**Chemistry 134**
**Prof. Jason Kahn**
**University of Maryland, College Park**
**General Chemistry and Energetics**
**Exam I (100 points)**

**Your Name:** ______________________________

**Your SID #:** ______________________________

**Your Section # or time:** ______________________

**October 13, 2016**

You have 53 minutes for this exam.

Explanations should be concise and clear. There is extra space on the last page if you need it.

You will need a calculator for this exam. No other study aids or materials are permitted.

Generous partial credit will be given, *i.e.*, if you don't know, guess.

**Useful Equations:**

---

$K_a = [H^+][A^-]/[HA]$    $pH = -\log([H^+])$    $(V-nb)(P+an^2/V^2) = nRT$

$R = 0.08206$ L·atm/mole K    $k_B = 1.38 \times 10^{-23}$ J/K    $\ln K_{eq} = -\Delta H°/(RT) + \Delta S°/R$

$R = 8.314$ J/mole K $= 1.987$ cal/mole K $= N_A k_B$    $\ln k = (-E_a/RT) + \ln A$

$°C = °K - 273.15$    $P(v)dv = Cv^2 exp(-mv^2/2kT)$    $x = \dfrac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

Integrated rate laws for 0, 1, 2 order:

$[A] = [A]_0 - kt$    $\ln[A] = \ln[A]_0 - kt$    $1/[A] = 1/[A]_0 + kt$

$t_{1/2} = [A]_0/(2k)$    $t_{1/2} = \ln 2/k$    $t_{1/2} = 1/(k[A]_0)$

**Honor Pledge: At the end of the examination time, please write out the following sentence and sign it, or talk to me about it:**

"I pledge on my honor that I have not given or received any unauthorized assistance on this examination."

## 1. States of Matter (35 pts)

The phase diagram at the right is for elemental iodine, $I_2$. Consider starting with gaseous iodine at (P = 2 atm, T = 600 K) and cooling it down at constant pressure, as indicated by the arrow.

(a; 6 pts) In one sentence, what happens to the iodine, at what temperatures, as T decreases?

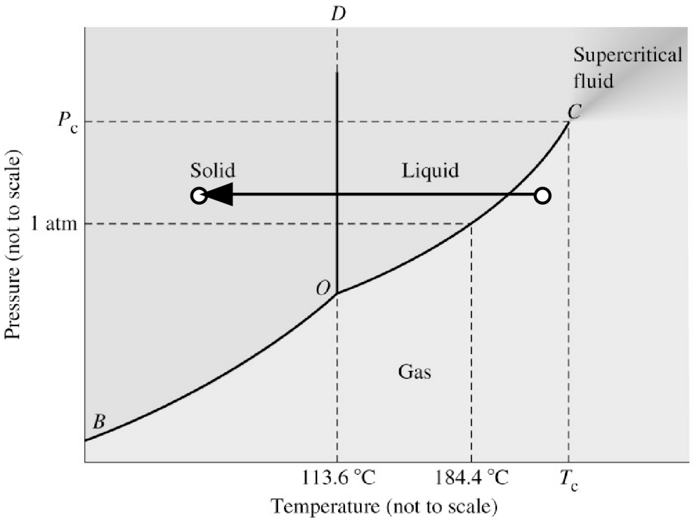


**Figure 9:** Phase diagram of iodine.

(b; 15 pts) We know that the corresponding cooling curve for $I_2$ at constant P = 2 atm goes through two intervals during which the temperature does not change as we remove heat. Physically, what is changing during each of those intervals, in terms of what the iodine is doing and the volume of the container? Indicate the points corresponding to these constant-temperature intervals on the phase diagram.

Score for the page____________

(c; 9 pts) If we heat iodine in the open air (in a hood), it will <u>sublime</u>, i.e. convert from solid directly to vapor, and will then <u>deposit</u> on a cold finger (a chilled metal tube, not a human finger). How can this work, given that the triple point is at below 1 atm – <u>why doesn't it form a liquid</u>? On the phase diagram, <u>indicate the process (as a curve in the P-T plane) of (nearly) complete deposition of a fixed total number of moles of iodine vapor</u>.

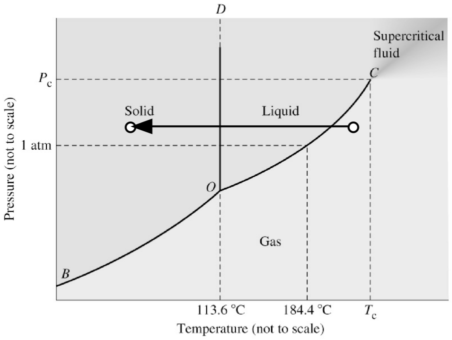


**Figure 9:** Phase diagram of iodine.

(d; 5 pts) Explain why the heat of vaporization for most substances is much larger than the heat of fusion.

## 2. Ideal and Non-ideal Gases (28 pts)

(a; 6 pts) What are the two assumptions that we make in applying the ideal gas law to real gases (what two properties of a real gas do we neglect)?

Score for the page____________

(b; 10 pts) Calculate the volume occupied by 1 mole of an ideal gas at 400 K and 1 atm pressure. If the gas were steam, what would its volume be after condensing it and cooling it to room temperature? (The density of water at 20 °C is 0.9982 g/cm$^3$ and its molecular weight is 18 g/mole.)

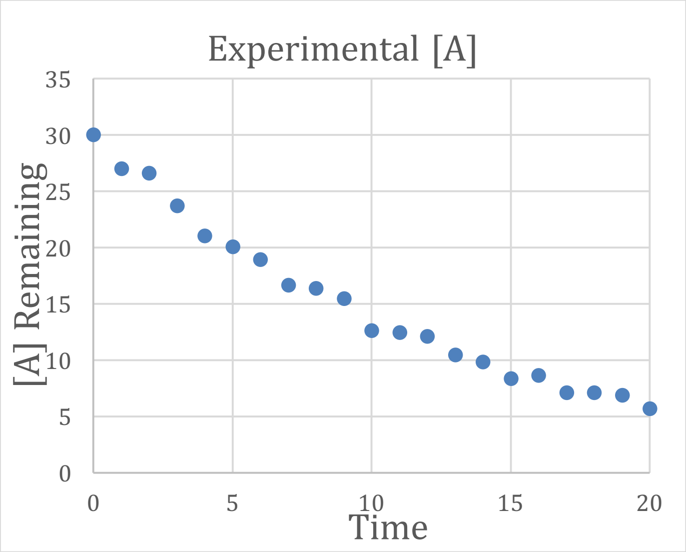
(b; 3 pts) We characterize deviations from ideal gas behavior by graphing $P_{real}V/nRT$. Show that this is the same as $P_{real}/P_{ideal}$. Not a trick question.

(c; 9 pts) Sketch a graph of ($P_{real}V/nRT$) vs. the actual pressure $P_{real}$ for (1) an ideal gas and (2) methane. Methane has significant intermolecular attractions, but we are at a temperature high enough so that it does not liquefy. Identify the features of the graph relating to violating each of the assumptions in (a).

Score for the page____________

## 4. Kinetics (25 pts)

Consider the time course at the right for [A] vs. time for the reaction A ⟶ B. It is hard to tell by eye whether it represents zero-order, first-order, or second-order kinetics, especially if we only observe the reaction at early time points. There are at least two ways to determine the rate law.



(a; 15 pts) Sketch how you would replot the data in linear forms to help decide on the reaction order: show three graphs, with labeled axes and the correct beginning, 10 min, and 20 min points. You do not have to come to a decision on the true reaction order.

Score for the page____________

(b; 10 pts) For the unrelated reaction D ⟶ C, you could use measurements of initial rates at different initial [D] to determine the reaction order with respect to D. Assuming the reaction is actually second order, sketch a graph of [D] vs. time curves for $[D]_0$ values 1, 2, and 5 M. Sketch the graph you would use to work up these data to get the rate law.

Score for the page____________

**3. Miscellaneous (12 pts)**

(a; 2 pts) What does the slope of an Arrhenius plot represent?

(b; 4 pts) If the rate constant for the elementary reaction P $\longrightarrow$ S at $[P]_0 = 1\ \mu M$ is $1.126 \times 10^{-6}\ s^{-1}$, what is the half life at $[P]_0 = 1$ nM?

(c; 6 pts) List and very briefly describe three kinds of intermolecular attractive forces.

| **Page** | **Score** |
|---|---|
| 2 | /21 |
| 3 | /20 |
| 4 | /22 |
| 5 | /15 |
| 6 | /10 |
| 7 | /12 |
| **Total** | **/100** |

Score for the page_____________