

Chemistry 134

Prof. Jason Kahn

University of Maryland, College Park

General Chemistry and Energetics

Exam I (100 points)

Your Name: Key

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:

$$K_a = [\text{H}^+][\text{A}^-]/[\text{HA}]$$

$$\text{pH} = -\log([\text{H}^+])$$

$$(V-nb)(P+an^2/V^2) = nRT$$

$$R = 0.08206 \text{ L}\cdot\text{atm}/\text{mole K}$$

$$k_B = 1.38 \times 10^{-23} \text{ J/K}$$

$$\ln K_{eq} = -\Delta H^\circ/(RT) + \Delta S^\circ/R$$

$$R = 8.314 \text{ J/mole K} = 1.987 \text{ cal/mole K} = N_A k_B$$

$$\ln k = (-E_a/RT) + \ln A$$

$$^\circ\text{C} = ^\circ\text{K} - 273.15$$

$$P(v)dv = Cv^2 \exp(-mv^2/2kT)$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Integrated rate laws for 0, 1, 2 order:

$$[\text{A}] = [\text{A}]_0 - kt$$

$$\ln[\text{A}] = \ln[\text{A}]_0 - kt$$

$$1/[\text{A}] = 1/[\text{A}]_0 + kt$$

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

$$t_{1/2} = \ln 2/k$$

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

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 ($P = 2 \text{ atm}$, $T = 600 \text{ K}$) 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?

The iodine condenses from gas to liquid at $T > 184.4^\circ\text{C}$ and then it freezes into solid at $T \approx 113.6^\circ\text{C}$.
 $+2(3.7)$
 $T = 184.4$

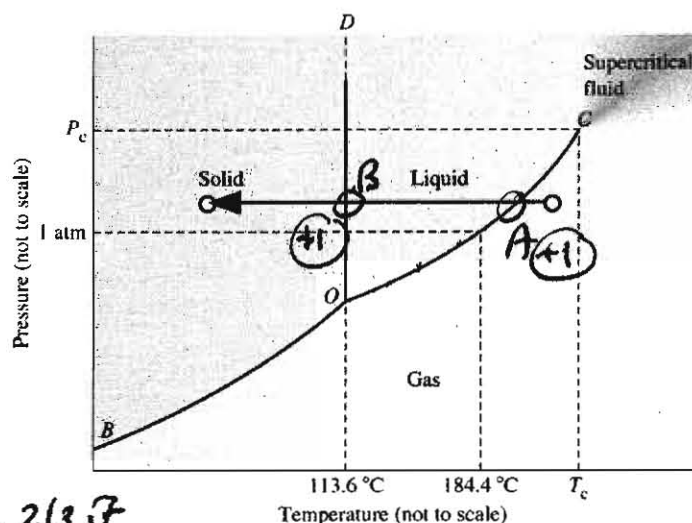


Figure 9: Phase diagram of iodine.

$+3$ each step

(b; 15 pts) We know that the corresponding cooling curve for I_2 at constant $P = 2 \text{ atm}$ 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.

$+1$ for having an answer to (a)

- At $T > 185$ when the I_2 condenses, the composition of the sample

$+3$ changes progressively from gas to liquid at constant T . At

A constant P , this is accompanied by a large decrease in

$+3$ volume. [Volume changes from $\approx \frac{nRT}{P}$ to n/ρ_{Liq} .]

- At $T \approx 113.6^\circ\text{C}$ the sample changes progressively from liquid to

$+3$ solid at constant T . The volume changes from n/ρ_{Liq} to

n/ρ_{Solid} but the fact that the liquid-gas coexistence line is nearly vertical suggests that the volume change

B is very small. (more precisely, the compressibility of solid and liquid is very similar).

$+3$

(+1 each for points on phase diagram)

(c; 9 pts) If we heat iodine in the open air (in a hood), it will sublime, i.e. convert from solid directly to vapor, and will then deposit 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 — why doesn't it form a liquid? On the phase diagram, 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.

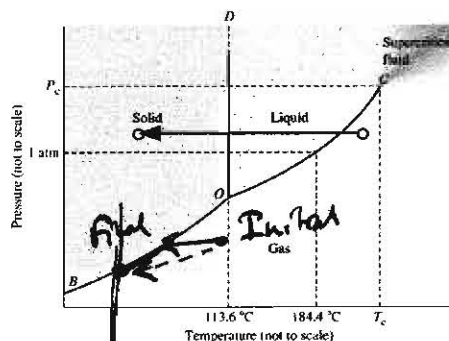


Figure 9: Phase diagram of iodine.

- The "1 atm" refers to the partial pressure of I_2 ~~gas~~ ^{plus} gas (or the pressure on pure solid or liquid I_2).

(+3) Therefore in the open air, ~~where~~ we are effectively at much lower pressure on the phase diagram, below the pressure at the triple point.

- As the I_2 ^{deposits} ~~condenses~~ on the cold finger, the P_{I_2} will drop until it reaches equilibrium at ~~constant~~ the temperature around the cold finger. (+3) for any line that crosses from (+3) for traveling down coexistence curve to 5

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

+3 for either
+5 for both

- Melting requires breaking ⁽⁺²⁾ enough of the intermolecular bonds to allow for movement of molecules and flow, whereas vaporization requires breaking all of the inter-molecular contacts. (+3)

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)?

(+3) - We ignore excluded volume - i.e. assume the gas is a point particle

(+3) - We ignore inter-molecular attractions - the net effect is that every molecule interacts independently with the wall of the container

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?

$$PV = nRT \quad V = \frac{1 \cdot 0.08206 \text{ L} \cdot \text{atm} / \text{mol} \cdot \text{K} \cdot 400 \text{ K}}{1 \text{ atm}} \quad +3$$

$\rho = 1 \text{ g/cc}$
~~0.00082~~ 1.0
MW = 18.02

$$V = 32.8 \text{ L (1 mol)} \quad +2$$

At 20°C water occupies $18 \text{ g} / (1 \text{ g/cm}^3) = 18 \text{ cm}^3$ or 0.018 L

(mole of) +2 +2

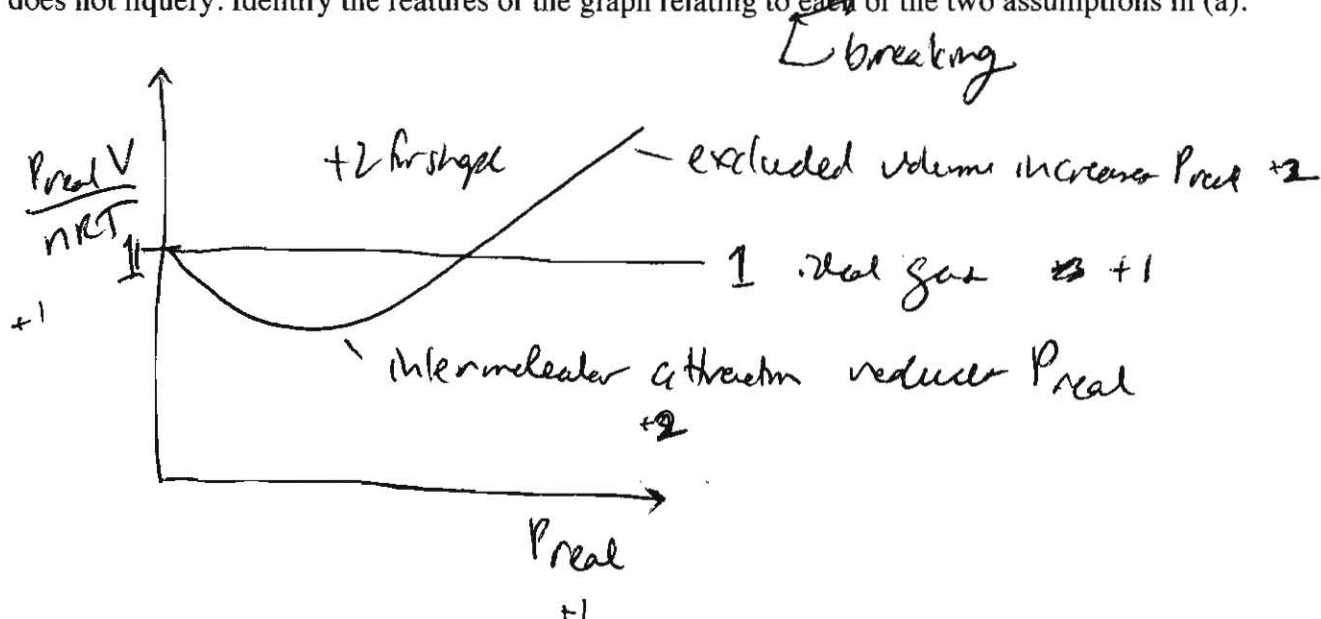
... that's why the steam engine works

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

$$P_{\text{ideal}} = \frac{nRT}{V} \quad \text{so} \quad P_{\text{real}}/P_{\text{ideal}} = \frac{P_{\text{real}}V}{nRT}$$

+1 +2

(c; 9 pts) Sketch a graph of $(P_{\text{real}}V/nRT)$ 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 each of the two assumptions in (a).

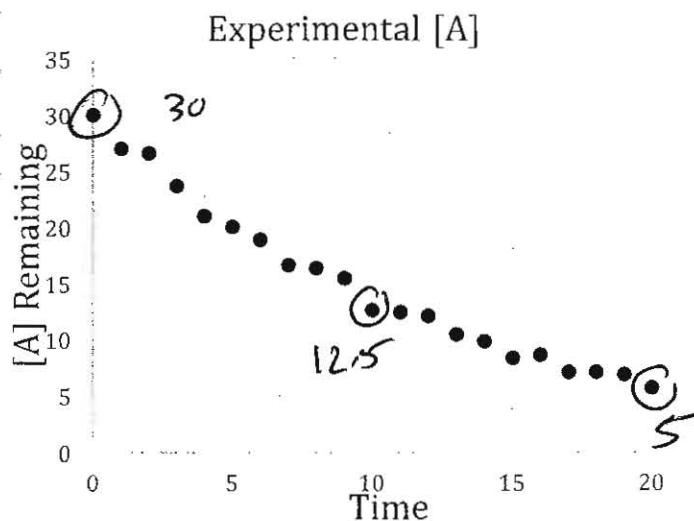


4. Kinetics (25 pts)

Consider the time course at the right for [A] vs. time for the reaction $A \rightarrow B$. 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.

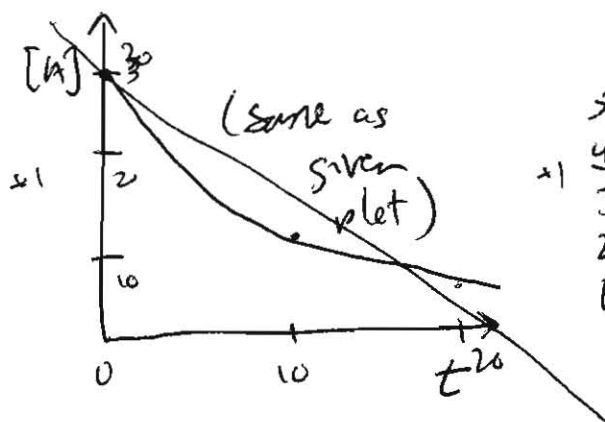
(a; 15 pts) Sketch how you would replot the data in linear forms to help decide on the reaction order. Show three sketches, with labeled axes and the correct beginning, 10 min, and end points. You do not

have to come to a decision on the true reaction order.

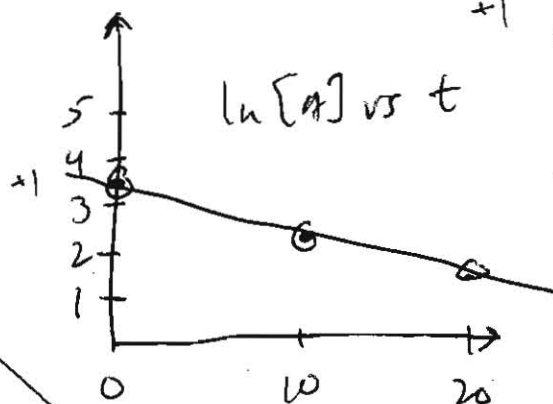


t	[A]	$\ln [A]$	$1/[A]$
0	30	3.4	0.033
10	12.5	2.5	0.08
20	5	1.6	0.200

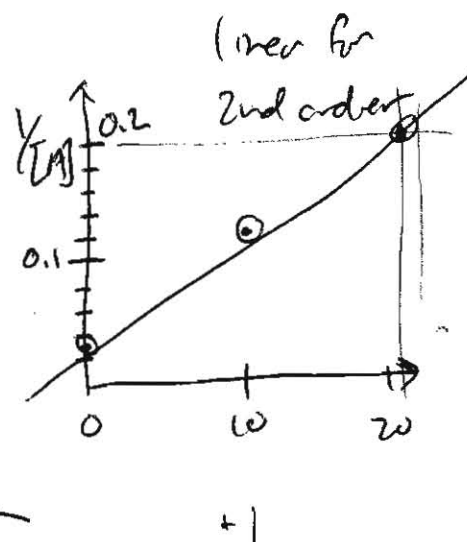
+1 each piece



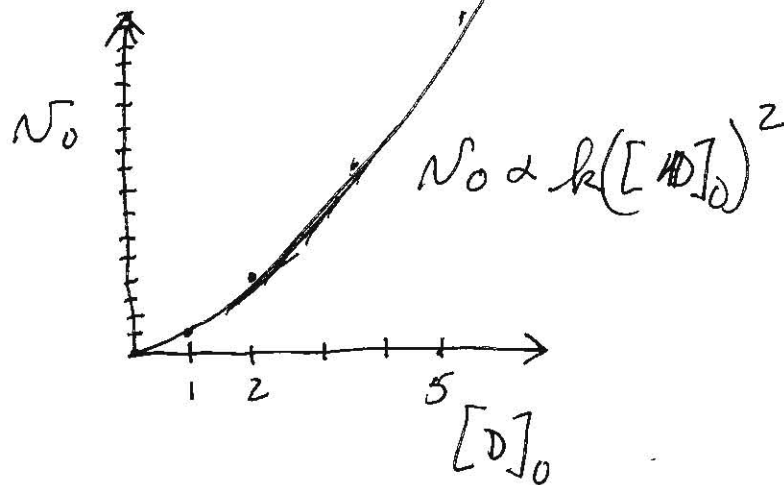
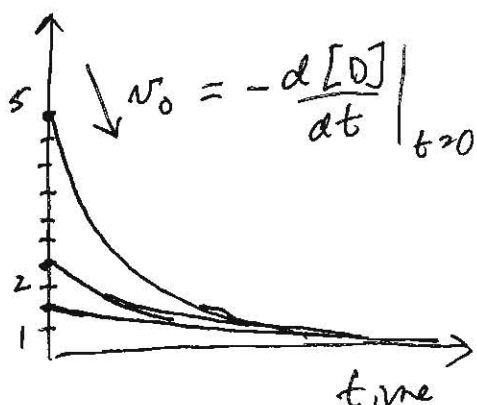
linear for
0 order
+1



linear for
1st order
+1



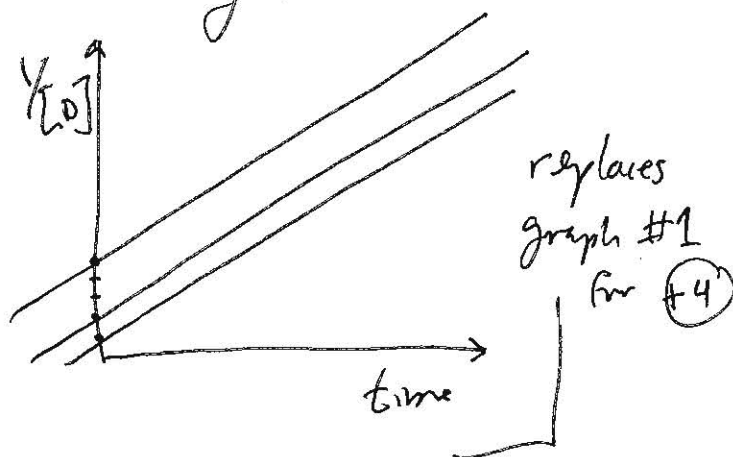
(b; 10 pts) For the unrelated reaction $D \rightarrow C$, you could use measurements of initial rates at different initial $[D]$ to determine the reaction order with respect to D . Assuming the reaction is actually second order, sketch a graph of $[D]$ vs. time curves for $[D]_0$ values 1, 2, and 5 M.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



+2 for idea of time course
 +2 for different initial slopes
 +2 for no crossing of lines
 +1

+3 for idea of v_0 vs. $[D]$
 +2 for parabola

Would actually use



3. Miscellaneous (12 pts)

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

$-E_a/R$, the activation energy

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

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.69}{1.126 \times 10^{-6}} = 6.16 \times 10^5 \text{ sec}$$

so $t_{1/2}$ @ $1 nM$ is the same ... 2 weeks

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

- Van der Waals interactions - induced-dipole induced dipole attraction between polarizable electron clouds
- dipole-dipole interactions ~~also~~ in polar liquids
- electrostatic attraction between ions
- the hydrophobic effect - ~~is~~
- hydrogen bonding

Page	Score
2	/21
3	/21
4	/22
5	/15
6	/9
7	/15
8	/12
Total	/100

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