Chemistry 236 -- Quiz 5

Lab Day ____

November 19, 2008 — Elective Experiments and Review

Pledge and signature:

I. (30) Elective Experiments. Do the TWO that correspond to your lab work. (Other choices will not be counted.)

A. Equilibrium and spectrophotometry. Justin Tyme studies an equilibrium complexation reaction of form $I_2 + M \leftrightarrow I_2{\bullet}M$ by spectrophotometry at a wavelength of 350 nm, where only the complex $I_2{\bullet}M$ 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 9.80×10^3 L mol^{-1} cm^{-1}. Tyme mixes 2.00 mL of 0.235 M M with 3.00 mL of 0.00165 M I_2 and measures an absorbance of 0.6566. (M = mol/L) Calculate (1) the transmittance, $^{I}/_{I_0}$; (2) the concentrations we call $[M]_0$ and $[I_2]_0$, (3) the concentration of $I_2{\bullet}M$ at equilibrium; (4) the concentrations of M and I_2 at equilibrium; and (5) the equilibrium constant K_c.

B . The Freeze. 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 $K_a = 1.75\times10^{-5}$ mol/kg.

1. Calculate the fraction dissociated α for a 0.250 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.)

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 0.355 m° HCl if the activity coefficients are taken to be 1.00.

C. Thermal Expansivity. Do either 1 OR 2, NOT both. They are unequal in credit.

1. (12) The density of ethanol in the range 20-90˚C can be represented as $\rho = 0.76302 \exp(bx + cx^2 + dx^3)$, where ρ is in g/mL and $x = t(˚\mathrm{C}) - 50˚\mathrm{C}$. (a) Obtain from this an expression for the thermal expansivity α for ethanol in this temperature range. (b) The coefficients b, c, and d, are -0.00118, -2.262×10^{-6}, and -1.3639×10^{-8}, respectively. Calculate ρ and α at $t = 40.0˚\mathrm{C}$.

2. (15) 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 108.663 g. Filled with water at 20.0°C ($\rho = 0.998207$ g/mL) to the low mark on the capillary extension, it weighs 132.344 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.

D. Physical Adsorption. In a setup like ours, the volume of the manifold is 61.3 mL, and the cell *V* is 12.8 mL. The total active volume is the sum of these two, and the room is at 22° C. [R = 8.3145 J mol^{-1} K^{-1} = 0.082058 L atm mol^{-1} K^{-1}; 1 atm = 1.0133×10^5 Pa; V_{STP} = 22414 cm^3]

1. The system is first evacuated, and the valve to the cell is shut, leaving it at $P \sim 0$. The manifold is charged with N_2 to $P = 302$ torr. Then the valve to the cell is opened. What is the new P?
2. Now the cell is charged with a sample of silica gel and carefully evacuated and degassed. Then the manifold is charged with N_2 to $P = 445$ torr. With the silica gel sample immersed in liquid N_2, the valve to the cell is opened, whereupon the N_2 pressure drops and settles at 36.5 torr. The "cold volume" has previously been determined to be 8.2 cm^3. Calculate the amounts (in STP cm^3) of N_2 (a) at the outset, in the manifold; (b) remaining in the gas phase at equilibrium, and (c) adsorbed on the silica gel.

E. Liquid-Vapor Equilibrium. I. M. Al-Knowing collects equilibrium data for the chloroform/acetone system at 35.2˚C and obtains the following results (where A ≡ acetone):

$x_{A,l}$	$x_{A,v}$	P(torr)	$x_{A,l}$	$x_{A,v}$	P(torr)
0.0000	0.0000	293	0.6034	0.6868	267
0.0821	0.0500	279.5	0.7090	0.8062	286
0.2003	0.1434	262	0.8147	0.8961	307
0.3365	0.3171	249	0.9397	0.9715	332
0.4188	0.4368	248	1.0000	1.0000	344.5
0.5061	0.5625	255			

1. From these data, answer the following questions:

   (a) What is the vapor pressure of pure acetone at 35.2˚C? Of pure chloroform?

   (b) For the solution having $x_{A,l} = 0.6034$, calculate P_A, P_B, $P_{A,id}$, $P_{B,id}$, γ_A, and γ_B (where "id" stands for ideal).

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

   (d) Are the deviations from ideality positive, negative, or neither?

2. In analyzing his data, Al-Knowing smartly employs a special cubic polynomial to obtain a smooth representation of his measured dependence of $x_{A,v}$ on $x_{A,l}$. Give this equation and explain briefly why it is wise to use this expression rather than a simple fit to $y = a + bx + cx^2 + dx^3$.

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 20. If you leave this space blank, your points will be distributed 12:12.

II. (26) Review.

A. (10) I. B. Thoro measures a quantity y 127 times and obtains an estimated mean $\bar{y} = 76.326$ and a sum of squares, $\mathbf{S} = \sum (y_i - \bar{y})^2$] = 29.74.

1. Calculate the estimated variance, standard deviation, and standard deviation in the mean (standard error).

2. What error limits should Thoro quote for 90% confidence in his mean?

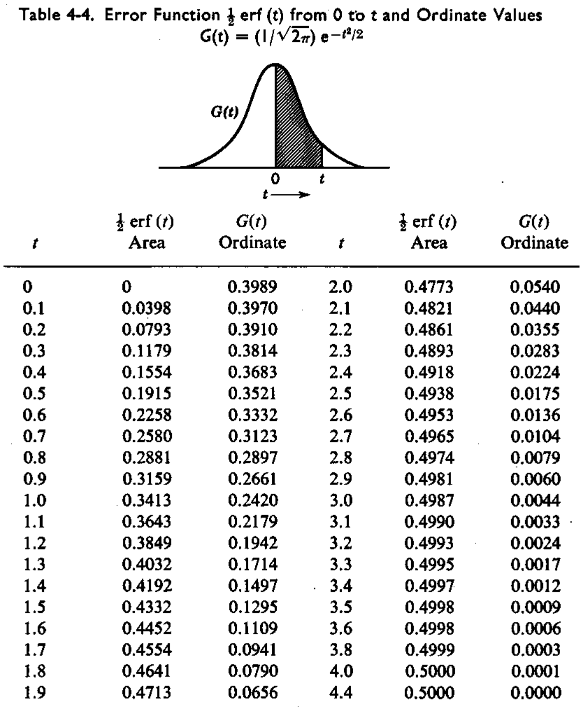

Table 4-4. Error Function $\frac{1}{2}\,\mathrm{erf}\,(t)$ from 0 to t and Ordinate Values $G(t) = (1/\sqrt{2\pi})\,e^{-t^2/2}$

t	$\frac{1}{2}\,\mathrm{erf}\,(t)$ Area	$G(t)$ Ordinate	t	$\frac{1}{2}\,\mathrm{erf}\,(t)$ 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	0.0283
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

B. (6) Consider the probablility distribution, $P(x) = cx^2$ for $0 \leq x \leq 2$, 0 elsewhere. Calculate

1. the normalization constant c.
2. the mean μ.
3. the variance σ^2.

C. (10) J. Walker studies the temperature dependence of a certain first-order reaction and obtains $k = 3.78(13) \times 10^{-4}\ \text{s}^{-1}$ [*i.e.*, $(3.78 \pm 0.13) \times 10^{-4}\ \text{s}^{-1}$] at 22.0˚C and $12.19(24) \times 10^{-4}\ \text{s}^{-1}$ 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. ($R = 3.3145\ \text{J mol}^{-1}\ \text{K}^{-1}$; neglect uncertainties in T.)