

Chemistry 236 — Hour Exam
December 2, 1998 — Tellinghuisen

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

(Signature)

- I. (35) Least Squares.** Statistician Marge Inovera has collected some data (x_i, y_i) which she thinks should follow the relationship, $y = a/x^2 + bx^2$.
- 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.)
- 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.)

B. (20)

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

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

(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.

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

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

(a) $9.0 \times \quad \times 4.000 =$

(b) $71.1113 - 2.000000 \times 10^3 + 3.57 \times 10^{-3} =$

(c) $\ln(3.1) =$

(d) $529 \div 2.000 =$

(e) $25.279 \times \sqrt{2.00} =$

C. (15) I. B. Thoro measures a quantity y 250 times and obtains an estimated mean $\bar{y} = 46.2311$ and an estimated variance $s^2 = 19.7442$. What error limits should Thoro quote for 80% 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.

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.

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

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?
- 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 ($\rho = 0.998206 \text{ g/mL}$) 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.)
- C. In analyzing our vapor pressure data for water, we assumed that $H_{m,\text{vap}}$ was independent of temperature. Over an extended T range, this becomes a poor approximation. Suppose we include the T -dependence in $H_{m,\text{vap}}$ by treating $C_P (= C_{P,m,g} - C_{P,m,l})$ as independent of T .
1. Obtain an expression for $H_{m,\text{vap}}(T)$, in terms of C_P and $H_{m,\text{vap}}$ at the triple point.
 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 C_P and $H_{m,\text{vap}}(273.16 \text{ K})$.

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

A. Equilibrium and spectrophotometry. May B. Knott studies an equilibrium complexation reaction of form $I_2 + M \rightleftharpoons I_2 \cdot M$ 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 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 $22.0^\circ C$.

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

2. A cuvette containing just I_2 in CCl_4 at a concentration of 8.50×10^{-4} mol/L yields a transmittance $T (= I/I_0)$ of 0.226 at $\lambda = 500$ nm. Calculate the absorbance A and the molar absorption coefficient ϵ for I_2 in CCl_4 .

3. A solution is prepared having initial concentrations $[I_2]_0 = 9.75 \times 10^{-4}$ mol/L and $[M]_0 = 1.755 \times 10^{-3}$ 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.

- 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_c in the lab text.)
1. Calculate the fraction dissociated for a 0.200 m° solution of acetic acid. Then calculate the freezing-point depression for this solution. ($K_f = 1.855 \text{ K kg/mol}$; assume activity coefficients are all 1.00.)
 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 β and a values given below.)

- C. Bomb Calorimetry. Strangelove 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 $\sim 25^\circ\text{C}$, 0.923 g of benzoic acid yields a temperature rise of 2.584 K. When the bomb is opened, Strangelove 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.
 2. Benzoic acid ($M = 122.13 \text{ g/mol}$) is $\text{C}_6\text{H}_5\text{COOH}$. Write a balanced equation for the complete combustion of 1.00 mol of benzoic acid in oxygen.
 3. Calculate U (E in SGN) and H for the complete combustion of 1.00 mol of benzoic acid in oxygen at 25.0°C .

Fundamental Constants and Conversion Factors

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

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

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

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