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

   $O_3 : \overline{C}_V = \left(\frac{3}{2} + \frac{3}{2} + 3(3) - 6\right) R = 6R$
   $CS_2 : \overline{C}_V = \left(\frac{3}{2} + 1 + 3(3) - 5\right) R = 6.5R$
   $C_3H_6 : \overline{C}_V = \left(\frac{3}{2} + \frac{3}{2} + 3(9) - 6\right) R = 24R$

   (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.

$$q = \sum_i g_i e^{-\beta\varepsilon_i} = 1 \cdot e^0 + 2 \cdot e^{-\beta E} = 1 + 2e^{-\beta E}$$

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

   Write the total partition function:

$$Q = q^N = \left(1 + 2e^{-\beta E}\right)^N$$

   Take the natural log:

$$\ln Q = N \ln\left(1 + 2e^{-\beta E}\right)$$

   Use the definition of average energy:

$$\langle U \rangle = -\frac{\partial \ln Q}{\partial \beta} = -\frac{\partial}{\partial \beta}\left[N \ln\left(1 + 2e^{-\beta E}\right)\right]$$

   Apply chain rule and simplify:

$$\langle U \rangle = -N \cdot \frac{1}{1 + 2e^{-\beta E}} \cdot \left(-2Ee^{-\beta E}\right)$$
$$\langle U \rangle = N \cdot \frac{2Ee^{-\beta E}}{1 + 2e^{-\beta E}}$$

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

Use the chain rule with β:

$$C_V = \frac{d\langle U\rangle}{dT} = \frac{d\langle U\rangle}{d\beta} \cdot \frac{d\beta}{dT}$$

$$\beta = \frac{1}{k_BT} \quad \Longrightarrow \quad \frac{d\beta}{dT} = -\frac{1}{k_BT^2}$$

Differentiate $\langle U\rangle$:

$$\frac{d\langle U\rangle}{d\beta} = N \cdot \frac{(1+2e^{-\beta E})(-2E^2e^{-\beta E}) - (2Ee^{-\beta E})(-2Ee^{-\beta E})}{(1+2e^{-\beta E})^2}$$

Simplify the numerator:

$$= -2E^2e^{-\beta E} - 4E^2e^{-2\beta E} + 4E^2e^{-2\beta E}$$

$$= -2E^2e^{-\beta E}$$

$$\frac{d\langle U\rangle}{d\beta} = -N \cdot \frac{2E^2e^{-\beta E}}{(1+2e^{-\beta E})^2}$$

Plug back in:

$$C_V = \left(-N \cdot \frac{2E^2e^{-\beta E}}{(1+2e^{-\beta E})^2}\right)\left(-\frac{1}{k_BT^2}\right)$$

$$\boxed{C_V = \frac{NE^2}{k_BT^2} \cdot \frac{2e^{-\beta E}}{(1+2e^{-\beta E})^2}}$$

$$\boxed{C_V = Nk_B\beta^2E^2 \cdot \frac{2e^{-\beta E}}{(1+2e^{-\beta E})^2}}$$

(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.

The single particle partition function remains the same. The partition function for the whole system would change as we have to correct for overcounting with $Q = \frac{q^N}{N!}$. The expressions for internal energy and heat capacity are the same since $\ln Q = \ln(q^N/N!) = N\ln q - \ln N!$, and when we take partial wrt beta the $\ln N!$ term disappears.

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.

Step 1 is isothermal:

$$P_1V_1 = P_2V_2 \implies P_2 = \frac{P_1V_1}{V_2} = \frac{1\,\text{atm} \cdot 1\,\text{L}}{2\,\text{L}} = 0.5\,\text{atm}$$

Step 2 is isobaric:

$$\frac{T_3}{T_2} = \frac{V_3}{V_2} \implies T_3 = T_2 \cdot \frac{V_3}{V_2} = 298\,\text{K} \cdot \frac{V_3}{2\,\text{L}}$$

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

Using the adiabatic relationship we derived:

$$\frac{T_1}{T_3} = \left(\frac{V_3}{V_1}\right)^{\frac{R}{\overline{C}_V}}$$

For a monoatomic ideal gas, $\overline{C}_V = \frac{3}{2}R$ so $\frac{R}{\overline{C}_V} = \frac{2}{3}$. Now we plug in:

$$\frac{298}{298 \cdot \frac{V_3}{2}} = V_3^{\frac{2}{3}} \qquad \implies \qquad \frac{2}{V_3} = V_3^{\frac{2}{3}}$$

Simplifying:

$$2 = V_3^{1+\frac{2}{3}} = V_3^{\frac{5}{3}} \implies V_3 = 2^{\frac{3}{5}}\text{L}$$

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

A closed, rigid 2.5 L flask contains a mixture of Ne(g) and F_2(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 $\frac{\mathrm{J}}{\mathrm{K}}$. How many mols of Ne are in the flask?

$$\begin{aligned}
n &= \frac{PV}{RT} = \frac{3.22\,\mathrm{atm} \times 2.5\,\mathrm{L}}{0.0821\,\frac{\mathrm{L \cdot atm}}{\mathrm{mol \cdot K}} \times 273\,\mathrm{K}} = 0.3705\,\mathrm{mol} \\
\Delta S &= \Delta S_{\mathrm{Ne}} + \Delta S_{\mathrm{F_2}} = 0.345\,\tfrac{\mathrm{J}}{\mathrm{K}} \\
&= n\overline{C_V}\ln\frac{T_2}{T_1} + n\overline{C_V}\ln\frac{T_2}{T_1} \quad (\text{for Ne and } \mathrm{F_2}) \\
&= x\frac{3}{2}R\ln\frac{288\,\mathrm{K}}{273\,\mathrm{K}} + (0.3705\,\mathrm{mol} - x)\frac{7}{2}R\ln\frac{288\,\mathrm{K}}{273\,\mathrm{K}} = 0.345\,\tfrac{\mathrm{J}}{\mathrm{K}} \\
0.345\tfrac{\mathrm{J}}{\mathrm{K}} &= 0.445\,\tfrac{\mathrm{J}}{\mathrm{K \cdot mol}} \cdot \left[\frac{3}{2}x + \frac{7}{2}(0.371\,\mathrm{mol}) - \frac{7}{2}x\right] \\
&= 0.445\,\tfrac{\mathrm{J}}{\mathrm{K \cdot mol}} \cdot [1.297\,\mathrm{mol} - 2x] \\
x &= \boxed{0.261\,\mathrm{mol\ Ne}}
\end{aligned}$$

(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: CH_3F, CH_3OH, CH_3SH. Briefly justify your answer.

$CH_3F < CH_3OH < CH_3SH$
Periodic trend for size: increases left and down the periodic table.

(e) (4 points) Considering real gases, rank the following gases in order of increasing volume at a pressure of 3 atm: CH_3F, CH_3OH, CH_3SH. Briefly justify your answer.

$CH_3OH < CH_3F < CH_3SH$.
Stronger IMFs lead to smaller volume. CH_3OH has hydrogen bonding, so strongest
CH_3F has larger dipole due to larger electronegativity difference

3. **Exam 3: Equilibrium**

(a) (8 points) Starting from:

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

show that:

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

Divide through by dV and use Clairaut's Theorem:

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

Apply the Maxwell relation $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$:

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

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

$$\mathrm{C(s, graphite)} + \mathrm{S_2(g)} \rightleftharpoons \mathrm{CS_2(g)} \qquad \Delta H^\circ = -13.3\,\frac{\mathrm{kJ}}{\mathrm{mol}}, \quad \Delta S^\circ = 3.93\,\frac{\mathrm{J}}{\mathrm{mol\cdot K}}$$

At $T = 3{,}000\,\mathrm{K}$, the system has total pressure 1.0 bar, volume 0.50 L, and equilibrium partial pressures $P_{\mathrm{S_2}} = 0.281\,\mathrm{bar}$, $P_{\mathrm{CS_2}} = 0.719\,\mathrm{bar}$

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

$$K = \frac{P_{\mathrm{CS_2}}}{P_{\mathrm{S_2}}} = \frac{0.719\,\mathrm{bar}}{0.281\,\mathrm{bar}} = \boxed{2.56}$$

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?

$$\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$K_2 = K_1 \exp\left[-\frac{\Delta H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right]$$

$$K_{500} = 2.56 \exp\left[-\frac{-13{,}300\,\frac{\mathrm{J}}{\mathrm{mol}}}{8.314\,\frac{\mathrm{J}}{\mathrm{mol\cdot K}}}\left(\frac{1}{500\,\mathrm{K}} - \frac{1}{3{,}000\,\mathrm{K}}\right)\right]$$

$$\boxed{K_{500} = 36.84}$$

(g) (8 points) What are the equilibrium pressures of $\mathrm{S_2(g)}$ and $\mathrm{CS_2(g)}$ at 500 K.

	$\mathrm{S_2}$	$\mathrm{CS_2}$
I	0.281	0.719
C	-x	+x
E	0.281 - x	0.719 + x

$$K = \frac{P_{\mathrm{CS_2}}}{P_{\mathrm{S_2}}} = \frac{0.719 + x}{0.281 - x} = 36.84$$

$$0.719 + x = 36.84(0.281 - x)$$

$$37.84x = 9.636$$

$$x = \frac{9.636}{37.84} = 0.255$$

$$P_{\mathrm{CS_2}} = 0.719 + 0.255 = \boxed{0.974\,\mathrm{bar}}$$

$$P_{\mathrm{S_2}} = 0.281 - 0.255 = \boxed{0.026\,\mathrm{bar}}$$

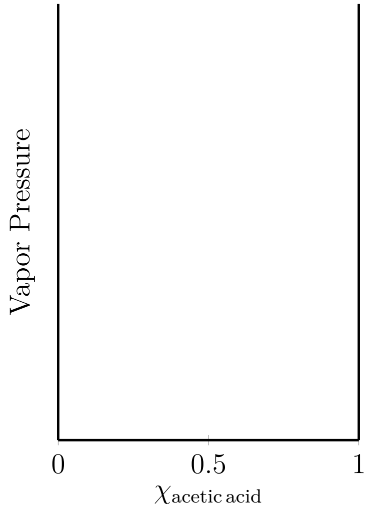
4. Exam 4: Kinetics

(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.

$$\begin{aligned} \mathrm{Cl}\cdot + \mathrm{O_3} &\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{ClO} + \mathrm{O_2} \\ \mathrm{ClO} &\xrightarrow{k_2} \mathrm{Cl}\cdot + \mathrm{O}\cdot \\ \mathrm{O}\cdot + \mathrm{O_3} &\xrightarrow{k_3} 2\,\mathrm{O_2} \quad \text{(rate-determining)} \end{aligned}$$

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

Since step 3 is rate determining, we have a rate law Rate $= k_3[\mathrm{O}\cdot][\mathrm{O_3}]$ From steady state:

$$k_2[\mathrm{ClO}] - k_3[\mathrm{O}\cdot][\mathrm{O_3}] = 0$$

Solving for $[\mathrm{O}\cdot]$

$$k_2[\mathrm{ClO}] = k_3[\mathrm{O}\cdot][\mathrm{O_3}] \rightarrow [\mathrm{O}\cdot] = \frac{k_2[\mathrm{ClO}]}{k_3[\mathrm{O_3}]}$$

Substitute into rate law:

$$\text{Rate} = k_3\left(\frac{k_2[\mathrm{ClO}]}{k_3[\mathrm{O_3}]}\right)[\mathrm{O_3}] = k_2[\mathrm{ClO}]$$

Steady state for second intermediate [ClO]:

$$k_1[\mathrm{Cl}\cdot][\mathrm{O_3}] - \left(k_{-1}[\mathrm{O_2}] + k_2\right)[\mathrm{ClO}] = 0 \rightarrow [\mathrm{ClO}] = \frac{k_1[\mathrm{Cl}\cdot][\mathrm{O_3}]}{k_{-1}[\mathrm{O_2}] + k_2}$$

Plugging into rate law:

$$\text{Rate} = k_2 \cdot \frac{k_1[\mathrm{Cl}\cdot][\mathrm{O_3}]}{k_{-1}[\mathrm{O_2}] + k_2}$$

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

One of the results we showed in Lecture 31 was:

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

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

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

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

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

Using the definition of the average value:

$$\begin{aligned}\langle u_x^2 \rangle &= \int_{-\infty}^\infty u_x^2 f(u_x)\,du_x \\ &= \left(\frac{m}{2\pi k_BT}\right)^{1/2} \int_{-\infty}^\infty u_x^2 e^{-\frac{mu_x^2}{2k_BT}}\,du_x\end{aligned}$$

Let $a = \frac{m}{2k_BT}$ in the Gaussian integral:

$$\begin{aligned}\langle u_x^2 \rangle &= \left(\frac{m}{2\pi k_BT}\right)^{1/2} \cdot \frac{\sqrt{\pi}}{2a^{3/2}} \\ &= \frac{1}{\sqrt{\pi}}a^{1/2} \cdot \frac{\sqrt{\pi}}{2a^{3/2}} = \frac{1}{2a} \\ &= \frac{1}{2}\cdot\frac{2k_BT}{m} = \boxed{\frac{k_BT}{m}}\end{aligned}$$

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

Each direction is independent and equivalent:

$$\begin{aligned}\langle u^2 \rangle &= \langle u_x^2 \rangle + \langle u_y^2 \rangle + \langle u_z^2 \rangle \\ &= 3\frac{k_BT}{m}\end{aligned}$$

Substitute into the kinetic energy expression:

$$\begin{aligned}\langle \epsilon \rangle &= \frac{1}{2}m\langle u^2 \rangle \\ &= \frac{1}{2}m\cdot\frac{3k_BT}{m} = \boxed{\frac{3}{2}k_BT}\end{aligned}$$

End of exam.