Problem 1: Energy of a Film

a) The best approach to take here is to find a general expression for \( C_A \) and then show that its derivative with respect to \( A \) is zero.

\[
C_A \equiv \frac{dQ}{dT} \bigg|_A
\]

\[
= T \left( \frac{\partial S}{\partial T} \right) \bigg|_A \quad \text{by the second law}
\]

\[
\left( \frac{\partial C_A}{\partial A} \right)_T = T \frac{\partial^2 S}{\partial A \partial T}
\]

\[
= T \frac{\partial}{\partial T} \left( \left( \frac{\partial S}{\partial A} \right)_T \right) \bigg|_A \quad \text{interchanging order of the derivatives}
\]

We use a Maxwell relation to find \( \left( \frac{\partial S}{\partial A} \right)_T \). Note that \( S \) and \( S \) are different variables. I would normally construct a magic square to fine the equivalent derivatives, but for clarity I will go through the more fundamental route here.

\[
dE = T \, dS + S \, dA
\]

\[
dF = dE - d(TS) = -S \, dT + S \, dA
\]

Since \( F \) is a state function, the cross derivatives must be equal.

\[
- \left( \frac{\partial S}{\partial A} \right)_T = \left( \frac{\partial S}{\partial T} \right)_A = -\frac{Nk}{A - b}
\]

Substitute this result into the expression for the derivative of the heat capacity.

\[
\left( \frac{\partial C_A}{\partial A} \right)_T = T \frac{\partial}{\partial T} \left( \frac{Nk}{A - b} \right) \bigg|_A = 0
\]

This shows that the heat capacity at constant area does not depend on the area: \( C_A(T, A) = C_A(T) \).
b) Now we find the exact differential for the energy and integrate up.

\[ dE = T dS + S dA \]

\[ = T \left( \frac{\partial S}{\partial T} \right)_A dT + \left[ T \left( \frac{\partial S}{\partial A} \right)_T + S \right] dA \]

\[ \Rightarrow \left( \frac{\partial E}{\partial A} \right)_T = 0 \]

\[ E(T, A) = E(T) \]

\[ = \int^{T}_{0} C_A(T') dT' + E(T = 0) \]

**Problem 2: Bose-Einstein Gas**

a) In this problem, we just follow the directions.

\[ dE = T dS - P dV \]

\[ = T \left( \frac{\partial S}{\partial T} \right)_V dT + \left[ T \left( \frac{\partial S}{\partial V} \right)_T - P \right] dV \]

\[ dF = dE - d(TS) = -S dT - P dV \]

\[ \Rightarrow - \left( \frac{\partial S}{\partial V} \right)_T = - \left( \frac{\partial S}{\partial T} \right)_V \]

\[ \left( \frac{\partial P}{\partial T} \right)_V = \left( 5/2 \right) a T^{3/2} + 3b T^2 = \left( \frac{\partial S}{\partial V} \right)_T \]

\[ \left( T \left( \frac{\partial S}{\partial V} \right)_T - P \right) = \left( 5/2 \right) a T^{5/2} + 3b T^3 - a T^{5/2} - b T^3 - c V^{-2} \]

\[ = \left( 3/2 \right) a T^{5/2} + 2b T^3 - c V^{-2} \]

Collecting this all together gives

\[ dE = \left( dT^{3/2} V + c T^2 V + f T^{1/2} \right) dT + ((3/2) a T^{5/2} + 2b T^3 - c V^{-2}) dV \]
b) Use the fact that the energy is a state function which requires that the cross derivatives must be equal.

\[
\frac{\partial}{\partial V} \left( \frac{\partial E}{\partial T} \right)_V = \frac{\partial}{\partial T} \left( \frac{\partial E}{\partial V} \right)_V
\]

\[dT^{3/2} + eT^2 = (15/4)aT^{3/2} + 6bT^2\]

\[\Rightarrow d = (15/4)a, \quad e = 6b\]

c) Use the results from b) to simplify the expression for \(dE\) in a).

\[dE = ((15/4)aT^{3/2}V + 6bT^2V + fT^{1/2})dT + ((3/2)aT^{5/2} + 2bT^3 - cV^{-2})dV\]

Integrate with respect to \(T\) first.

\[E = (3/2)aT^{5/2}V + 2bT^3V + (2/3)fT^{3/2} + \mathcal{F}(V)\]

\[\left( \frac{\partial E}{\partial V} \right)_T = (3/2)aT^{5/2} + 2bT^3 + \mathcal{F}'(V) \quad \text{from above}\]

\[= (3/2)aT^{5/2} + 2bT^3 - cV^{-2} \quad \text{from } dE\]

\[\Rightarrow \mathcal{F}' = -cV^{-2}, \quad \mathcal{F} = cV^{-1} + K_E\]

\[E = (3/2)aT^{5/2}V + 2bT^3V + (2/3)fT^{3/2} + cV^{-1} + K_E\]

d) Proceed just as we did above for \(E\).

\[dS = \left( \frac{\partial S}{\partial T} \right)_VdT + \left( \frac{\partial S}{\partial V} \right)_T dV\]

\[C_V/T \quad \left( \frac{\partial P}{\partial T} \right)_V \quad \text{from a)}\]

\[= (dT^{1/2} + eTV + fT^{-1/2})dT + ((5/2)aT^{3/2} + 3bT^2)dV\]

Integrate with respect to \(T\) first.

\[S = \underbrace{(2/3)dVT^{3/2}}_{(5/2)aVT^{3/2}} + \underbrace{(1/2)eVT^2}_{3bVT^2} + \underbrace{fT^{1/2}}_{2fT^{1/2}} + \mathcal{G}(V)\]
\[
\left( \frac{\partial S}{\partial V} \right)_T = \frac{5}{2}aT^{3/2} + 3bT^2 + G'(V) \quad \text{from above}
\]
\[
= \frac{5}{2}aT^{3/2} + 3bT^2 \quad \text{from } dS
\]
\[
\Rightarrow G'(V) = 0, \quad G(V) = K_S
\]
\[
S(T, V) = \frac{5}{2}aVT^{3/2} + 3bVT^2 + 2fT^{1/2} + K_S
\]

**Problem 3: Paramagnet**

a) This is virtually identical in approach to problem 1.

\[
C_M \equiv \left. \frac{dQ}{dT} \right|_M
\]
\[
= T \left( \frac{\partial S}{\partial T} \right)_M \quad \text{by the second law}
\]
\[
\left( \frac{\partial C_M}{\partial M} \right)_T = T \frac{\partial^2 S}{\partial M \partial T}
\]
\[
= T \frac{\partial}{\partial T} \left( \left( \frac{\partial S}{\partial M} \right)_T \right)_M \quad \text{interchanging order of the derivatives}
\]

We will need \( H(T, M) \) for what follows.

\[
M = \frac{A}{T - T_0}H \quad \Rightarrow \quad H = \frac{M}{A}(T - T_0)
\]

We use a Maxwell relation to find \( (\partial S/\partial M)_T \).

\[
dE = TdS + HdM
\]
\[
dF = dE - d(TS) = -SdT + HdM
\]

Since \( F \) is a state function, the cross derivatives must be equal.

\[
-\left( \frac{\partial S}{\partial M} \right)_T = \left( \frac{\partial H}{\partial T} \right)_M = \frac{M}{A}
\]
Substitute this result into the expression for the derivative of the heat capacity.

\[ \left( \frac{\partial C_M}{\partial M} \right)_T = T \frac{\partial}{\partial T} \left( -\frac{M}{A} \right)_M = 0 \]

This shows that the heat capacity at constant magnetization does not depend on the magnetization: \( C_M(T, M) = C_M(T) \).

b)

\[ dE = T \, dS + H \, dM \]

\[ = T \left( \frac{\partial S}{\partial T} \right)_M dT + \left( T \left( \frac{\partial S}{\partial M} \right)_T + H \right) dM \]

\[-MT/A + H = -M T_0/A\]

Do the \( T \) integration first.

\[ E(T, M) = \int_0^T C_M(T') \, dT' + f(M) \]

\[ \left( \frac{\partial E}{\partial M} \right)_T = f'(M) \]

\[ = -\frac{MT_0}{A} \]

\[ \Rightarrow f(M) = -\frac{M^2 T_0}{2A} + K_E \]

\[ E(T, M) = \int_0^T C_M(T') \, dT' - \frac{M^2 T_0}{2A} + K_E \]

c)

\[ dS = \left( \frac{\partial S}{\partial T} \right)_M dT + \left( \frac{\partial S}{\partial M} \right)_T dM \]

\[ = \frac{C_M(T)}{T} dT' - M/A \text{ from a) } \]

\[ S(T, M) = \int_0^T \frac{C_M(T')}{T'} \, dT' + g(M) \]

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\[
\left( \frac{\partial S}{\partial M} \right)_T = g'(M) \quad \text{from above}
\]
\[
= \frac{M}{A} \quad \text{from } dS
\]
\[
\Rightarrow g(M) = -\frac{M^2}{2A} + K_S
\]
\[
S(T, M) = \int_0^T \frac{C_M(T')}{T'} dT' - \frac{M^2}{2A} + K_S
\]

**Problem 4:** Sargent Cycle

a) The equation of state, \( PV = NkT \), shows that if \( V \) is held constant, increasing \( P \) increases \( T \). Thus \( T_3 > T_2 \). Similarly if \( P \) is held constant, increasing \( V \) increases \( T \). Therefore \( T_4 > T_1 \).

For an adiabatic process \( PV^{\gamma} = P_0V_0^{\gamma} \), or equivalently \( TV^{\gamma-1} = T_0V_0^{\gamma-1} \). Since \( \gamma - 1 > 0 \), increasing \( V \) adiabatically decreases \( T \). This tells us that \( T_4 < T_3 \) and \( T_1 < T_2 \). We can put this all together as follows.

\[
\begin{align*}
T_1 < T_2 < T_3 \quad &\Rightarrow \quad T_3 \text{ is the hottest} \\
T_1 < T_4 < T_3 \quad &\Rightarrow \quad T_1 \text{ is the coldest}
\end{align*}
\]

b) For an isotherm

\[
\left( \frac{\partial P}{\partial V} \right)_T = \frac{\partial}{\partial V} \left( \frac{NkT}{V} \right)_T = -\frac{NkT}{V^2} = -\frac{P}{V}.
\]
For an adiabatic path
\[
\left( \frac{\partial P}{\partial V} \right)_S = \frac{\partial}{\partial V} \left( \frac{P_0 V_0^\gamma}{V^\gamma} \right)_T = -\gamma \frac{P}{V}.
\]

Since \( \gamma > 1 \), “adiabats” descend more steeply than isotherms. In the following phase diagrams, illustrating two extreme versions of the Sargent cycle, isotherms have been indicated by dashed lines.

\[ T_4 > T_2 \]

\[ T_4 < T_2 \]

c) The definition of an engine’s efficiency together with the first law of thermodynamics leads to \( \eta = 1 - (|Q_C|/|Q_H|) \). So the problem is reduced to finding expressions for the heat taken in at high temperature \( |Q_H| \) and that dumped at low temperature \( |Q_C| \). Note that by definition there is no heat transfer along the adiabatic parts of the path. The temperature increases in going from 2 to 3, so \( Q_H = C_V (T_3 - T_2) \) in a constant \( V \) process. The temperature of the gas decreases going from 4 to 1, so \( Q_C = C_P (T_1 - T_4) \) or \( |Q_C| = C_P (T_4 - T_1) \) in a constant \( P \) process. Therefore,
\[
\eta = 1 - \frac{|Q_C|}{|Q_H|} = 1 - \frac{C_P (T_4 - T_1)}{C_V (T_3 - T_2)} = 1 - \gamma \frac{T_4 - T_1}{T_3 - T_2}.
\]

d) For a fluid \( dW \)(work done on a substance) = \( -PdV \).
\[
W \equiv \int dW = W_{1\to 2} + W_{2\to 3} + W_{3\to 4} + W_{4\to 1}
\]
\[
W_{1\to 2} = -\int_1^2 P \, dV = -P_1 V_1^\gamma \int_1^2 V^{-\gamma} \, dV
\]
\[
\begin{align*}
W_{2\rightarrow3} &= 0 \quad \text{since} \quad dV \equiv 0 \\
W_{3\rightarrow4} &= -\int_3^4 P \, dV = -P_v \gamma \int_3^4 V^{-\gamma} \, dV \\
W_{4\rightarrow1} &= -\int_4^1 P \, dV = -P_1 \int_4^1 dV \\
&= -P_1(V_1 - V_4) = P_4 V_4 - P_1 V_1 \\
W &= Nk(T_4 - T_1) \\
&= Nk[T_4 - T_1 + \frac{1}{\gamma - 1}(T_2 - T_1 + T_4 - T_3)] \\
&= Nk\left[\frac{\gamma}{\gamma - 1}(T_4 - T_1) - \frac{1}{\gamma - 1}(T_3 - T_2)\right]
\end{align*}
\]
\( \Delta E = \Delta W + \Delta Q = 0 \) for a complete cycle

\( \Rightarrow Q = -W = |Q_H| - |Q_C| \)

\[-W = \frac{Nk}{\gamma - 1} [(T_3 - T_2) - \gamma(T_4 - T_1)] \quad \text{from d)}\]

Alternatively we know that

\[ |Q_H| - |Q_C| = C_V(T_3 - T_2) - C_P(T_4 - T_1) \]

\[ = C_V[(T_3 - T_2) - \gamma(T_4 - T_1)] \]

Equating the two expressions gives

\[ \frac{Nk}{\gamma - 1} = C_V \]

or

\[ Nk = C_V(\gamma - 1) = C_P - C_V \]

**Problem 5: Entropy Change**

We assume that the mixing is done at constant pressure so we will be using the constant pressure heat capacity, \( C_P \). We will also assume \( C_P \) is independent of \( T \) in the region of interest. Take each mass of fluid by some reversible path between the initial and final states to determine \( \Delta E \) and \( \Delta S \). Note that the path taken between the same initial and final states in the actual mixing is irreversible.
No work is done on either fluid in the mixing process. Therefore for each mass of fluid

\[ dE = dQ + dW = 0 \]

\[ = T dS \]

\[ = T \left( \frac{\partial S}{\partial T} \right)_P dT + T \left( \frac{\partial S}{\partial P} \right)_T \frac{dP}{T} = 0 \]

\[ = C_P dT \]

Simple integration then gives the results

\[ \Delta E_1 = C_P (T_F - T_1), \quad \Delta E_2 = C_P (T_F - T_2) \]

The system as a whole is isolated, so

\[ 0 = \Delta Q_1 + \Delta Q_2 = \Delta E_1 + \Delta E_2 = C_P (T_F - T_1) + C_P (T_F - T_2) \]

\( C_P \) drops out of the final line above, and rearrangement gives us the final temperature:

\[ T_F = (T_1 + T_2)/2. \]

Now compute the \( \Delta S \)s for the reversible paths.

\[ dS = \left( \frac{\partial S}{\partial T} \right)_P dT + \left( \frac{\partial S}{\partial P} \right)_T \frac{dP}{T} = 0 \]

\[ \Delta S_1 = \int_{T_1}^{T_F} \frac{C_P}{T} dT = C_P \ln \frac{T_F}{T_1} \]

\[ \Delta S_2 = \int_{T_2}^{T_F} \frac{C_P}{T} dT = C_P \ln \frac{T_F}{T_2} \]

\[ \Delta S_T = \Delta S_1 + \Delta S_2 \]
\[
C_P \ln \left( \frac{T_F}{T_1} + \ln \frac{T_F}{T_2} \right) = C_P \ln \frac{T_F^2}{T_1 T_2}
\]
\[
= 2C_P \ln \frac{T_F}{\sqrt{T_1 T_2}} = 2C_P \ln \left\{ \frac{T_1 + T_2}{2\sqrt{T_1 T_2}} \right\}
\]
\[
= 2MC_P \left| \begin{array}{c}
\text{unit mass} \\
\text{not } = 0 \text{ is positive}
\end{array} \right| \ln \left\{ \frac{T_1 + T_2}{2\sqrt{T_1 T_2}} \right\}
\]

If \( \Delta S_T \) is to be positive for all positive \( T_1 \) and \( T_2 \) for which \( T_1 \neq T_2 \), the argument of the logarithm must be greater than 1, which requires that \( T_1 + T_2 > 2\sqrt{T_1 T_2} \) for all positive \( T_1 \neq T_2 \). We now prove that this is indeed true.

\[
(T_1 - T_2)^2 > 0 \quad \text{square of a real number not } = 0 \text{ is positive}
\]
\[
T_1^2 - 2T_1 T_2 + T_2^2 > 0
\]
\[
T_1^2 + 2T_1 T_2 + T_2^2 > 4T_1 T_2 \quad \text{add } 4T_1 T_2 \text{ to both sides}
\]
\[
(T_1 + T_2)^2 > 4T_1 T_2
\]
\[
T_1 + T_2 > 2\sqrt{T_1 T_2}
\]