Chem 322: Physical Chemistry II

Spring 2026 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.

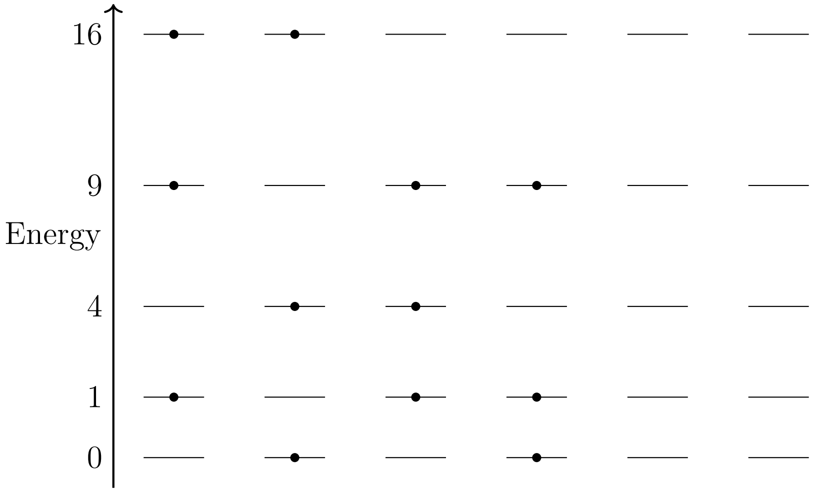
Signature: ____________________

Instructions

- Do not turn the page until instructed. You have 3 hours for the exam.
- Ensure you have all pages of the exam. The exam consists of one cover page and 4 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. **Statistical Mechanics**

   (a) (8 points) Consider a system of 3 distinguishable electrons that obey the Pauli Exclusion Principle, subject to a constraint that the total energy must be even. Draw all available macrostates, and write the partition function Q for the system.



$$\begin{aligned} Q &= \sum g e^{-\beta E_i} \\ &= \boxed{6\left(e^{-26\beta} + e^{-20\beta} + e^{-14\beta} + e^{-10\beta}\right)} \end{aligned}$$

Consider a different system with this partition function:

$$Q = \frac{1}{N!}\left(2 + e^{-2\beta\epsilon}\right)^N$$

   (b) (4 points) Describe the system modeled, including the allowed energy levels, types/numbers of particles, degeneracy etc.

   N indistinguishable partciles, 2 energy levels, 0 with degeneracy 2 and 2ϵ with degeneracy 1.

   (c) (10 points) Derive an expression for U for the provided Q.

$$\begin{aligned} \ln Q &= \ln\left[\frac{1}{N!}\left(2 + e^{-2\beta\varepsilon}\right)^N\right] \\ &= -\ln N! + N\ln\left(2 + e^{-2\beta\varepsilon}\right) \\ U &= -\frac{\partial \ln Q}{\partial \beta} \\ &= -N\frac{\partial}{\partial\beta}\ln\left(2 + e^{-2\beta\varepsilon}\right) \\ &= -N\left(\frac{-2\varepsilon e^{-2\beta\varepsilon}}{2 + e^{-2\beta\varepsilon}}\right) \\ &= \boxed{\frac{2N\varepsilon e^{-2\beta\varepsilon}}{2 + e^{-2\beta\varepsilon}}} \end{aligned}$$

2. **Thermodynamics**

   (a) (16 points) How many moles of air at 400 K must be added to a constant volume container containing 10 g of CCl_4($M = 153.82\,\frac{\text{g}}{\text{mol}}$) at 340 K to reach a final temperature of 360 K? Treat air as a mixture of diatomic linear molecules. Data for CCl_4:

$$T_m = 250\,\text{K} \qquad T_b = 350\,\text{K} \qquad \overline{C}_{V,\ell} = 130\,\tfrac{\text{J}}{\text{mol}\cdot\text{K}} \qquad \Delta S_{\text{vap}} = 85.8\,\tfrac{\text{J}}{\text{mol}\cdot\text{K}}$$

$$\begin{aligned}
n_{\text{CCl}_4} &= \frac{10\,\text{g}}{153.82\,\frac{\text{g}}{\text{mol}}} = 0.065\,\text{mol} \\
\overline{C}_V &= 12\,(8.314\,\tfrac{\text{J}}{\text{mol}\cdot\text{K}}) = 99.8\,\tfrac{\text{J}}{\text{mol}\cdot\text{K}} \\
\Delta H_{\text{vap}} &= T_b\,\Delta S_{\text{vap}} = (350\,\text{K})(85.8\,\tfrac{\text{J}}{\text{mol}\cdot\text{K}}) = 30{,}030\,\tfrac{\text{J}}{\text{mol}} \\
q_{\text{air}} &= -q_{\text{CCl}_4} \\
-n\left(\frac{7}{2}R\right)(T_f - T_i) &= n\,C_{V,\ell}\,\Delta T_{340\to350} + n\,\Delta H_{\text{vap}} + n\,C_{V,g}\,\Delta T_{350\to360} \\
-n\left(\frac{7}{2}\cdot 8.314\,\tfrac{\text{J}}{\text{mol}\cdot\text{K}}\right)(360\,\text{K} - 400\,\text{K}) &= (0.065\,\text{mol})(130\,\tfrac{\text{J}}{\text{mol}\cdot\text{K}})(10\,\text{K}) \\
&\quad + (0.065\,\text{mol})(30{,}030\,\tfrac{\text{J}}{\text{mol}}) \\
&\quad + (0.065\,\text{mol})(99.8\,\tfrac{\text{J}}{\text{mol}\cdot\text{K}})(10\,\text{K}) \\
n\,(1{,}163.96\,\tfrac{\text{J}}{\text{mol}}) &= 2{,}101\,\text{J} \\
n_{\text{air}} &= \boxed{1.81\,\text{mol}}
\end{aligned}$$

3. **Equilibrium**

   Consider the following equilibrium:

$$H_2S\,(g) \longleftrightarrow 2\,H\,(g) + S\,(g) \qquad K = 0.420$$

   (a) (4 points) Circle all stressors that would cause the equilibrium to shift right.

   ■ **Increase volume** ☐ Add S(g) ■ **Add Ne, constant pressure** ☐ Add catalyst

   The system is at equilibrium (EQ1), and the temperature is increased at constant volume. Immediately afterwards, but before equilibrium is reestablished:

   (b) (2 points) What happens to Q?

   ☐ Q increases ■ **Q stays the same** ☐ Q decreases ☐ Cannot be determined

   (c) (2 points) How does Q compare to K?

   ☐ $Q > K$ ☐ $Q = K$ ■ $Q < K$ ☐ Cannot be determined

   The system reestablishes equilibrium (EQ2). Fill in the blanks with $>, <, =, X$.

   (d) (2 points) mol H(g) at EQ1 ___$<$___ mol H(g) at EQ2

   (e) (2 points) Total pressure at EQ1 ___$<$___ Total pressure at EQ2

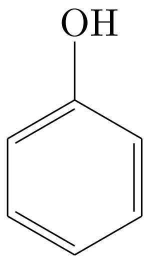
4. **Colligative Properecties and Maxwell–Boltzmann**

(a) (8 points) Find the most probable energy E_{mp} for a system has an energy distribution:

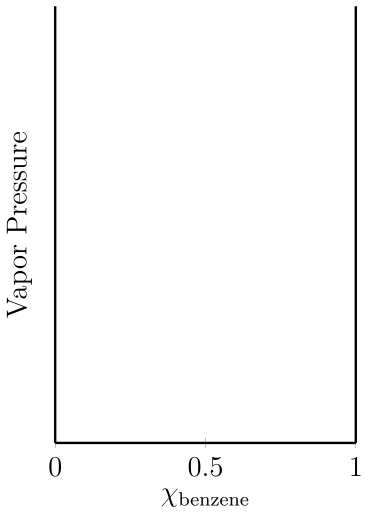
$$f(E) \propto E^2 e^{-E/kT}$$

$$\begin{aligned}
\frac{df}{dE} &= 2Ee^{-E/k_BT} + E^2 e^{-E/k_BT}\left(-\frac{1}{k_BT}\right) \\
0 &= e^{-E/k_BT}\left(2E - \frac{E^2}{kT}\right) \\
0 &= 2E - \frac{E^2}{k_BT} \\
0 &= E\left(2 - \frac{E}{k_BT}\right) \\
&\boxed{E_{\text{mp}} = 0, 2k_BT}
\end{aligned}$$

(b) (8 points) Benzene and phenol are mixed together. When mixed together, the temperature of the solution decreases. It forms an azeotrope when the mol fraction of benzene is 0.25. Draw and label the ideal and real vapor pressure curves, as well as and the azeotropic point.



Phenol



(c) (8 points) A solution is prepared by dissolving 25 g of $CaCl_2$($M = 110.98\,\frac{\text{g}}{\text{mol}}$) in 50 g of water($M = 18.02\,\frac{\text{g}}{\text{mol}}$). Given $K_b = 0.512\,\frac{\text{K·kg}}{\text{mol}}$, calculate the boiling point of the solution.

$$\begin{aligned}
n(\text{CaCl}_2) &= \frac{25\,\text{g}}{110.98\,\frac{\text{g}}{\text{mol}}} = 0.225\,\text{mol} \\
m_{\text{solvent}} &= 50\,\text{g} = 0.050\,\text{kg} \\
m &= \frac{0.225\,\text{mol}}{0.050\,\text{kg}} = 4.51\,\frac{\text{mol}}{\text{kg}} \\
\Delta T_b &= iK_bm \\
&= 3 \times 0.512\,\frac{\text{K·kg}}{\text{mol}} \times 4.51\,\frac{\text{mol}}{\text{kg}} = 6.92\,\text{K} \\
T_b &= 100\,^\circ\text{C} + 6.92\,^\circ\text{C} \\
&= \boxed{106.9\,^\circ\text{C}}
\end{aligned}$$

5. Kinetics and Mechanisms

Consider the following mechanism for the formation of sulfur trioxide from sulfur dioxide.

(Overall) $$2\,SO_2(g) + O_2(g) \longrightarrow 2\,SO_3(g)$$

(Step 1) $$SO_2 + O_2 \xrightleftharpoons[k_{-1}]{k_1} SO_4$$

(Step 2) $$SO_4 \xrightarrow{k_2} SO_3 + O^\bullet$$

(Step 3) $$O^\bullet + SO_2 \xrightarrow{k_3} SO_3$$

(a) (14 points) Write the rate law. You do not need the most simplified form, stop after eliminating the intermediate.

$$v(t) = \frac{d[SO_3]}{dt} = k_2[SO_4] + k_3[O][SO_2]$$

$$\frac{d[SO_4]}{dt} = k_1[SO_2][O_2] - k_{-1}[SO_4] - k_2[SO_4] = 0$$

$$[SO_4] = \frac{k_1[SO_2][O_2]}{k_{-1} + k_2}$$

$$\frac{d[O^\bullet]}{dt} = k_2[SO_4] - k_3[O^\bullet][SO_2] = 0$$

$$[O^\bullet] = \frac{k_2[SO_4]}{k_3[SO_2]} = \frac{k_1 k_2[O_2]}{k_3(k_{-1} + k_2)}$$

$$\boxed{v(t) = k_2 \cdot \frac{k_1[SO_2][O_2]}{k_{-1} + k_2} + k_3[SO_2] \cdot \frac{k_1 k_2[O_2]}{k_3(k_{-1} + k_2)}}$$

$$= 2k_2 \cdot \frac{k_1[SO_2][O_2]}{k_{-1} + k_2}$$

(b) (12 points) In Chem 120, we study the first–order decomposition of hydrogen peroxide, which takes about 30 days (43,200 minutes) without a catalyst. Adding a catalyst ($Fe(NO_3)_3$) reduces the reaction time to 20 minutes. If the uncatalyzed activation energy is 50 $\frac{\text{kJ}}{\text{mol}}$, what is the catalyzed activation energy at SATP?

$$\frac{k_2}{k_1} = \frac{t_1}{t_2} = \frac{43{,}200\,\text{min}}{20\,\text{min}} = 2160$$

$$k = Ae^{-E_a/(RT)}$$

$$\frac{k_2}{k_1} = \frac{Ae^{-E_{a,2}/(RT)}}{Ae^{-E_{a,1}/(RT)}} = e^{(E_{a,1} - E_{a,2})/(RT)}$$

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_{a,1} - E_{a,2}}{RT}$$

$$E_{a,2} = E_{a,1} - RT\ln\left(\frac{k_2}{k_1}\right)$$

$$E_{a,2} = 50\,\tfrac{\text{kJ}}{\text{mol}} - (8.314\,\tfrac{\text{J}}{\text{mol}\cdot\text{K}})(298\,\text{K})\ln(2160)$$

$$E_{a,2} = \boxed{31.0\,\tfrac{\text{kJ}}{\text{mol}}}$$

End of exam.