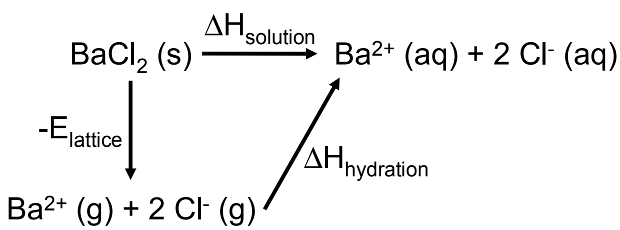
CHEM 121
Spring 2006
Quiz 9

Name: ____

1a. (8 Points) Use the following data to calculate the enthalpy of hydration ($\Delta H_{hydration}$) for calcium chloride and for calcium iodide.

	$E_{lattice}$ (kJ/mole)	$\Delta H_{solution}$ (kJ/mole)
$CaCl_2$ (s)	-2247	-46
CaI_2 (s)	-2059	-104

By Hess's Law $\Delta H_{solution}$ may be thought of as the sum of $-E_{lattice}$ and $\Delta H_{hydration}$, as shown below.



Thus,

$$\Delta H_{solution} = \Delta H_{hydration} + -E_{lattice}$$

$$\Delta H_{hydration} = \Delta H_{solution} + E_{lattice}$$

For $CaCl_2$

$$\Delta H_{hydration} = \Delta H_{solution} + E_{lattice} = -46 \text{ kJ/mole} + -2247 \text{ kJ/mole} = -2293 \text{ kJ/mole}$$

For CaI_2

$$\Delta H_{hydration} = \Delta H_{solution} + E_{lattice} = -104 \text{ kJ/mole} + -2059 \text{ kJ/mole} = -2163 \text{ kJ/mole}$$

For $CaCl_2$ $\Delta H_{hydration}$ is -2293 kJ/mole and for CaI_2 $\Delta H_{hydration}$ is -2163 kJ/mole.

b. (6 Points) Based on your answers to part a, which ion, Cl^- or I^-, is interacting more strongly with water? Explain why this should be so.

Since $\Delta H_{hydration}$ is higher for $CaCl_2$, and the Ca^{2+} ion is the same for both salts, Cl^- ion must be interacting more strongly with water (*when the ion-dipole interactions form between Cl^- ion and water they release more energy as heat than the ion-dipole interactions between I^- ion and water do***). We know that Cl^- is a smaller ion (size increases down a group in the periodic table) and the interaction between an ion and a dipole should follow Coulomb's Law (if not exactly, then approximately). Since Coulomb's Law predicts that the strength of (energy involved in) the**

interaction should be inversely proportional to distance between the ion and the dipole, we would expect the smaller Cl^- to have the stronger interaction with water.

A more formal proof of the qualitative argument made above for the differences in $\Delta H_{hydration}$.

We can write $\Delta H_{hydration}$ for each salt as follows (again by Hess's Law).

$$\Delta H_{hydration}(CaCl_2) = \Delta H_{hydration}(Ca^{2+}) + 2\ \Delta H_{hydration}(Cl^-)$$

$$\Delta H_{hydration}(CaI_2) = \Delta H_{hydration}(Ca^{2+}) + 2\ \Delta H_{hydration}(I^-)$$

We can then write

$$\Delta H_{hydration}(CaCl_2) - \Delta H_{hydration}(CaI_2) = \Delta H_{hydration}(Ca^{2+}) + 2\ \Delta H_{hydration}(Cl^-) - \Delta H_{hydration}(Ca^{2+}) - 2\ \Delta H_{hydration}(I^-)$$

$$\Delta H_{hydration}(CaCl_2) - \Delta H_{hydration}(CaI_2) = 2(\Delta H_{hydration}(Cl^-) - \Delta H_{hydration}(I^-))$$

$$(\Delta H_{hydration}(CaCl_2) - \Delta H_{hydration}(CaI_2))/2 + \Delta H_{hydration}(I^-) = \Delta H_{hydration}(Cl^-)$$

$$\Delta H_{hydration}(Cl^-) = (-2293 + 2163\ \text{kJ/mole})/2 + \Delta H_{hydration}(I^-)$$

$$\Delta H_{hydration}(Cl^-) = -65\ \text{kJ/mole} + \Delta H_{hydration}(I^-)$$

Since we know that $\Delta H_{hydration}(I^-)$ is negative (ion-dipole interactions are stabilizing interactions), we also know that $\Delta H_{hydration}(Cl^-)$ is a more negative number. This means that the ion-dipole interaction between Cl^- and water is stronger.

2. (8 Points) The freezing point of pure *t*-butanol is 25.50 °C and K_f is 9.1 °C·kg·mole^{-1}. Usually *t*-butanol absorbs water on exposure to air. If the freezing point of a 10.0-g sample of *t*-butanol is 24.59 °C, how many grams of water are present in the sample? You are given $\Delta T = K_f \cdot m_{solute}$.

Rearrange the freezing point depression formula to solve for m_{solute}.

$$m_{solute} = \frac{\Delta T}{K_f} = \frac{(25.50 - 24.59)^\circ\text{C}}{9.1\ {}^\circ\text{C}\cdot\text{kg}\cdot\text{mole}^{-1}} = \frac{0.91\,\text{mole}}{9.1\,\text{kg}} = 0.10\frac{\text{mole}}{\text{kg}}$$

Convert molality of water in t-butanol to grams of water.

$$10.0\,\text{g}\ t\text{-butanol}\left(\frac{0.10\,\text{mole H}_2\text{O}}{1.00\text{x}10^3\ \text{g}\ t\text{-butanol}}\right)\left(\frac{18.0148\,\text{g}}{1\,\text{mole H}_2\text{O}}\right) = 0.018\,\text{g}$$

The sample of *t*-butanol contains 0.018 g of water.

3. (8 Points) At a certain temperature, the vapor pressure of pure benzene (C_6H_6) is 0.930 atm. A solution was prepared by dissolving 10.0 g of a nondissociating, nonvolatile solute in 78.11 g of benzene at that temperature. The vapor pressure of the solution was found to be 0.900 atm. Assuming that the solution behaves ideally, determine the molar mass of the solute. You are given that $p_{solution} = \chi_{solvent} \cdot p^0_{solvent}$.

Rearrange the equation to solve for $\chi_{solvent}$.

$$\chi_{solvent} = \frac{p_{solution}}{p^0_{solvnet}} = \frac{0.900\,\text{atm}}{0.930\,\text{atm}} = 0.967_7$$

Let y = moles of solute present.

Calculate moles of benzene present.

$$78.11\,\text{g}\left(\frac{1\,\text{mole}}{78.113\,\text{g}}\right) = 0.9999_6\ \text{mole}$$

Use the definition of mole fraction to find moles of the solute present.

$$\chi_{solvent} = \frac{0.9999_6\ \text{mole}}{\text{y} + 0.9999_6\ \text{mole}} = 0.967_7$$

$$\text{y} = \frac{0.032_2\ \text{mole}}{0.967_7} = 0.033_3\ \text{mole}$$

The compound's molar mass is thus,

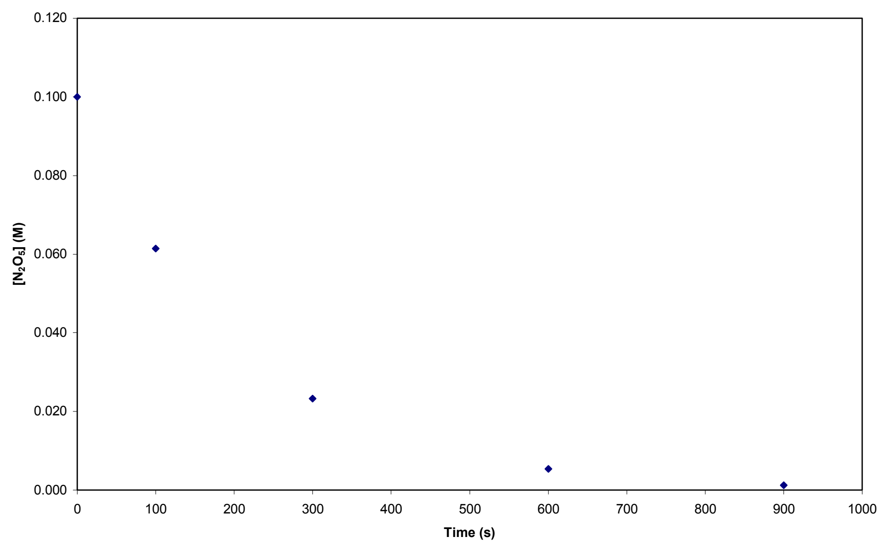
$$\frac{10.0\,\text{g}}{0.033_3\ \text{mole}} = 3.0x10^2\ \text{g}\cdot\text{mole}^{-1}$$

The compound's molar mass is 3.0x10^2 g·mole^{-1}.

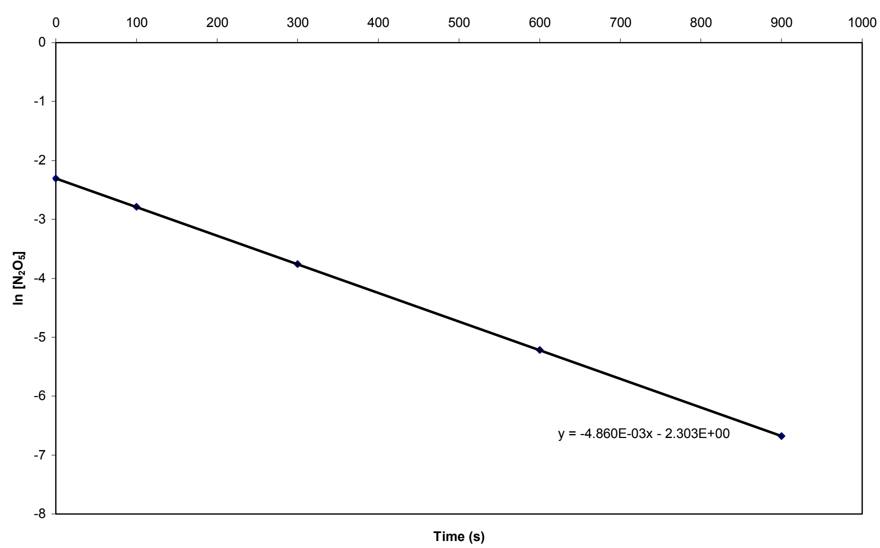
4. (10 Points) Attach problem 15-84 to this sheet.

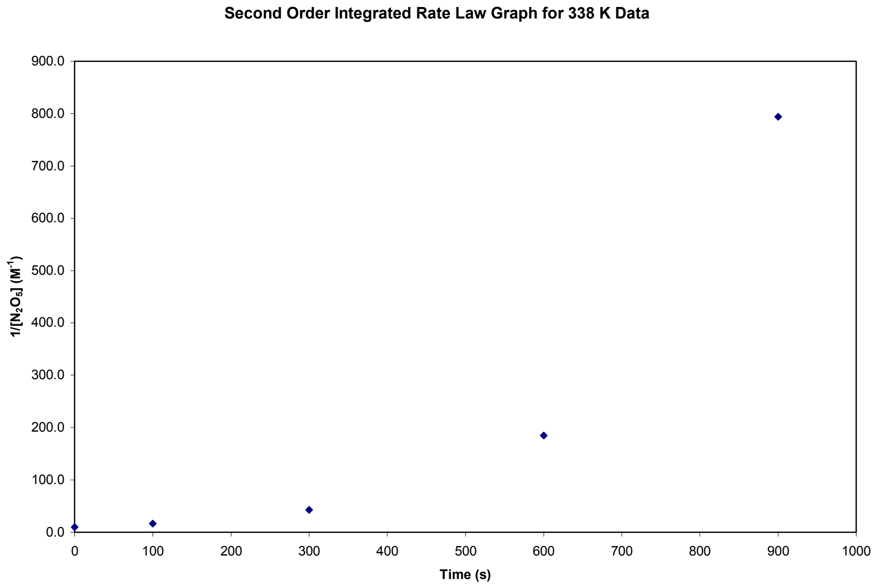
Prepare three graphs, one for each integrated rate law, for one of the temperatures.

Zeroth Order Integrated Rate Law Graph for 338 K Data

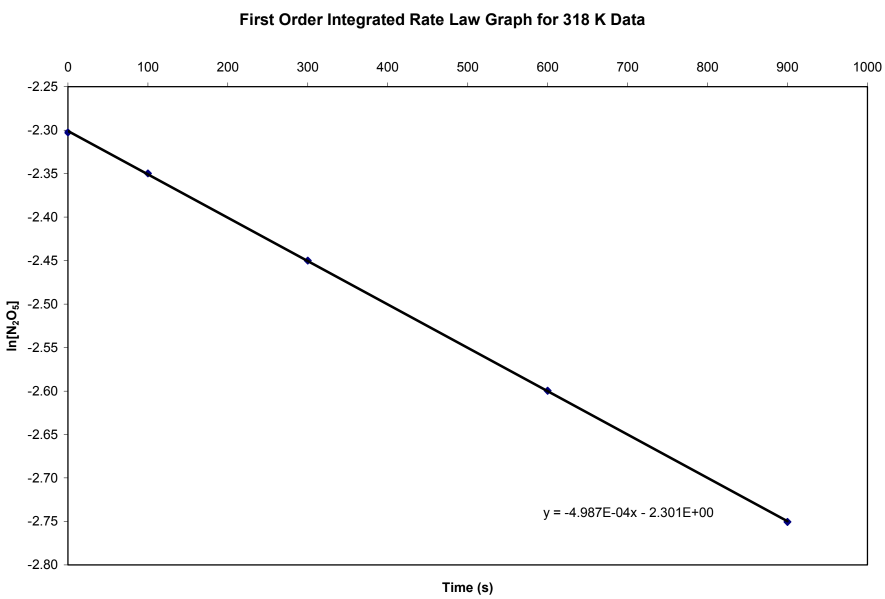


First Order Integrated Rate Law Graph for 338 K Data





The first order integrated rate law graph is clearly linear. From the slope of the best fit line on this graph, find *k* at this temperature to be 4.86×10^{-3} s^{-1}.



Prepare a first order integrated rate law graph at the second temperature (see above) to find *k* at this temperature, which is 4.99×10^{-4} s^{-1}.

The form of the Arrhenius equation given as equation 15.11 in the book can be used to calculate E_a from these two points.

$$ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

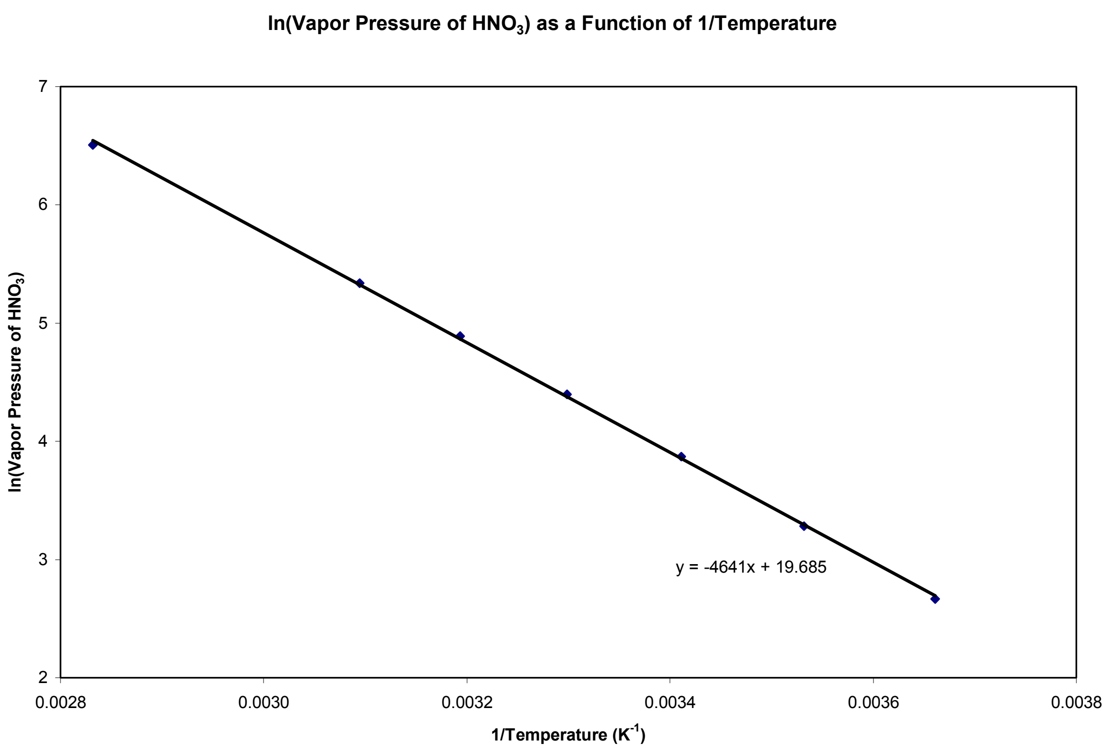
$$E_a = \frac{R \cdot ln\left(\frac{k_2}{k_1}\right)}{\left(\frac{1}{T_1} - \frac{1}{T_2}\right)} = \frac{\left(8.31451\,\mathrm{J \cdot K^{-1} \cdot mole^{-1}}\right) ln\left(\frac{4.86\mathrm{x}10^{-3}\ \mathrm{s}^{-1}}{4.99\mathrm{x}10^{-4}\ \mathrm{s}^{-1}}\right)}{\left(\frac{1}{318} - \frac{1}{338}\right)\mathrm{K}^{-1}}$$

$$E_a = \frac{\left(8.31451\,\mathrm{J \cdot mole^{-1}}\right)\left(2.276_1\right)}{\left(0.00314_4 - 0.00295_8\right)} = \frac{18.92_5\ \mathrm{J \cdot mole^{-1}}}{0.00018_6} = 1.0_2 x 10^2\ \mathrm{kJ \cdot mole^{-1}}$$

The activation energy for this reaction is 1.0x10^2 kJ/mole.

5. (10 Points) Attach problem 16-80 to this sheet.

Equation 16.4 from the book ($ln\left(p_{vap}\right) = -\frac{\Delta H_{vap}}{R}\left(\frac{1}{T}\right) + C$ **) suggests that there is a linear relationship between the vapor pressure of a liquid, p_{vap} and 1/T (in K) where the slope of the line will be –ΔH_{vap}/R. Graphing the given data in that way yields the following.**



The slope of this line is -4.64$_1$x10^3 K. Substituting this into the equation for the slope ($slope = -\frac{\Delta H_{vap}}{R}$ **) gives ΔH_{vap} = +38.6 kJ/mole.**

Boiling will occur when p_{vap} equals the ambient pressure. For the normal boiling point ambient pressure is 760.0 mmHg, by definition. Substituting p_{vap} = 760.0 mm Hg into the equation of the best fit line through the data shown above, and solving for T, gives the boiling temperature of nitric acid.

$$ln\left(p_{vap}\right) = -\left(4.64_1 x10^3 \text{ K}\right)\left(\frac{1}{T}\right) + 19.685$$

$$T = -\frac{4.64_1 x10^3 \text{ K}}{ln\left(760.0\right) + 19.685} = -\frac{4.64_1 x10^3 \text{ K}}{6.633_3 - 19.685} = \frac{4.64_1 x10^3 \text{ K}}{13.051_7} = 355._5 \text{ K}$$

$$T = 355._5 \text{ K} - 273.15 = 82.\ °\text{C}$$

The normal boiling point of liquid HNO_3 is 82. °C.