NAME:

Instructions:

1. Keep this exam closed until instructed to begin.

2. Please write your name on this page but not on any other page.

3. Please silence any noisy electronic devices you have.

4. Attached sheet(s) provide potentially useful constants and equations. You may detach these from the exam.

5. To receive full credit for your work, please
   (a) show all your work, using only the exam papers, including the back of this sheet if necessary;
   (b) specify the correct units, if any, for your final answers;
   (c) use an appropriate number of significant digits for final numerical answers;
   (d) stop writing and close your exam immediately when time is called.

Other notes:

• The first page portion of the exam is worth 40 points. Partial credit for these problems is not necessarily available.

• Your 2 best scores of the 3 remaining problems will count towards the other 60 points. Partial credit is available for these problems, so try each problem and do not erase any of your work.
1. **40 points.**

(a) Use the Sackur-Tetrode equation to predict the standard molar entropy of atomic iodine I(g) at 573 K and 1.00 bar.

(b) Calculate the entropy change when we heat calcium chloride from 298 K to 323 K, assuming that the heat capacity remains a constant 72.59 J K\(^{-1}\) mol\(^{-1}\) over this temperature range.

(c) The container shown below separates an ideal gas into two compartments with a movable, thermally conducting wall between them. The conditions in each compartment are labeled.

\[
\begin{array}{c|c}
500 \text{ K} & 600 \text{ K} \\
2.00 \text{ mol} & 4.00 \text{ mol} \\
10.0 \text{ L} & 20.0 \text{ L} \\
8.3 \text{ bar} & 10.0 \text{ bar} \\
\end{array}
\]

Circle **each** statement below that correctly describes how the system will change.

i. the wall will move to the right

ii. the wall will move to the left

iii. heat will flow to the right

iv. heat will flow to the left

v. until the volume on both sides is the same

vi. until the temperature on both sides is the same

vii. until the pressure on both sides is the same

viii. until the number of moles on both sides is the same
2. In the text, we described the reversible, isothermal expansion of 1.00 mol of an ideal gas from 2.48 L at 10.00 bar and 298 K to a final pressure of 1.00 bar. Repeat the process from the same starting point, but this time set the final pressure $P_2$ to 0.100 bar. Calculate the following parameters:

(a) $V_2 =$

(b) $\Delta E =$

(c) $w =$

(d) $\Delta S =$

(e) $\Delta F =$

3. In many systems, the canonical distribution accurately describes populations in each degree of freedom (translations, rotations, and vibrations), but the effective temperature for each degree of freedom is different. Consider a sample of I$_2$ gas ($\omega_e = 214.5$ cm$^{-1}$, $B_e = 0.0559$ cm$^{-1}$) that initially has a vibrational temperature $T_{\text{vib}} = 653$ K, a rotational temperature $T_{\text{rot}} = 437$ K, and a translational temperature $T_{\text{trans}} = 298$ K. We then isolate the sample, and wait for these different degrees of freedom to exchange energy until the temperatures are equal. What is the final temperature (now the same for all motions) of the sample?
4. Figure 17.17 from the book (reproduced at left below) shows the $P$ vs $V$ graphs of three expansions: (a) the reversible isothermal, (b) the irreversible isothermal, and (c) the reversible adiabatic. In the empty graph at right, plot the corresponding curves for $T$ vs $S$ of these three processes, letting all three processes start from the same initial point $(T_1, S_1)$. Be quantitative if possible, otherwise sketch an approximate curve. Label the curves a, b, and c.
### Fundamental Constants

- **Avogadro's number**: \( N_A \) = \( 6.0221367 \cdot 10^{23} \) mol\(^{-1} \)
- **Bohr radius**: \( a_0 = \frac{4\pi\varepsilon_0\hbar^2}{m_e^2} \) = 5.29177249 \cdot 10^{-11} \) m
- **Boltzmann constant**: \( k_B = 1.380658 \cdot 10^{-23} \) J K\(^{-1} \) = 0.6950 cm\(^{-1} \) K
- **electron rest mass**: \( m_e = 9.1093897 \cdot 10^{-31} \) kg
- **fundamental charge**: \( e = 1.6021773 \cdot 10^{-19} \) C
- **permittivity factor**: \( 4\pi\varepsilon_0 = 1.113 \cdot 10^{-10} \) C\(^2\) J\(^{-1}\) m\(^{-1} \)
- **gas constant**: \( R = 8.314510 \) J K\(^{-1}\) mol\(^{-1} \)
  - \( R = 0.08314510 \) L bar K\(^{-1}\) mol\(^{-1} \)
  - \( R = 0.08206 \) L atm K\(^{-1}\) mol\(^{-1} \)
- **hartree**: \( E_h = \frac{m_e^4}{(4\pi\varepsilon_0)^2\hbar^2} \) = 4.35980 \cdot 10^{-18} \) J
- **Planck’s constant**: \( h = 6.6260755 \cdot 10^{-34} \) J s
  - \( h = 1.05457266 \cdot 10^{-34} \) J s
- **proton rest mass**: \( m_p = 1.672631 \cdot 10^{-27} \) kg
- **neutron rest mass**: \( m_n = 1.6749286 \cdot 10^{-27} \) kg
- **speed of light**: \( c = 2.99792458 \cdot 10^8 \) m s\(^{-1} \)

### Unit Conversions

<table>
<thead>
<tr>
<th>K</th>
<th>cm(^{-1} )</th>
<th>kJ mol(^{-1} )</th>
<th>kcal mol(^{-1} )</th>
<th>erg</th>
<th>kJ</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{kHz} = )</td>
<td>( 4.799 \cdot 10^{-8} )</td>
<td>( 3.336 \cdot 10^{-8} )</td>
<td>( 3.990 \cdot 10^{-10} )</td>
<td>( 9.537 \cdot 10^{-11} )</td>
<td>( 6.626 \cdot 10^{-24} )</td>
</tr>
<tr>
<td>( \text{MHz} = )</td>
<td>( 4.799 \cdot 10^{-5} )</td>
<td>( 3.336 \cdot 10^{-5} )</td>
<td>( 3.990 \cdot 10^{-7} )</td>
<td>( 9.537 \cdot 10^{-8} )</td>
<td>( 6.626 \cdot 10^{-21} )</td>
</tr>
<tr>
<td>( \text{GHz} = )</td>
<td>( 4.799 \cdot 10^{-2} )</td>
<td>( 3.336 \cdot 10^{-2} )</td>
<td>( 3.990 \cdot 10^{-4} )</td>
<td>( 9.537 \cdot 10^{-5} )</td>
<td>( 6.626 \cdot 10^{-18} )</td>
</tr>
<tr>
<td>( K = )</td>
<td>1</td>
<td>8.314 \cdot 10^{-3}</td>
<td>1.987 \cdot 10^{-3}</td>
<td>1.381 \cdot 10^{-16}</td>
<td>1.381 \cdot 10^{-26}</td>
</tr>
<tr>
<td>( \text{cm}^{-1} = )</td>
<td>1.4388</td>
<td>1</td>
<td>1.196 \cdot 10^{-2}</td>
<td>2.859 \cdot 10^{-3}</td>
<td>1.986 \cdot 10^{-16}</td>
</tr>
<tr>
<td>( \text{kJ mol}^{-1} = )</td>
<td>1.203 \cdot 10^{2}</td>
<td>83.59</td>
<td>1</td>
<td>0.2390</td>
<td>1.661 \cdot 10^{-14}</td>
</tr>
<tr>
<td>( \text{kcal mol}^{-1} = )</td>
<td>5.032 \cdot 10^{2}</td>
<td>3.498 \cdot 10^{2}</td>
<td>4.184</td>
<td>1</td>
<td>6.948 \cdot 10^{-14}</td>
</tr>
<tr>
<td>( \text{eV} = )</td>
<td>1.160 \cdot 10^{4}</td>
<td>8.066 \cdot 10^{3}</td>
<td>96.49</td>
<td>23.06</td>
<td>1.602 \cdot 10^{-12}</td>
</tr>
<tr>
<td>( \text{hartree} = )</td>
<td>3.158 \cdot 10^{5}</td>
<td>2.195 \cdot 10^{5}</td>
<td>2.625 \cdot 10^{3}</td>
<td>6.275 \cdot 10^{2}</td>
<td>4.360 \cdot 10^{-11}</td>
</tr>
<tr>
<td>( \text{erg} = )</td>
<td>7.243 \cdot 10^{15}</td>
<td>5.034 \cdot 10^{15}</td>
<td>6.022 \cdot 10^{13}</td>
<td>1.439 \cdot 10^{13}</td>
<td>1</td>
</tr>
<tr>
<td>( \text{J} = )</td>
<td>7.243 \cdot 10^{22}</td>
<td>5.034 \cdot 10^{22}</td>
<td>6.022 \cdot 10^{20}</td>
<td>1.439 \cdot 10^{20}</td>
<td>10^{7}</td>
</tr>
<tr>
<td>( \text{dm}^3 \text{ bar} = )</td>
<td>7.243 \cdot 10^{24}</td>
<td>5.034 \cdot 10^{24}</td>
<td>6.022 \cdot 10^{22}</td>
<td>1.439 \cdot 10^{22}</td>
<td>1.000 \cdot 10^{9}</td>
</tr>
<tr>
<td>( \text{kJ} = )</td>
<td>7.243 \cdot 10^{25}</td>
<td>5.034 \cdot 10^{25}</td>
<td>6.022 \cdot 10^{23}</td>
<td>1.439 \cdot 10^{23}</td>
<td>10^{10}</td>
</tr>
</tbody>
</table>

**Distance**: 1 å = \( 10^{-10} \) m

**Mass**: 1 amu = \( 1.66054 \cdot 10^{-27} \) kg

**Energy**: 1 J = \( 1 \) kg m\(^2\) s\(^{-2}\) = \( 10^7 \) erg

**Force**: 1 N = \( 1 \) kg m s\(^{-2}\) = \( 10^5 \) dyn

**Electrostatic Charge**: 1 C = 1 A s = 2.9979 \cdot 10^9 \) esu

**Magnetic Field Strength**: 1 T = \( 1 \) kg s\(^{-2}\) A\(^{-1}\) = \( 10^4 \) gauss

**Pressure**: 1 Pa = \( 1 \) N m\(^{-2}\) = \( 1 \) kg m\(^{-1}\) s\(^{-2}\)

1 bar = \( 10^5 \) Pa = 0.98692 atm
entropy \quad S_{\text{Boltzmann}} = k_B \ln \Omega \quad S_{\text{Gibbs}} = -Nk_B \sum_i \mathcal{P}(i) \ln \mathcal{P}(i)

partition func.s \quad q(T) = \sum \mathcal{g}(\mathcal{e})e^{-\mathcal{e}/(k_B T)} \quad q_{\text{rot}} \approx \frac{k_B T}{B} \quad q_{\text{vib}} \approx \frac{1}{1 - e^{-\omega_\mathcal{e}/(k_B T)}}

q_{\text{trans}}(T, V) = q'_{K} q'_{U} = \left(\frac{2\pi m k_B T}{\hbar^2}\right)^{3/2} V \text{ (ideal gas)}

collisions \quad \nu_{\text{rms}} = \sqrt{\frac{3k_B T}{m}} \quad \langle \nu \rangle = \sqrt{\frac{8k_B T}{\pi m}} \quad \langle \nu_{AB} \rangle = \sqrt{\frac{8k_B T}{\pi \mu}} \quad \gamma = \rho \sigma \langle \nu_{AA} \rangle \quad \lambda = \frac{1}{\sqrt{2} \rho \sigma} \quad \rho = \frac{N}{V} = \frac{PN_A}{RT}

thermo derivatives \quad dE = TdS - PdV + \mu_1 d_n_1 + \ldots \quad dH = TdS + VdP + \mu_1 d_n_1 + \ldots

\quad dF = -SdT - PdV + \mu_1 d_n_1 + \ldots \quad dG = -SdT + VdP + \mu_1 d_n_1 + \ldots

isobaric heating: \quad \Delta S = nC_{P_m} \ln \left(\frac{T_f}{T_i}\right)

isothermal exp: \quad w_{\text{rev}} = -nRT \ln \left(\frac{V_2}{V_1}\right) \quad w_{\text{int}} = -P_{\text{min}} \Delta V \quad \Delta S = nR \ln \left(\frac{V_f}{V_i}\right)

adiabatic exp: \quad w_{\text{rev}} = C_V \Delta T \quad \frac{V_2}{V_1} = \left(\frac{T_2}{T_1}\right) = \left(\frac{P_2}{P_1}\right) = -\frac{C_{V_m} / R}{C_{P_m} / R}

Sackur-Tetrode: \quad S_m = R \left\{ \frac{5}{2} + \ln \left[ \left(\frac{2\pi m k_B T}{\hbar^2}\right)^{3/2} \frac{RT}{N_A P}\right] \right\}

Clausius/Clapeyron: \quad \frac{dP}{dT} = \frac{\Delta H_{\phi}}{T \Delta \phi / V} \quad \ln P(\text{bar}) = \frac{\Delta_{\text{vap}} H}{R} \left[ \frac{1}{T_b} - \frac{1}{T} \right]

Gibbs phase: \quad d = k - p + 2

Raoult’s law: \quad P_A = P_A^* X_A

Henry’s law: \quad P_B = k_X X_B \quad k_X = \lim_{X_B \to 0} \left(\frac{P_B}{X_B}\right)

colligative props. \quad \Delta T_f = -\frac{RT^* X_B}{\Delta_{\text{fus}} H} \quad \Pi = RT[\text{B}]

reactions: \quad \Delta_{\text{rxn}} G = \Delta_{\text{rxn}} G^* + RT \ln \Xi \quad \ln K_{\text{eq}}(T) = -\frac{\Delta_{\text{rxn}} G^*}{RT} = -\frac{\Delta_{\text{rxn}} H^*}{RT} + \frac{\Delta_{\text{rxn}} S^*}{R}

rate constants: \quad k_{\text{SCT}} = p\sigma_{AB} \left(\frac{8k_B T}{\pi \mu}\right)^{1/2} e^{-E_a/(RT)} N_A \quad k_{\text{TST}} = \frac{k_B T}{C h} e^{\Delta S^*/R} e^{-\Delta H^*/(RT)}