

Chem 322: Physical Chemistry II

Spring 2025 Exam 4
Professor Yuting Chen

Name: _____

This is an open note exam. You may use your prepared eight-page cheat sheet and calculator, but no other external resources. No other electronics may be in your possession. The Hamilton College Honor Code applies to this exam.

By my signature below, I affirm on my honor the work represented in this exam is solely my own, and that I did not give or receive assistance on this exam. Violating the Honor Code will result in automatic failure of the course.

Signature: _____

Instructions

- Do not turn the page until instructed. You have 4 hours for the exam.
- Ensure you have all pages of the exam. The exam consists of one cover page and 8 pages of questions.
- Write your answers in the spaces indicated. Anything written on the backs of pages will not be graded. If you need more space, ask for scratch paper.
- Write legibly and show all of your work clearly and logically. Even if the final answer is correct, you may not receive credit if your work is incomplete, indecipherable, or unable to be followed.
- Grading is based on the consistency of your work. If you make an error in one step, you may still receive credit for later steps if your other steps are consistent, so it is in your best interest to attempt all parts of a problem.
- Include units for all of your answers. Report answers with a reasonable number of significant figures unless otherwise specified.

1. **Exam 1: Statistical Mechanics**

(a) (5 points) **Equipartition**

Use the equipartition theorem to determine the constant volume molar heat capacity of the following molecules *at the high temperature limit*: O_3 , CS_2 , C_3H_6

(b) (2 points) **Partition Function**

A system consists of N non-interacting, distinguishable particles. Each particle can occupy one of two energy levels: $\varepsilon_0 = 0$ with degeneracy 1 or $\varepsilon_1 = E$ with degeneracy 2.

Write an expression for the single-particle partition function q .

(c) (5 points) Derive an expression for the average internal energy of the whole system.

(d) (8 points) Derive an expression for the heat capacity of the whole system.

(e) (5 points) Suppose the system is instead made of indistinguishable particles. How would your approach change for evaluating q , Q , U , and C_V ? Do not evaluate anything, but you should explain what quantities remain the same, what quantities would be different.

2. Exam 2: Thermodynamics

PV Diagram

A monoatomic ideal gas initially has a pressure P_1 of 1 atm, a volume V_1 of 1 liter, and a temperature T_1 of 298 K. The gas undergoes the following reversible processes in sequence:

- Isothermal expansion from $V_1 = 1$ L to $V_2 = 2$ L
- Isobaric cooling from V_2 to an unknown volume V_3
- Adiabatic compression, back to the initial state ($P = 1$ atm, $V = 1$ liter, $T = 298$ K)

(a) (3 points) Find the temperature T_3 after the isobaric cooling in terms of V_3 .

(b) (6 points) Determine the unknown volume V_3 .

(c) (8 points) **Thermodynamics**

A closed, rigid 2.5 L flask contains a mixture of Ne(g) and F₂(g) with a total pressure of 3.32 atm at 0 °C. The system is heated to 15 °C. The change in entropy for this process is 0.345 $\frac{\text{J}}{\text{K}}$. How many mols of Ne are in the flask?

(d) (4 points) **Real Gases**

Electronegativities: C - 2.5, O - 3.5, F - 4.0, S - 2.5

Considering real gases, rank the van der Waals constant b for the following gases: CH₃F, CH₃OH, CH₃SH. Briefly justify your answer.

(e) (4 points) Considering real gases, rank the following gases in order of increasing volume at a pressure of 3 atm: CH₃F, CH₃OH, CH₃SH. Briefly justify your answer.

3. Exam 3: Equilibrium

(a) (8 points) Starting from:

$$C_V = T \left(\frac{\partial S}{\partial T} \right)_V$$

show that:

$$\left(\frac{\partial C_V}{\partial V} \right)_T = T \left(\frac{\partial^2 P}{\partial T^2} \right)_V$$

Consider the following equilibrium stored in a constant–pressure vessel:



At $T = 3,000 \text{ K}$, the system has total pressure 1.0 bar, volume 0.50 L, and equilibrium partial pressures $P_{\text{S}_2} = 0.281 \text{ bar}$, $P_{\text{CS}_2} = 0.719 \text{ bar}$

(b) (2 points) What is the value of the equilibrium constant K at 3000 K?

Temperature decreases to 500 K. Circle the correct response:

(c) (2 points) Immediately Q :

increases decreases stays the same

(d) (2 points) Immediately ΔG_{toeq} is:

positive equal to zero negative

(e) (2 points) Immediately ΔG_T becomes:

more positive equal to zero more negative

(f) (4 points) What is K at 500 K?

(g) (8 points) What are the equilibrium pressures of $\text{S}_2(\text{g})$ and $\text{CS}_2(\text{g})$ at 500 K.

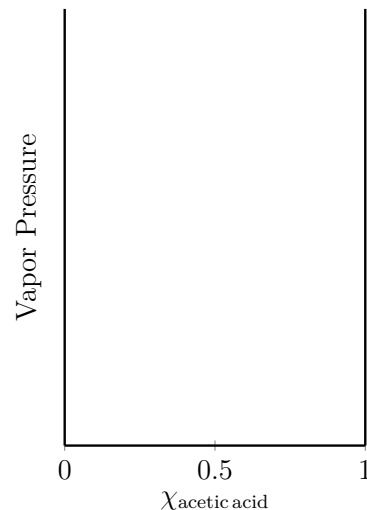
4. Exam 4: Kinetics

(a) (5 points) Colligative Properties

Acetic acid (bp = 118 °C) behaves ideally when mixed with water, but with *n*-octane (bp = 109 °C) it behaves as a real mixture. A 50% by mass mixture of acetic acid and *n*-octane has a boiling point of 105 °C, but no azeotropes are formed.

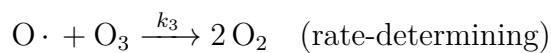
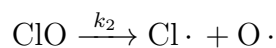
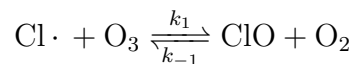
Qualitatively sketch and label the following two lines:

- one for the acetic acid/water solution
- one for the acetic acid/*n*-octane solution



(b) (10 points) Mechanisms

Consider the following mechanism for the decomposition of ozone.



Use the steady state approximation to determine the rate law of this reaction.

(c) (6 points) **Maxwell-Boltzmann**

One of the results we showed in Lecture 31 was:

$$\langle u^2 \rangle = \frac{3k_B T}{m} \implies \langle \epsilon \rangle = \frac{1}{2} m \langle u^2 \rangle = \frac{3}{2} k_B T$$

In this problem, we will re-derive this result using the velocity distribution instead of the speed distribution.

$$f(u_x) = \left(\frac{m}{2\pi k_B T} \right)^{1/2} e^{-mu_x^2/2k_B T}$$

First compute the average value $\langle u_x^2 \rangle$. Here are some potentially useful integrals:

$$\int_0^\infty e^{-ax^2} dx = \frac{1}{2} \sqrt{\frac{\pi}{a}}, \quad \int_0^\infty x^2 e^{-ax^2} dx = \frac{1}{2} \cdot \frac{\sqrt{\pi}}{2a^{3/2}}, \quad \int_{-\infty}^\infty e^{-ax^2} dx = \sqrt{\frac{\pi}{a}}, \quad \int_{-\infty}^\infty x^2 e^{-ax^2} dx = \frac{\sqrt{\pi}}{2a^{3/2}}$$

- (d) (4 points) Generalize your result to 3 dimensions to show that $\langle u^2 \rangle = \frac{3k_B T}{m}$, and show that $\langle \epsilon \rangle = \frac{3}{2} k_B T$.