Chem 322: Physical Chemistry II

Spring 2026 Exam 2
Professor Yuting Chen

Name: ____

This is an open note exam. You may use your prepared two-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: ____

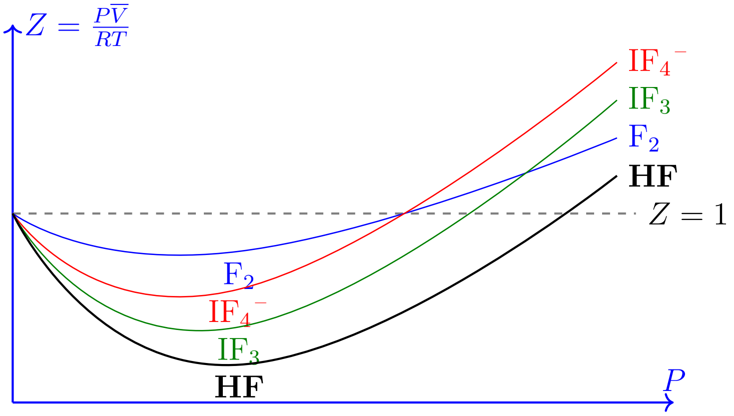
Instructions

- 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 7 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. **Real Gases**

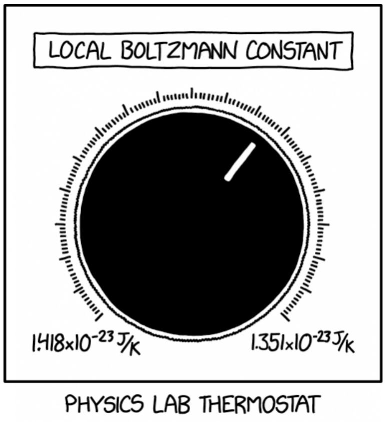
   (a) (8 points) Sketch a Z vs P diagram for IF_3, IF_4^-, F_2, HF.

   vdw "a": F_2, IF_4^-, IF_3, HF   vdw "b": HF, F_2, IF_3, IF_4^-



   (b) (4 points) Name a molecule that could slot in the middle position for both vdw "a" and "b". So $A < B <$ your molecule $< C < D$. Briefly justify your answer using periodic trends.

   ClF_3 as Cl is smaller than I and is closer to F in electronegativity, thus reducing the magnitude of the dipole.



I didn't want to squeeze the first two problems onto one page, so here's something to take up the empty space.

2. **Reaction Enthalpies**

Consider the following reaction:

$$\mathrm{N_2H_4(g) + O_2(g) \longrightarrow N_2(g) + 2\,H_2O\,(g)}$$

Species	ΔH_f° (kJ/mol)
H_2O (g)	-241.82
N_2H_4(g)	50.63

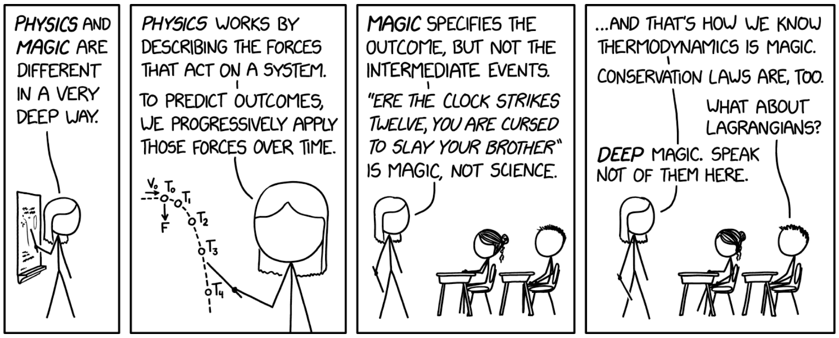
Bond	Bond enthalpy (kJ/mol)
O=O	498
N≡N	945
O−H	467

$$\mathrm{N\,(g) + 3\,H\,(g) \longrightarrow NH_3(g)} \quad \Delta H^\circ_{\text{rxn}} = -1164\ \text{kJ}$$

(a) (8 points) Find the N−N bond enthalpy using the above data.

N−H bond enthalpy is given by $\frac{1{,}164\,\frac{\text{kJ}}{\text{mol}}}{3} = 388\,\frac{\text{kJ}}{\text{mol}}$

$$\begin{aligned}
\Delta H^\circ_{\text{rxn}} &= \sum n\Delta H_f^\circ(\text{products}) - \sum n\Delta H_f^\circ(\text{reactants}) \\
&= \left[0 + 2\,\text{mol}(-241.83\,\tfrac{\text{kJ}}{\text{mol}})\right] - \left[0 + 1\,\text{mol}(50.63\,\tfrac{\text{kJ}}{\text{mol}})\right] \\
&= -534.27\,\text{kJ} \\
\Delta H^\circ_{\text{rxn}} &= \sum \text{bonds broken} - \sum \text{bonds formed} \\
-534.3\,\text{kJ} &= \left[4(388\,\tfrac{\text{kJ}}{\text{mol}}) + x + 1(498\,\tfrac{\text{kJ}}{\text{mol}})\right] - \left[1(945\,\tfrac{\text{kJ}}{\text{mol}}) + 4(467\,\tfrac{\text{kJ}}{\text{mol}})\right] \\
x &= 228.7\,\tfrac{\text{kJ}}{\text{mol}}
\end{aligned}$$



3. **First Law**

A system of argon gas is initially at 25 °C, 1.63 atm, and a volume of 750 mL. Heat is added and the system reaches a final temperature of 50 °C, a final volume of 1.5 L, and a final pressure of 0.88 atm. 101.325 J=1 L · atm

(a) (5 points) Determine ΔU without using the first law.

$$\begin{aligned} n &= \frac{PV}{RT} = \frac{(1.63\,\text{atm})(0.750\,\text{L})}{(0.08206\,\frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}})(298\,\text{K})} \\ &= 0.050\,\text{mol} \\ \Delta U &= \int_{T_1}^{T_2} C_V\,dT = n\int_{T_1}^{T_2}\frac{3}{2}R\,dT \\ &= n\frac{3}{2}R(T_2 - T_1) \\ &= (0.05\,\text{mol})\frac{3}{2}(8.314\,\tfrac{\text{J}}{\text{mol}\cdot\text{K}})(323\,\text{K} - 298\,\text{K}) \\ &= 15.59\,\text{J} \end{aligned}$$

Use equipartition

$$\begin{aligned} U &= \frac{3}{2}nRT \\ \Delta U &= \frac{3}{2}nR(T_2 - T_1) \\ &= (0.05\,\text{mol})\frac{3}{2}(8.314\,\tfrac{\text{J}}{\text{mol}\cdot\text{K}})(323\,\text{K} - 298\,\text{K}) \\ &= 15.59\,\text{J} \end{aligned}$$

We can apply the first law by breaking up this into two steps.

Step 1: Reversible Isothermal expansion to the final pressure

Step 2: Isobaric expansion to final conditions

(b) (6 points) Determine the work and heat associated with step 1, in J.

$$\begin{aligned} V_2 &= \frac{nRT}{P_2} = \frac{0.05\,\text{mol}\,(0.0821\,\frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}})(298\,\text{K})}{0.88\,\text{atm}} \\ &= 1.39\,\text{L} \\ w &= -nRT\ln\frac{V_2}{V_1} = -(0.05\,\text{mol})(8.314\,\tfrac{\text{J}}{\text{mol}\cdot\text{K}})(298\,\text{K})\ln\frac{1.39}{0.75} \\ &= -76.43\,\text{J} \\ q &= -w = 76.43\,\text{J} \end{aligned}$$

(c) (6 points) Determine the work and heat associated with step 2, in J.

$$\begin{aligned} w &= -P\Delta V = -0.88\,\text{atm}(1.5\,\text{L} - 1.39\,\text{L})\left(\frac{101.325\,\text{J}}{1\,\text{L}\cdot\text{atm}}\right) \\ &= -9.81\,\text{J} \\ q &= n\overline{C_P}\Delta T = 0.05\,\text{mol}\left(\frac{5}{2}\cdot 8.314\,\tfrac{\text{J}}{\text{mol}\cdot\text{K}}\right)(323\,\text{K} - 298\,\text{K}) \\ &= 25.98\,\text{J} \end{aligned}$$

We are now going to compare different first steps for the two step process.

(d) (2 points) Which first step has the greater work associated with it?

A. Reversible isothermal expansion to the final pressure

[✓ B. Reversible isothermal expansion to the final volume]

C. The work done is equal in both cases

(e) (2 points) Which would result in the greater ΔU for the overall two step process?

A. Reversible isothermal expansion to the final pressure in the first step, followed by going to the same final conditions

B. Reversible isothermal expansion to the final volume in the first step, followed by going to the same final conditions

[✓ C. The ΔU is equal in both cases]

4. **Concepts!**

Circle the correct choice for each of the following.

(a) (2 points) Highest residual entropy

☐ $CH_4(g)$ ■ $CF_2H_2(g)$ ☐ $CF_4(l)$

(b) (2 points) Larger energy level spacing (assuming PIAB energy levels)

■ 2 mol $CH_4(g)$ at 1 L ☐ 1 mol $CF_2H_2(g)$ at 2 L ☐ Cannot be determined

(c) (2 points) Highest standard molar entropy

☐ $CH_4(g)$ ■ $CF_2H_2(g)$ ☐ $CF_4(l)$ ☐ Cannot be determined

(d) (2 points) Greater number of accessible microstates after heating 1 mol $CH_4(g)$ from 150 K to 200 K.

■ Isobaric heating ☐ Isochoric heating ☐ Both are equal ☐ Cannot be determined

A rigid container has 2 mol of Ne(g) at 200 K. 2 mol of Ar(g) at 300 K are added.

(e) (2 points) What is the final temperature of the mixture?

☐ $<$ 250 K ■ $=$ 250 K ☐ $>$ 250 K ☐ Cannot be determined

An insulated container with a moveable, frictionless piston has 2 mol of Ne(g) at 200 K under constant external pressure. 2 mol of Ar(g) at 300 K are added, causing the piston to move.

(f) (2 points) What is the final temperature of the mixture?

■ $<$ 250 K ☐ $=$ 250 K ☐ $>$ 250 K ☐ Cannot be determined

An insulated container with a moveable, frictionless piston has 2 mol of Ar(g) at 200 K under constant external pressure. 2 mol of $Cl_2(g)$ at 300 K are added, causing the piston to move.

(g) (2 points) What is the final temperature of the mixture?

☐ $<$ 250 K ☐ $=$ 250 K ☐ $>$ 250 K ■ Cannot be determined

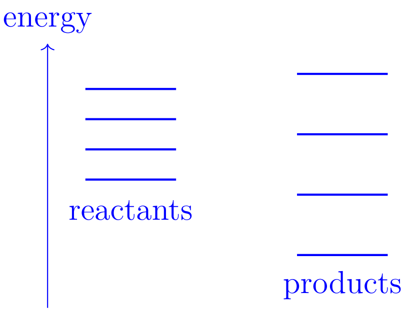
5. **A bit of everything**

$$\mathrm{C(s)} + 2\,\mathrm{Cl_2(g)} \longrightarrow \mathrm{CCl_4(l)} \quad \Delta H^\circ_{\mathrm{rxn}} = -135.4\,\mathrm{kJ}$$

(a) (3 points) What type of reaction is this? (*Circle all that apply*):

☐ bond making ☐ bond breaking ■ formation ☐ endothermic
■ exothermic ☐ spontaneous ☐ non-spontaneous

(b) (4 points) Draw an energy level diagram for this reaction, illustrating both ΔH and ΔS.



(c) (10 points) Using the data provided and the equation at the top, find the C−Cl bond enthalpy.

ΔH_f° Cl(g) = 121.7 $\frac{\mathrm{kJ}}{\mathrm{mol}}$ ΔH_f° C(g) = 716.7 $\frac{\mathrm{kJ}}{\mathrm{mol}}$ $\Delta H^\circ_{\mathrm{vap}}$ $\mathrm{CCl_4(l)}$ = 45.9 $\frac{\mathrm{kJ}}{\mathrm{mol}}$

We need gas phase to do bond enthalpies:

$$\mathrm{C(g)} + 2\,\mathrm{Cl_2(g)} \longrightarrow \mathrm{CCl_4(g)} \quad \Delta H = ?$$

$$\begin{aligned}
\mathrm{C(s)} + 2\,\mathrm{Cl_2(g)} &\longrightarrow \mathrm{CCl_4(l)} & \Delta H &= -135.4\,\mathrm{kJ}\\
\mathrm{C(g)} &\longrightarrow \mathrm{C(s)} & \Delta H &= -716.7\,\mathrm{kJ}\\
\mathrm{CCl_4(l)} &\longrightarrow \mathrm{CCl_4(g)} & \Delta H &= 45.9\,\mathrm{kJ}\\
\hline
\mathrm{C(g)} + 2\,\mathrm{Cl_2(g)} &\longrightarrow \mathrm{CCl_4(g)} & \Delta H &= -806.3\,\mathrm{kJ}
\end{aligned}$$

Breaking: 2 Cl–Cl Forming: 4 C–Cl

$$\begin{aligned}
\Delta H_{\mathrm{rxn}} &= \textstyle\sum(\text{bonds broken}) - \sum(\text{bonds formed})\\
\Delta H_{\mathrm{rxn}} &= 2(\mathrm{Cl{-}Cl}) - 4(\mathrm{C{-}Cl})\\
-806.3\,\mathrm{kJ} &= 2(243.4\,\mathrm{kJ}) - 4(\mathrm{C{-}Cl})\\
-806.3\,\mathrm{kJ} &= 486.8\,\mathrm{kJ} - 4(\mathrm{C{-}Cl})\\
-4(\mathrm{C{-}Cl}) &= -1{,}293.1\,\mathrm{kJ}
\end{aligned}$$

$$\boxed{(\mathrm{C{-}Cl}) = 323.3\,\tfrac{\mathrm{kJ}}{\mathrm{mol}}}$$

$$\begin{aligned}
\tfrac{1}{2}\mathrm{Cl_2(g)} &\longrightarrow \mathrm{Cl(g)} & \Delta H^\circ &= +121.7\\
\mathrm{C(s)} &\longrightarrow \mathrm{C(g)} & \Delta H^\circ &= +716.7\\
\mathrm{CCl_4(l)} &\longrightarrow \mathrm{CCl_4(g)} & \Delta H^\circ &= +45.9\,\mathrm{k}\\
\mathrm{CCl_4(l)} &\longrightarrow \mathrm{C(s)} + 2\,\mathrm{Cl_2(g)} & \Delta H^\circ &= +135.4\\
\hline
\mathrm{C(g)} + 4\,\mathrm{Cl(g)} &\longrightarrow \mathrm{CCl_4(g)} & \Delta H^\circ &= -1{,}293.
\end{aligned}$$

This is energy released when forming 4 (C-Cl) bonds, so we divide by 4 and flip to get bond enthalpy

$$\frac{1{,}293.0\,\mathrm{kJ}}{4} = \boxed{323.3\,\tfrac{\mathrm{kJ}}{\mathrm{mol}}}$$

6. **Entropy**

Consider a system of four distinguishable particles confined in a rigid container divided into two compartments, L and R, each containing two particles. The total energy is $E_{tot} = 5$, and each particle can occupy single particle energy levels $E_i = 0, 1, 2, 3, 4, 5$.

We will consider two cases for the divider:

Adiabatic divider No energy can be transferred as heat. Particle exchange is not allowed.

Diathermal divider Energy can be exchanged as heat, but particles cannot be exchanged

The particles are initially in a configuration where $E_L = 3$ and $E_R = 2$. For this problem you may leave your answer in terms of fundamental constants R, k_B etc.

(a) (2 points) Using concepts and no calculations, briefly explain which has higher entropy.

Diathermal will have more entropy since more there are more accessible microstates when energy can be transfered across the divider.

(b) (4 points) Calculate the entropy of the whole system for the adiabatic divider.

$$\begin{aligned}
&E_L = 3 \quad E_R = 2\\
&W_L : (0,3), (1,2), (2,1), (3,0) \implies W_L = 4\\
&W_R : (0,2), (1,1), (2,0) \implies W_R = 3\\
&W = W_L \times W_R = 12\\
&S = k_B \ln W = k_B \ln(12)
\end{aligned}$$

(c) (8 points) Calculate the entropy of the whole system for the diathermal divider.

E_L	W_L	W_R	W
0	(0,0)	(0,5),(1,4),(2,3),(3,2),(4,1),(5,0)	$1 \times 6 = 6$
1	(0,1),(1,0)	(0,4),(1,3),(2,2),(3,1),(4,0)	$2 \times 5 = 10$
2	(0,2),(1,1),(2,0)	(0,3),(1,2),(2,1),(3,0)	$3 \times 4 = 12$
3	(0,3),(1,2),(2,1),(3,0)	(0,2),(1,1),(2,0)	$4 \times 3 = 12$
4	(0,4),(1,3),(2,2),(3,1),(4,0)	(0,1),(1,0)	$5 \times 2 = 10$
5	(0,5),(1,4),(2,3),(3,2),(4,1),(5,0)	(0,0)	$6 \times 1 = 6$

$$\begin{aligned}
W_{\text{tot}} &= 6 + 10 + 12 + 12 + 10 + 6 = 56\\
S &= k_B \ln 56
\end{aligned}$$

7. **Entropy of a mixture**

A flexible container with volume $V = 16.39\,\mathrm{L}$ contains a mixture of NH_3 and N_2 gas at standard conditions. 1,800 J of heat is added, and the temperature rises by $42\,^\circ\mathrm{C}$.

(a) (14 points) What percentage of this process's change in entropy ΔS is attributed to N_2?

$$\begin{aligned} n_{\text{total}} &= \frac{PV}{RT} \\ &= \frac{(1.000\,\mathrm{atm})(16.39\,\mathrm{L})}{(0.0821\,\frac{\mathrm{L\cdot atm}}{\mathrm{mol\cdot K}})(298\,\mathrm{K})} \\ &= 0.670\,\mathrm{mol} \end{aligned}$$

Let $x = \text{mol } NH_3$, so mol $N_2 = 0.670 - x$.

$$\begin{aligned} q &= n\overline{C_P}\Delta T + n\overline{C_P}\Delta T \\ 1{,}800\,\mathrm{J} &= (8.314\,\tfrac{\mathrm{J}}{\mathrm{mol\cdot K}})(42\,\mathrm{K})\left[\frac{9}{2}(0.670 - x) + 10x\right] \\ \frac{1{,}800\,\mathrm{J}}{(8.314\,\frac{\mathrm{J}}{\mathrm{mol\cdot K}})(42\,\mathrm{K})} &= \frac{9}{2}(0.670 - x) + 10x \\ 5.155\,\mathrm{mol} &= 3.015\,\mathrm{mol} + 5.5x \\ x &= \boxed{0.389\,\mathrm{mol}\ \mathrm{NH_3}} \\ 0.670 - x &= \boxed{0.281\,\mathrm{mol}\ \mathrm{N_2}} \end{aligned}$$

At constant pressure: $\Delta S = n\overline{C_P}\ln(\frac{T_f}{T_i})$ with $T_f = 340\,\mathrm{K}$ and $T_i = 298\,\mathrm{K}$.

$$\begin{aligned} \Delta S_{N_2} &= (0.281\,\mathrm{mol})\left(\frac{9}{2}\right)(8.314\,\tfrac{\mathrm{J}}{\mathrm{mol\cdot K}})\ln\left(\frac{340\,\mathrm{K}}{298\,\mathrm{K}}\right) \\ &= 1.386\,\tfrac{\mathrm{J}}{\mathrm{K}} \\ \Delta S_{NH_3} &= (0.389\,\mathrm{mol})(10)(8.314\,\tfrac{\mathrm{J}}{\mathrm{mol\cdot K}})\ln\left(\frac{340\,\mathrm{K}}{298\,\mathrm{K}}\right) \\ &= 4.264\,\tfrac{\mathrm{J}}{\mathrm{K}} \\ \frac{1.386}{1.396 + 4.265} &= \boxed{24.5\%} \end{aligned}$$

End of exam.