Chemistry 236 — Quiz 3
November 29, 2006 — Tellinghuisen

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

(Signature)

R = 8.3145 J mol^{-1} K^{-1} = 0.082058 L atm mol^{-1} K^{-1} = 1.9872 cal mol^{-1} K^{-1}; 1 atm = 1.0133×10^5 Pa

I. (14) Elective Experiments. Do ONE and only one of the following three problems. You must choose one that matches one of your lab electives.

A. BET Stuff. In a setup like ours, the volume of the manifold is 64.3 mL, and the cell V is 14.8 mL. The total active volume is the sum of these two, and the room is at 22° C.

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 = 203 torr. Then the valve to the cell is opened. What is the new P?
2. The cell and manifold are charged with N_2 to P = 195 torr. With the valve to the cell still open, the "fat" part of the cell is immersed in liquid N_2 at 77 K. The pressure drops to 141 torr. Calculate the effective volume (cold volume) that is at 77 K.
3. When you filled the manifold with N_2 to a pressure exceeding 800 Torr and then cooled the cell by immersing it in the liquid N_2 contained in your dewar, the pressure dropped and then leveled out at a value greater than 760 Torr. What does this tell us?

1. P = 165 Torr

2. V_{cold} = 10.7 mL

3. P > 760 Torr means that the temperature of the liquified N_2 in the cell is > the boiling point T. (In fact you were to have used this measurement to determine the T.) This can happen when O_2 condenses in the Dewar flask, giving a solution that boils above the BP for pure N_2.

B . Spectro-K. I_2 forms 1:1 complexes with all aromatic substances in a manner similar to that studied for mesitylene. Let us suppose that for such an arene, K_c = 7.7 L/mol at 22°C.

1. 5.0 mL of 0.00087 M I_2 in heptane is mixed with 10 mL of 2.15 M arene in heptane in a 25.0-mL volumetric flask, and heptane is added to bring the volume to the mark. Calculate the concentrations of all three substances in the equilibrium mixture at 22°C.
2. I_2 in heptane has peak absorptivity of 925 L mol^{-1} cm^{-1} at 525 nm. Assuming that only I_2 absorbs at this wavelength, calculate the absorbance at 525 nm in a 2.0-cm cuvette of (a) the original I_2 stock solution, (b) the I_2 in the mix IF there were no reaction with arene, (c) the I_2 in the actual equilibrium mixture.

1. $[I_2]_0 = 1.74 \times 10^{-4}$ M, and $[A]_0 = 0.86$ M

   Solving for the concentrations at equilibrium, we obtain

   $[I_2{\bullet}A] = 1.51_2 \times 10^{-4}$ M, $[I_2] = 2.2_8 \times 10^{-4}$ M, $[A] \approx 0.86$ M

2. $A = \varepsilon\, c\, l$

   (a) $A = 1.61$

   (b) $A = 0.32_2$

   (c) $A = 0.042_2$

C. Binary. The following data have been obtained for mixtures of water (A) and hydrogen peroxide (B) at 60°C:

$x_{A,l}$	$x_{A,v}$	P(kPa)	$x_{A,l}$	$x_{A,v}$	P(kPa)
0.000	0.000	2.35	0.700	0.967	12.86
0.100	0.301	3.00	0.900	0.995	17.77
0.300	0.696	5.03	1.000	1.000	19.92
0.500	0.888	8.33			

1. For the solution having mole fraction $x_{A,l} = 0.300$, calculate P_A, P_B, $P_{A,id}$, $P_{B,id}$, γ_A, and γ_B (where "id" stands for ideal).
2. Calculate a_A and a_B for this same mixture.
3. Briefly describe how you determined the compositions of your samples when you did this experiment.

1. $P_A = 3.50_1$ kPa, $P_{A,id} = 5.97_6$ kPa, $\gamma_A = 0.586$

   $P_B = 1.52_9$ kPa, $P_{B,id} = 1.64_5$ kPa, $\gamma_B = 0.930$

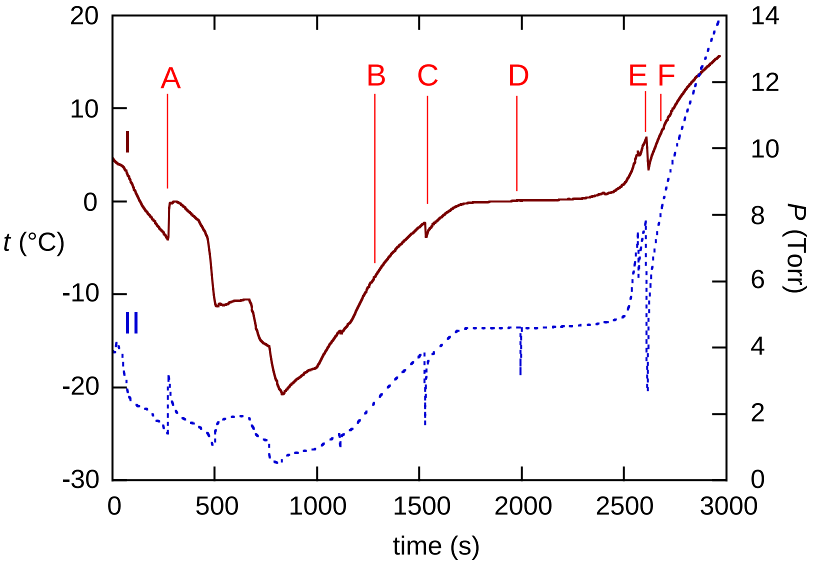
2. $a_A = 0.176$, $a_B = 0.651$

3. We measured the refractive index of each solution and compared it with a calibration curve of refractive index vs composition, obtained from a series of samples of known prepared composition.

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. (14) Core Experiments.

A. **(5)** This figure shows the time dependence of *T* and *P* in the Triple Point experiment. Tell which curve (I & II) is which, and identify (by letter) points where (1) solid, liquid, and vapor are present simultaneously in equilibrium; (2) solid (only) is in equilibrium with vapor; (3) liquid (only) is in equilibrium with vapor; and (4) supercooled water spontaneously froze.

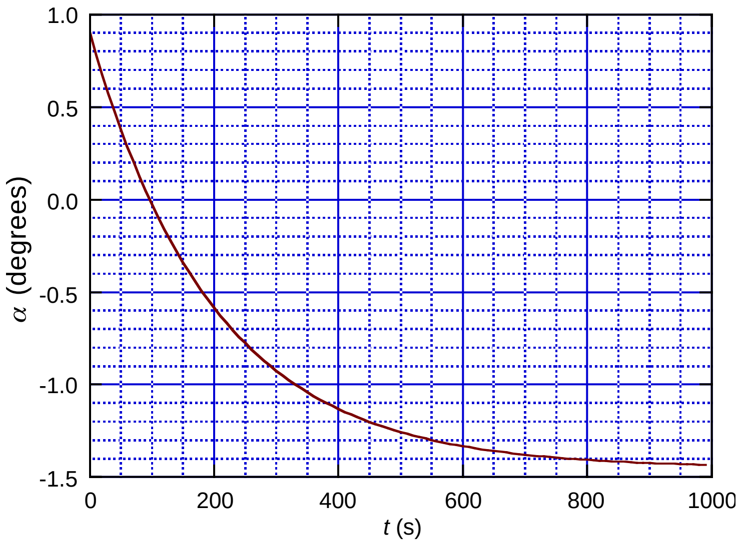


I is *T*, II is *P*.

(1) D (2) B

(3) F (4) A

B. **(5)** The figure to the right represents optical rotation data for a hypothetical sugar we shall call *picanose*. From this figure, give approximate values for the following quantities: (1) α_0, (2) α_∞, (3) the inversion time (in s), (4) the half-life of picanose, and (5) the effective rate constant k_{eff}.



(1) 0.9°

(2) –1.45 ° (1.5° O.K.)

(3) ~100 s

(4) ~140 s

(5) ~0.005 s^{-1}

C. **(4)** The resistance of a thermistor varies approximately exponentially with T^{-1}. [<u>Hint</u>: This is the same functional relationship you used to analyze vapor pressure data and estimate kinetics activation energies.] A particular thermistor shows a reistance of 11.27 kΩ at the ice point and 1.872 kΩ at 28.77°C. When immersed in a bath, its resistance is 8.93 kΩ. What is the apparent temperature of the bath?

276.56_7 K = 3.42°C

III. (8) Statistics and KaleidaGraph.

A. **(4)** You desire to fit some data to (1) a cubic polynomial in *x* with a constant term (4 adjustable parameters), and (2) a declining exponential plus a background (3 parameters). Using `a, b, c,` and `d` for the adjustable parameters, and `x` for the independent variable, write EXACTLY what you might enter in the "Define Fit" box of the **`General`** fit routine to execute these fits.

1. `a + b*x + c*x^2 + d*x^3; a = 1; b = 1; c = 1; d = 1` (etc.)
2. `a + b*exp(-c*x); a = ?; b = ?; c = ?`

B. **(4)** On fitting (unweighted) some thermistor calibration data, you obtain the results shown here.

1. If there are 22 data points, how many *degrees of freedom* are there in this fit?

   $\nu = 22 - 3 = 19$

2. If the precision for measuring *T* is limited by this calibration fit, estimate s_T.

   $s_T = (\text{Chisq}/\nu)^{1/2} = 0.005_1$ K

y = a + b*(x-25) + c*(x-25)^2		
	Value	Error
a	0.050861789	0.001247068
b	0.0036498518	0.0002037433
c	-0.00074572609	3.839555e-05
Chisq	0.00049905721	NA
R	0.96765516	NA

3. If this fit is redefined as a quadratic function of *x* instead of (*x*–25), which (if any) of the quantities shown in the results box will change and which will not?

   `c` and its error, `Chisq`, and `R` are unchanged; the others all change.