \right] \rightarrow S_{E_a} = c \left[ \quad \right]^{1/2} = c \cdot 0.04509$$

$$S_{E_a} = 2.923 \frac{\text{J}}{\text{mol}} \rightarrow \boxed{E_a = 64.7 \pm 2.6 \frac{\text{kJ}}{\text{mol}}}$$

- C. (20)

1. Smith and Voleri carry out measurements of the vapor pressure of water from  $-20^\circ\text{C}$  to  $20^\circ\text{C}$  and estimate from their analysis of the data,  $\Delta H_{\text{vap}} = 40.738 \pm 0.127 \text{ kJ/mol}$  and  $\Delta H_{\text{sub}} = 47.597 \pm 0.050 \text{ kJ/mol}$ . Calculate from these data  $\Delta H_{\text{fus}}$  and its uncertainty, and give your result with the correct number of significant figures.

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

$$S_{\Delta H_{\text{fus}}}^2 = S_{\Delta H_{\text{sub}}}^2 + S_{\Delta H_{\text{vap}}}^2 = (0.127)^2 + (0.050)^2 \rightarrow S_{\Delta H_{\text{fus}}} = 0.136 \frac{\text{kJ}}{\text{mol}} \rightarrow \boxed{6.86 \pm 0.14 \frac{\text{kJ}}{\text{mol}}}$$

2. Morely Smartt does very careful vapor pressure measurements on water and obtains  $\Delta H_{\text{vap}} = 44.001 \pm 0.003 \text{ kJ/mol}$ , while Bud Wizer breezes through and obtains  $44.8 \pm 0.9 \text{ kJ/mol}$ . The literature value reads  $44.012 \text{ kJ/mol}$ . Which of the two determinations — Smartt's or Wizer's — is the greater cause for "concern"? Explain.

$$\text{true value} - \text{Smartt} = 0.011 \frac{\text{kJ}}{\text{mol}} = 3.7 \sigma \leftarrow \text{very improbable!}$$

$$\text{true value} - \text{Wizer} = -0.8 \text{ " } < 1 \sigma \leftarrow \text{quite reasonable.}$$

- D. (15) I. B. Thoro measures a quantity  $y$  120 times and obtains an estimated mean  $\bar{y} = 76.32$  and an estimated variance  $s^2 [= 1/(n-1) \sum (y_i - \bar{y})^2] = 9.74$ . What error limits should Thoro quote for 90% confidence in his mean? (See integral table below, last page.)

$$S = 3.12 \rightarrow S_{\bar{x}} = \frac{S}{\sqrt{N}} = 0.285$$

90%  $\leftrightarrow$  half area = 0.45  $\rightarrow t \cong 1.65$ . This is in units of  $S_{\bar{x}}$ , so 90% confidence corresponds to  $\pm 0.47$ .

### III. (75) Experiments. [DO 3 ONLY — 25 points each.]

- A. Thermal expansivity by dilatometry. At the end of a long day of meniscus measuring, Otto Motive discovers that his dilatometer contains an air bubble. Through painstaking effort he determines that the bubble has a volume of 1.28 mL and seeks to use this information to correct his results. Suppose the volume of the dilatometer is 25.35 mL and the liquid being measured has a true value of  $\alpha = 9.7 \times 10^{-4} \text{ K}^{-1}$ . If the measurements are being done near  $25^\circ\text{C}$  and at an atmospheric pressure of 747 torr, how large would be the error introduced by the bubble? (Treat the air as an ideal gas.)

$$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \rightarrow \Delta V \approx \alpha V \cdot \Delta T$$

$$\text{For air, } V = \frac{nRT}{P} \rightarrow \alpha = \frac{1}{T}$$

Calculate  $\Delta V$  for  $25 \rightarrow 26^\circ\text{C}$  :

$$\text{liquid: } \Delta V \approx 9.7 \times 10^{-4} \text{ K}^{-1} \cdot 1 \text{ K} \times (25.35 - 1.28) \text{ mL} = 0.02335 \text{ mL}$$

$$\text{air: } \Delta V \approx \frac{1}{298.5} \cdot 1 \text{ K} \cdot 1.28 \text{ mL} = 4.29 \times 10^{-3} \text{ mL}$$

$$\Delta V_{\text{total}} = 0.0276 \rightarrow \alpha_{\text{apparent}} \approx \frac{\Delta V_{\text{total}}}{V \Delta T} = 1.09 \times 10^{-3} \approx 12\% \text{ high}$$

$$\text{Also, } \frac{1.28}{25.35} \cdot \alpha_{\text{air}} + \frac{24.07}{25.35} \alpha_{\text{liq}} = 1.09 \times 10^{-3}$$

- B. Equilibrium and spectrophotometry. Justin Tyme studies an equilibrium complexation reaction of form  $\text{I}_2 + \text{M} \leftrightarrow \text{I}_2 \cdot \text{M}$  by spectrophotometry at a wavelength of 350 nm, where only the complex  $\text{I}_2 \cdot \text{M}$  absorbs light. He uses absorption cells (cuvettes) having a path length of 1.000 cm and does the experiments at  $22.0^\circ\text{C}$  in  $\text{CCl}_4$  solvent, which is inert with respect to the reaction and does not absorb light at 350 nm.

Suppose that  $\epsilon_{350}$  is known to be  $9.8 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$ . Tyme mixes 2.00 mL of 0.330 M M with 3.00 mL of 0.00155 M  $\text{I}_2$  and measures an absorbance of 0.6566. (M = mol/L) Calculate (1) the transmittance,  $I/I_0$ ; (2) the concentration of  $\text{I}_2 \cdot \text{M}$ ; (3) the concentrations of M and  $\text{I}_2$  at equilibrium; and (4) the equilibrium constant  $K_c$ .

$$(1) I/I_0 = 10^{-A} = 10^{-0.6566} = \boxed{0.2205}$$

$$(2) A = \epsilon c l \rightarrow c = A / \epsilon l = \boxed{6.7 \times 10^{-5} \frac{\text{mol}}{\text{L}}}$$

$$(3) [\text{I}_2]_0 = \frac{3.00}{5.00} \times 0.00155 \frac{\text{mol}}{\text{L}} = 9.3 \times 10^{-4} \frac{\text{mol}}{\text{L}}$$

$$[\text{I}_2]_{\text{eq}} = \boxed{8.63 \times 10^{-4} \frac{\text{mol}}{\text{L}}}$$

$$[\text{M}]_0 = \frac{2.00}{5.00} \times 0.330 \frac{\text{mol}}{\text{L}} = 0.132 \frac{\text{mol}}{\text{L}} \rightarrow [\text{M}]_{\text{eq}} = \boxed{0.1319 \frac{\text{mol}}{\text{L}}}$$

$$(4) K_c = \frac{[\text{I}_2 \cdot \text{M}]}{[\text{I}_2][\text{M}]} = \boxed{0.588}$$

C. Vapor Pressure. Marian Haste carries out the triple point experiment on water, collecting data in the range  $-20^{\circ}\text{C}$  to  $0^{\circ}\text{C}$  for sublimation and  $0^{\circ}\text{C}$  to  $19^{\circ}\text{C}$  for vaporization.

- Marian analyzes her vaporization data using the usual integrated form of the Clausius-Clapeyron equation and then compares her results with values from Table 2.2 in the text by Woodbury, which is titled "Heats of fusion and vaporization at normal melting and boiling temperatures." Explain what is wrong with this comparison and give quantitative expressions that would render a more appropriate comparison to be made between Marian's experimental results and "literature."

Even though Marian analyzed her data treating  $\Delta H_{\text{vap}}$  as independent of  $T$ , her value is for  $T \approx 10^{\circ}\text{C}$ , whereas the "literature" value is for  $100^{\circ}\text{C}$ . For a proper comparison, use

$$\Delta H_T^{\circ} = \Delta H_{100^{\circ}\text{C}}^{\circ} + \int_{100^{\circ}\text{C}}^T \Delta C_p^{\circ} dT$$

to convert the literature value to  $10^{\circ}\text{C}$ . Better, use  $\Delta H_{25^{\circ}\text{C}}^{\circ} \rightarrow 10^{\circ}\text{C}$ .

- Is there any reason why Marian stopped the vapor pressure measurements around  $20^{\circ}\text{C}$ ? Why not use a heat gun to warm the sample up to  $25^{\circ}\text{C}$ ,  $30^{\circ}\text{C}$ , or even higher?

[This is because the vapor P is controlled by the coldest part of the system.] Yes! Any attempt to heat the sample above room  $T$  will lead to condensation of liquid on the colder walls of the apparatus, including in the pressure gage. To go to higher  $T$ , it would be necessary to heat the entire apparatus.

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  $\alpha$  is proportional to the optical path length, the concentration of solute, and to 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  $20^{\circ}\text{C}$ , are  $+66.4$ ,  $+52.5$ , and  $-88.5$ , respectively.

- 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  $[S]_0$ ,  $k_{\text{eff}}$ , and the time  $t$ .

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

$$\hookrightarrow [S] = [S]_0 e^{-k_{\text{eff}} t} \Rightarrow [\text{glucose}] = [\text{fructose}] = [S]_0 (1 - e^{-k_{\text{eff}} t})$$

{ Note: sucrose  $\rightarrow$  glucose + fructose }

- Honey does her experiments at  $20^{\circ}\text{C}$ , using solutions that contain 100.0 g sucrose per liter, in a polarimeter that has a path length of 20.0 cm. Calculate the rotation  $\alpha$  expected in her experiments (a) at the start ( $\alpha_0$ ), and (b) after the inversion has proceeded to completion ( $\alpha_{\infty}$ ).

$$\alpha_0 = [\alpha]_{\lambda, \text{suc}}^{20^{\circ}\text{C}} \cdot [\text{sucrose}]_0 \cdot l = 66.4 \cdot 0.1000 \cdot 2.00 = 13.28^{\circ}$$

$$\alpha_{\infty} \approx \frac{[S]_0}{2} \cdot l \cdot \left\{ [\alpha]_{\lambda, \text{gluc}}^T + [\alpha]_{\lambda, \text{fruc}}^T \right\} = 0.100 [52.5 - 88.5] = -3.6^{\circ}$$

- Obtain an expression for  $\alpha(t)$ , in terms of  $k_{\text{eff}}$ , the time  $t$ ,  $\alpha_0$ , and  $\alpha_{\infty}$ .

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

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

E. **Bomb Calorimetry.** Strangelove uses bomb calorimetry to measure the heat of combustion of n-octane [ $C_8H_{18}(l)$ ,  $M = 114.23 \text{ g/mol}$ ] and an unknown. The instrument is calibrated using benzoic acid ( $Q_{\text{specific}} = -26.413 \text{ kJ/g}$ ).

- In one experiment at  $\sim 25^\circ\text{C}$ , 0.923 g of benzoic acid yields a temperature rise of 1.375 K. Then under the same conditions (same fill of water, T, etc.), 1.237 g of the unknown produces a temperature rise of 1.122 K. Calculate  $Q_{\text{specific}}$  for the unknown.

$$Q = Q_{\text{spec}} \cdot m = C \cdot \Delta T \Rightarrow Q_{\text{BA}} = m_{\text{BA}} \cdot Q_{\text{spec, BA}} = C \cdot \Delta T_{\text{BA}}$$

$$\leftarrow Q_{\text{unk}} = m_{\text{unk}} \cdot Q_{\text{spec, unk}} = C \cdot \Delta T_{\text{unk}}$$

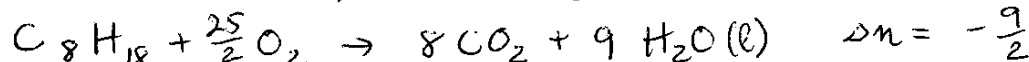
$$\frac{Q_{\text{spec, unk}}}{Q_{\text{spec, BA}}} = \frac{\Delta T_{\text{unk}}}{\Delta T_{\text{BA}}} \cdot \frac{m_{\text{BA}}}{m_{\text{unk}}} = \frac{1.122}{1.375} \cdot \frac{0.923}{1.237} = 0.60887 \Rightarrow Q_{\text{spec, unk}} = -16.082 \frac{\text{kJ}}{\text{g}}$$

- Under the same conditions, 0.754 g of n-octane yields a temperature rise of 2.025 K. Calculate (a) the specific heat of combustion per gram of n-octane, (b)  $\Delta U$  of combustion, and (c)  $\Delta H$  of combustion for n-octane.

$$(a) Q_{\text{spec, oct}} = \frac{2.025}{1.375} \cdot \frac{0.923}{0.754} \cdot (-26.413 \frac{\text{kJ}}{\text{g}}) = -47.618 \frac{\text{kJ}}{\text{g}}$$

$$(b) \Delta \bar{u} = M \cdot Q_{\text{spec}} = -5439.4 \frac{\text{kJ}}{\text{mol}} \quad \left\{ Q_{\text{spec}} \text{ is a form of } \Delta u \right\}$$

$$(c) \Delta \bar{H} = \Delta \bar{u} + \Delta(PV) = \Delta \bar{u} + (\Delta n)RT$$



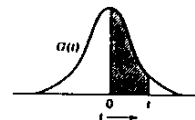
$$\hookrightarrow \Delta \bar{H} = -5450.55 \frac{\text{kJ}}{\text{mol}}$$

- In the determination of  $Q_{\text{specific}}$  for the unknown (1, above), suppose the masses are uncertain by 0.002 g and the temperature changes are uncertain by 0.015 K. What is the uncertainty in the determined value of  $Q_{\text{specific}}$  for the unknown?

$$\left(\frac{\Delta Q}{Q}\right)^2 = \left(\frac{\Delta m_1}{m_1}\right)^2 + \left(\frac{\Delta m_2}{m_2}\right)^2 + \left(\frac{\Delta(\Delta T_1)}{\Delta T_1}\right)^2 + \left(\frac{\Delta(\Delta T_2)}{\Delta T_2}\right)^2 = 3.05 \times 10^{-4}$$

$$\hookrightarrow \frac{\Delta Q}{Q} = 0.017 \rightarrow \Delta Q = 0.28 \frac{\text{kJ}}{\text{g}}$$

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



$t$	$\frac{1}{2} \text{erf}(t)$ Area	$G(t)$ Ordinate	$t$	$\frac{1}{2} \text{erf}(t)$ 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	0.0281
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 and Conversion Factors

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

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

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

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