

Chemistry 236 — Hour Exam
December 3, 1997 — Tellinghuisen

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

(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.)

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

- 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°C and $11.49(44) \times 10^{-4} \text{ s}^{-1}$ at 35.0°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.)
- C. (20)
1. Smith and Voleri carry out measurements of the vapor pressure of water from -20°C to 20°C and estimate from their analysis of the data, $H_{\text{vap}} = 40.738 \pm 0.127 \text{ kJ/mol}$ and $H_{\text{sub}} = 47.597 \pm 0.050 \text{ kJ/mol}$. Calculate from these data H_{fus} and its uncertainty, and give your result with the correct number of significant figures.
 2. Morely Smartt does very careful vapor pressure measurements on water and obtains $H_{\text{vap}} = 44.001 \pm 0.003 \text{ kJ/mol}$, while Bud Wizer breezes through and obtains $44.8 \pm 0.9 \text{ kJ/mol}$. The literature value reads 44.012 kJ/mol . Which of the two determinations — Smartt's or Wizer's — is the greater cause for "concern"? Explain.
- 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.)

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°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.)

- B. Equilibrium and spectrophotometry. Justin Tyme studies an equilibrium complexation reaction of form $\text{I}_2 + \text{M} \rightleftharpoons \text{I}_2 \cdot \text{M}$ 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°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 $9.8 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$. Tyme mixes 2.00 mL of 0.330 M M with 3.00 mL of 0.00155 M 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 I_2 at equilibrium; and (4) the equilibrium constant K_c .

- C. Vapor Pressure. Marian Haste carries out the triple point experiment on water, collecting data in the range -20°C to 0°C for sublimation and 0°C to 19°C for vaporization.
1. 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."
 2. Is there any reason why Marian stopped the vapor pressure measurements around 20°C ? Why not use a heat gun to warm the sample up to 25°C , 30°C , or even higher?
- 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 is proportional to the optical path length, the concentration of solute, and to the specific rotation $[\alpha]^T$. 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. 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 .
 2. Honey does her experiments at 20°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 expected in her experiments (a) at the start (α_0), and (b) after the inversion has proceeded to completion (α_{∞}).
 3. Obtain an expression for $\alpha(t)$, in terms of k_{eff} , the time t , α_0 , and α_{∞} .

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

Fundamental Constants and Conversion Factors

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

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

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

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