Chemistry 236 -- Quiz 5

Lab Day ____

December 2, 2009 — Elective Experiments and Review

Pledge and signature:

I. (35) Elective Experiments. Do only ONE of the following three problems; pick one that correspond to your lab work. (Other choices will not be counted.)

A. Equilibrium and spectrophotometry. May B. Knott studies the equilibrium complexation reaction I_2 + M □ I_2•M by spectrophotometry. She is able to ascertain that only the uncomplexed reagent I_2 (not M and not I_2•M) absorbs light at 540 nm. Consequently she elects to monitor the equilibrium at that wavelength, using absorption cells (cuvettes) having a path length of 1.000 cm. The experiments are done at 22.0°C in CCl_4 solvent, which is inert with respect to the reaction and which also does not absorb light at 540 nm.

1. A cuvette containing just I_2 in CCl_4 at a concentration of 1.511□10^{-3} mol/L yields an absorbance *A* of 0.992 at □= 540 nm. Calculate the <u>transmittance</u> *T* and the molar absorption coefficient □for I_2 in CCl_4 at this wavelength.

2. A solution is prepared by mixing 3.00 mL of the I_2/CCl_4 solution mentioned just above with 5.00 mL of a solution of M in CCl_4 having [M] = 1.555□10^{-3} mol/L. After equilibrium is established, a cuvette containing this mixture yields *A* = 0.228 at 540 nm. Calculate the concentrations of all three substances in this mixture and use these to evaluate K_c for the reaction. [Assume that volumes are additive for these dilute solutions.]

3. In separate experiments with another system, K_c is found to be 1.105 at 20°C and 0.633 at 40°C. Both values are uncertain by 3.0%. Calculate ΔH° and ΔS° for this reaction, under the usual assumption that these are constant over this T range. Also, calculate ΔG° at 20° and its uncertainty, and the uncertainty in ΔH°. Then use the 10% rule to properly state this ΔG° and ΔH° and their uncertainties. [$R = 8.3145$ J mol^{-1} K^{-1}]

B. Thermal Expansivity. [Hint: Precision is *very* important in all these calculations.]

1. The data given here concern a dilatometer like that you used in the lab. It has a capillary extension of diameter 1.000 mm. Neglect buoyancy corrections and the thermal expansivity of Pyrex glass in your calculations.

   The empty, dry dilatometer weighs 106.863 g. Filled with water at 20.0°C (ρ= 0.998207 g/mL) to the low mark on the capillary extension, it weighs 133.344 g. Later, containing a sample of an alcohol, the capillary reading is h = 3.3 mm at 22.3°C and rises to h = 107.2 mm at 25.6°C. Calculate V_b for the dilatometer and estimate the thermal expansivity α for the alcohol over this T range.

2. Assuming that the h measurements just given are uncertain by 0.2 mm, and the T measurements by 0.1°C, calculate the uncertainties in Δh, ΔT, and α. Then use the 10% rule to properly state α and its uncertainty.

3. A pycnometer is fitted with a capillary extension (*i.e.*, like those used in our lab) having an internal diameter of 1.000 mm. In the initial calibration with water, I. B. Allwette measures the capillary height to be 33.7 mm above the zero level. The apparent mass of pycnometer and water is 48.112 g, while the apparent mass of the empty pcynometer is 22.379 g. At the temperature of the h measurement, the density of water is 0.998011 g/mL. Neglecting air buoyancy effects, calculate (a) the volume of water in the capillary extension, (b) the volume V_0 of the pycnometer at the zero mark, and (c) the uncertainty in this V_0 due to the 0.2 mm uncertainty in h alone.

4. An unknown liquid is measured next, giving an apparent mass (pycnometer + sample) of 56.777 g for a capillary height of 19.3 mm. Calculate it's density.

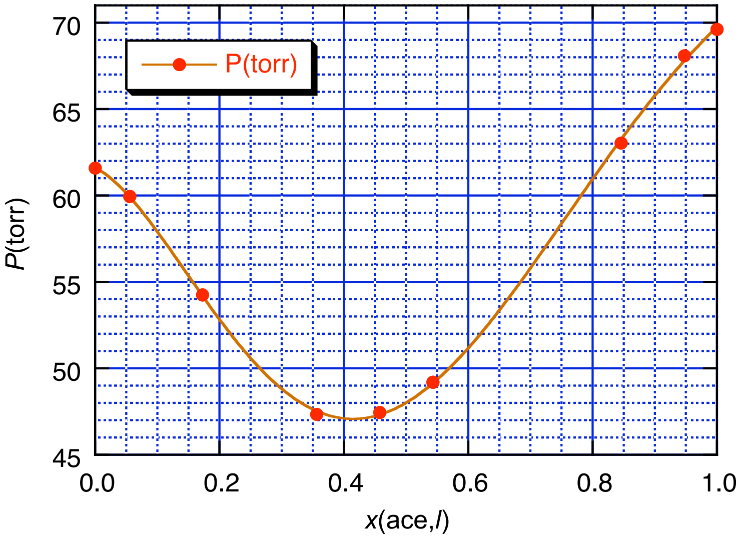
5. Taking the density of air to be 1.19 mg/mL, correct your results for V_0 and the density of the unknown for buoyancy of air.

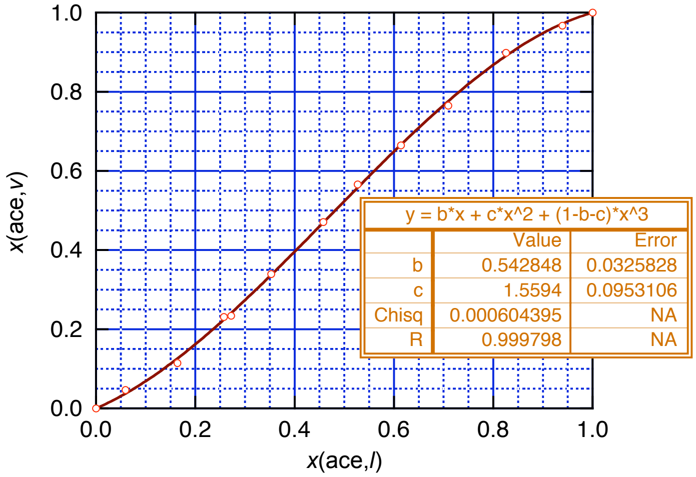
C. Liquid-Vapor Equilibrium. I. M. Al-Knowing collects equilibrium data for the chloroform/acetone system at 0.0˚C and processes them according to our specified procedures, obtaining the illustrated plots and fitted curves.

1. Use the fitted curves in these figures to answer the following questions, reading *P*s to the nearest 0.1 torr and *x* s to 0.01:

(a) What are the vapor pressures of pure acetone and pure chloroform at 0.0°C?

(b) Letting A = acetone, calculate P_A, P_B, $P_{A,id}$, $P_{B,id}$, γ_A, and γ_B for a liquid acetone mole fraction of 0.70 (where "id" stands for ideal).





y = b*x + c*x^2 + (1-b-c)*x^3

	Value	Error
b	0.542848	0.0325828
c	1.5594	0.0953106
Chisq	0.000604395	NA
R	0.999798	NA

(c) If this system behaved ideally, what would be the values of *P* and $x_{A,v}$ for this $x_{A,l}$?

(d) Does this system form an azeotrope? If so, is it maximum- or minimum-boiling?

(e) Sketch the approximate vapor-composition curves on the first figure, showing clearly the point you obtain for *x*(ace,*l*) = 0.70. Also, indicate the liquid, vapor, and two-phase regions of the diagram.

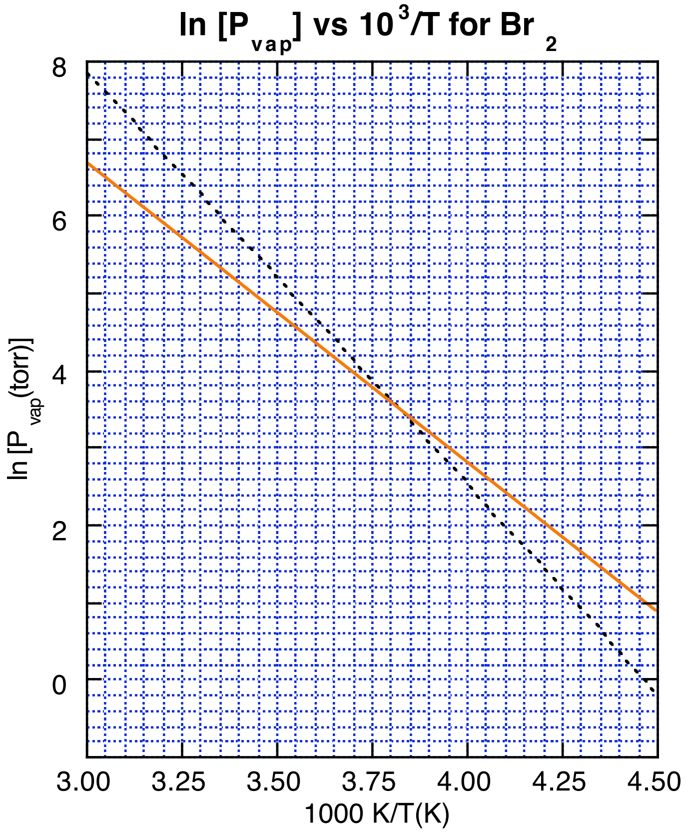
2. Why was the indicated function used in the second plot? How would you modify this function to go to 4th order in *x*? (Give its KaleidaGraph form.)

3. The smooth curve in the first figure represents an unweighted fit to a 5th-order polynomial (6 parameters) and gives Chisq = 0.21547. Estimate the standard deviation in *P* from this fit. Similarly, estimate the standard deviation in *x*(ace,*v*) from the 2nd fit.

Before beginning Part II, enter here the names of your lab partners and the number of peer points you wish to award to each. The total must not exceed 24, and the maximum to any one partner is 18. If you leave this space blank, your points will be distributed 12:12. (Members of teams of two receive 24 each.)

II. (15) Review.

A. (10) Consider the accompanying figure, which shows the natural log of the vapor pressure of Br_2 as a function of $1/T$, for both solid and liquid phases. Using this figure, estimate (1) the triple point T and P; (2) the normal boiling point T; (3) $\square H_{\mathrm{m,vap}}$; (4) $\square H_{\mathrm{m,sub}}$; and (5) $\square H_{\mathrm{m,fus}}$. [$R$ = 8.3145 J mol$^{\square 1}$ K$^{\square 1}$]



B. (5) In KG Exercise 3 and again in analyzing your sucrose inversion data, you used the General routine to fit the data to an exponential plus a background.

1. Give the mathematical equation you used for the inversion data, in terms of the parameters, $\square_0$, $\square$, and k_{eff}, and the variables $\square$ and t. (Derive if necessary, using definitions of $\square_0$ and $\square$.)

2. Using a, b, and c for the parameters, and x for the independent variable, write exactly what you had to enter in the Define Fit box for this fit.