1. \[ \frac{dS}{dt} = \frac{d}{dt}(S_i(E_i) + S_e(E_e)) = \frac{dS_i}{dt} \frac{dE_i}{dE} + \frac{dS_e}{dt} \frac{dE_e}{dE} \]

\[ \frac{1}{T_i} = \frac{dS_i}{dE_i}, \quad \frac{1}{T_e} = \frac{dS_e}{dE_e} \]

\[ \frac{dE}{dt} = \frac{d}{dt}(E - E_i) = -\frac{dE_i}{dt} \]

\[ \frac{dS}{dt} = \frac{dE_i}{dt} \left( \frac{1}{T_i} - \frac{1}{T_e} \right) > 0 \]

Key equation to start with

Assume \( T_i > 0, \ T_e < 0 \), then \( \frac{1}{T_i} - \frac{1}{T_e} \) is

Sum of two positive terms and is positive. Since

\[ \frac{dE_i}{dt} \left( \frac{1}{T_i} - \frac{1}{T_e} \right) > 0 \]

This implies \( \frac{dE_i}{dt} > 0 \), i.e., energy of \( E_i \) increases with time, which means heat transfer from negative temperature system to positive.

Note: what if \( 0 > T_i > T_e \)?
2. If \( S = a + b \ln y \) then

\[
\frac{1}{F} = \frac{aS}{2u} = \frac{a}{2u} \frac{a + b \ln y}{y} = \frac{b}{y}
\]

so \( U = bT \) and \( C_V = \frac{du}{dT} = b \)

need to discover or determine \( T \) from known \( S = S(U) \)

3. There are \( 4 \times 4 = 16 \) microstates since any value of die \( A \) can combine with any value of die \( 2 \).

There are \( 7 \) macrostates corresponding to the sums

\[ 2, 3, 4, 5, 6, 7, 8 \]

Their multiplicities are as follows:

<table>
<thead>
<tr>
<th>Sum, ( S )</th>
<th>( S_2(S) )</th>
<th>Accessible microstates</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1</td>
<td>1+1</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>1+2, 2+1</td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td>1+3, 3+1, 2+2</td>
</tr>
<tr>
<td>5</td>
<td>4</td>
<td>1+4, 4+1, 2+3, 3+2</td>
</tr>
<tr>
<td>6</td>
<td>3</td>
<td>2+4, 4+2, 3+3</td>
</tr>
<tr>
<td>7</td>
<td>2</td>
<td>3+4, 4+3</td>
</tr>
<tr>
<td>8</td>
<td>1</td>
<td>4+4</td>
</tr>
</tbody>
</table>
Problem 4

Key step was to understand what this process looks like. Adiabatic and isothermal expansions correspond to decreases in pressure. Follows from \( V^2 P = \text{const} \) (big \( V \) implies smaller \( P \)) or from \( PV = \text{const} \) for isothermal.

Can now answer parts:

(a) From \( U = \frac{1}{2} PV \) we conclude

\[
\Delta U = \frac{1}{2} \Delta (PV) = \frac{1}{2} (P_f V_f - P_i V_i) \\
= \frac{1}{2} V_0 (P_f - P_i) < 0 \quad \text{so} \quad \Delta U < 0
\]

since \( P_f < P_i \). Note how I didn't need to compute what happens for each step and I didn't need to know any details of the expansion, just that the final pressure is lower than the initial pressure.
4b: Work $W$ is given by

$$W = -\int_{V_0}^{V_0/2} P_1(V) dV - \int_{V_0/2}^{V_0} P_2(V) dV$$

$$= -\int_{V_0}^{V_0/2} (P_1(V) - P_2(V)) dV$$

It is the area between the compression and expansion curves (shaded). The sign of $W$ is given by which curve is higher. Here, the compression curve lies above the expansion curve, more work is added than removed. Conclude $W > 0$.

4c: Always compute heat $Q$ after computing $\Delta U$ and $W$. From conservation of energy

$$Q_{tot} = \Delta U_{tot} - W_{tot} < 0$$

since $\Delta U_{tot} < 0$ and $W_{tot} > 0 \Rightarrow -W_{tot} < 0$.

4d: $U = NF \frac{1}{2} \Rightarrow \Delta U = NF \frac{k}{2} \Delta T$

so $\Delta U < 0 \Rightarrow \Delta T < 0$
Problem 5

Let's collect information before making a plot.

We are told \( C_p \approx 75 \frac{J}{K} \) in liquid phase so

\[
\frac{C_p}{R} = \frac{75}{8/3} \approx \frac{70}{8} \approx 9 \quad 270 < T < 370
\]

So part of curve will look like this:

\[
\begin{array}{c}
\text{\( C_p \) vs. \( T \)}
\end{array}
\]

\[
\begin{array}{c}
270 \quad 370 \quad T
\end{array}
\]

We know from reading Schroeder page 32 bottom that, when substance melts or boils,

\[
C_p = \infty \quad \text{at } T = 270, \approx 370
\]

(Nearly all students missed this fact).

For ice with \( T < 270 \), we have solid so expect \( f = 6 \)

and \( C_p \approx C_v \approx N \cdot \frac{k_B}{2} = 3Nk = 3R \) for one mole

\( \text{(neglect)} \)
From Fig 1.14 on p. 30 of Schroeder that you memorized for the quiz, $C_p(t)$ increases from zero at $T=0$ but reaches 3R by $T \approx 270$ for lead and aluminum but is below 3R for diamond. So all we can predict is that $C_p(t)$ will increase from zero and will not get higher than 3R and could fall below 3R when ice melts. So reasonable guess is:

\[ \frac{C_p}{R} \quad 3 \quad \text{ does not exceed 3 by time } T \approx 270 \]

Gas phase was trickiest. According to Fig 1.18 on page 30 that give $C_v(t)$ for Hz. Rotational degrees of freedom have already activated when water boils, $T_2 400K$.

So for $T \geq 400K$, there are 3 rotational and 3 translational degrees of freedom so $C_v = N \frac{F k}{c} = 3R$.

But for ideal gas $C_p = C_v + R$ so

\[ C_p = 4R \quad \text{ when all rotational and translational degrees are active} \]
Since water is non-collinear molecule, total degrees of freedom given by formula on page 2 of guest:

\[ \tilde{f} = 2(3K-6) + 6 = 6(K-1) = 6(3-1) \]

\[ \tilde{f} = 12 \]

So at highest temperatures, when rot., trans., vibrational degrees of freedom active expect

\[ C_p = R + C_v = R + R \cdot \frac{\tilde{f}}{2} = 7R \]

Putting everything together, we make this prediction for \( C_p/T \) vs \( T \) for water:

![Diagram showing the behavior of \( C_p/T \) with temperature.](image-url)