Homework 6 Solution due 9 am on Mar 5 (Tu), 2019.
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You may discuss with your friends AFTER you have made due efforts of your own to solve the problems. I trust you. I wish you to fully understand the solutions when you submit your homeworks (and get the full credit).

No solution without your justification will get any credit.

1 [Heat pump]
We could import heat from the external world (outdoors) into a room to warm it up. The set up of the analysis is always the same, Fig. DH6.1:

\[
\begin{array}{c}
\text{T}_H \\
\text{Q}_H \\
\text{W} \\
\text{Q}_L \\
\text{T}_L
\end{array}
\]

Figure DH6.1: Heat pump operation requires: \( Q_L > 0, W > 0 \) and \( Q_H < 0 \).

\( W \) is what we invest, and \(|Q_H|\) is our gain, so \(|Q_H|/W\) is called the coefficient of performance.

If the room temperature \( T_H = 298 \) K and the low-temperature heat source is the \( T_L = 288 \) K underground device, what is the limit of the coefficient of performance?

\textbf{Soln.}
For one cycle the total energy input to the heat pump must be zero:

\[ Q_H + Q_L + W = 0. \tag{DH6.1} \]

For a single cycle the entropy increase of the device must be zero, so with the aid of Clausius’ inequality (\( \Delta S \geq Q/T \)), we have

\[ 0 = \Delta S \geq \frac{Q_H}{T_H} + \frac{Q_L}{T_L}, \text{ that is, } \frac{Q_H}{T_H} + \frac{Q_L}{T_L} \leq 0. \tag{DH6.2} \]

Thus,

\[ \frac{Q_H}{T_H} + \frac{-W - Q_H}{T_L} \leq 0 \tag{DH6.3} \]

or

\[ Q_H \left( \frac{1}{T_H} - \frac{1}{T_L} \right) = |Q_H| \left( \frac{1}{T_L} - \frac{1}{T_H} \right) \leq \frac{W}{T_L}. \tag{DH6.4} \]

Therefore, the coefficient of performance is

\[ \frac{|Q_H|}{W} \leq \frac{1}{T_L} \left/ \left( \frac{1}{T_L} - \frac{1}{T_H} \right) \right\} = \frac{T_H}{T_H - T_L}. \tag{DH6.5} \]
For our case this is 298/10, about 30, a tremendous gain.

2 [Explosion in a cylinder with a piston]
Inside a thermally insulated (i.e., adiabatic) empty (i.e., vacuum) cylinder of volume $10V$ is a small can of volume $V$ containing one mole of a monatomic ideal gas at temperature $15T$. The one wall of the cylinder can move outward, if the internal pressure is higher than the external one which is $P_{ex} = RT/V$. The can is punctured and the gas escapes and eventually reaches a new equilibrium state (see Fig. DH6.2).

![Diagram of explosion in a cylinder with a piston](image)

Figure DH6.2: Initially, the can is filled with a gas (Left) and is inside a vacuum box of volume $10V$. Then, it is punctured and the gas escapes to reach the final equilibrium state (Right).

(1) Find the final temperature $T_F$ and the volume $V_F$ of the gas in the cylinder.

(2) What is the total entropy change due to puncturing the can?

**Soln.**
(1) The initial internal energy is $E = 15C_V T$. Let $V_F$ be the final volume of the gas. Then, $V_F - 10V$ is the volume of the displaced external gas. This requires the system to do work (irreversible, because $P \neq P_{ex}$): $|W| = P_{ex}(V_F - 10V)$, so the final internal energy is

$$E - P_{ex}(V_F - 10V).$$  

(DH6.6)

Thus the final temperature of the gas is

$$T_F = (E - P_{ex}(V_F - 10V))/C_V = 15T - \frac{2}{3}T(V_F/V - 10).$$  

(DH6.7)

Since the equation of state implies that

$$P_{ex}V_F = RT_F \Rightarrow \frac{V_F}{V} = \frac{T_F}{T},$$  

(DH6.8)

we get

$$T \frac{V_F}{V} = 15T - \frac{2}{3}T(V_F/V - 10).$$  

(DH6.9)

That is,

$$\frac{5}{3} \frac{V_F}{V} = 15 + \frac{20}{3} = \frac{65}{3}$$  

(DH6.10)
or
\[ \frac{V_F}{V} = 65 \times \frac{5}{5} = 13. \]  
\[ \text{(DH6.11)} \]
Therefore,
\[ T_F = \frac{P_F V_F}{R} = \frac{RT V_F}{R V} = 13T. \]  
\[ \text{(DH6.12)} \]

or we can use (DH6.7) as
\[ T_F = 15T - \frac{2}{3}T (13 - 10) = 13T, \]  
\[ \text{(DH6.13)} \]
consistent.

(2) We may use the equation of state \( S = S(E, V) \):
\[ \Delta S = C_V \log \frac{E_F}{E_I} + R \log \frac{V_F}{V_I} = C_V \log \frac{T_F}{T_I} + R \log \frac{V_F}{V_I}. \]  
\[ \text{(DH6.14)} \]
Thus,
\[ \Delta S = C_V \log \frac{13}{15} + R \log 13. \]  
\[ \text{(DH6.15)} \]
This is OK, but numerically we get
\[ \Delta S = \frac{3}{2} \times 8.314 \times (-0.1431) + 8.314 \times 2.56 = -1.8 + 21.3 = 19.5 \text{ J/K\cdot mol}. \]  
\[ \text{(DH6.16)} \]

3. [General ideal gas]
Experimentally, the internal energy of a gas is volume-independent under constant temperature, and \( PV \) is a function of \( T \) only, say \( PV = \phi(T) \). Show that \( \phi(T) \propto T \). You may use the following Maxwell’s relation
\[ \left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial P}{\partial T} \right)_V, \]  
\[ \text{(DH6.17)} \]
which we will show in a month. \(^1\)

Soln.
The first law tells us
\[ dE = TdS - PdV. \]  
\[ \text{(DH6.18)} \]

\(^1\) You will understand (in Section 17) the following simple algebra:
\[ \left( \frac{\partial S}{\partial V} \right)_T = \frac{\partial (S, T)}{\partial (V, T)} = \frac{\partial (S, T)}{\partial (V, P)} \frac{\partial (V, P)}{\partial (V, T)} = \frac{\partial (V, P)}{\partial (V, T)} \left( \frac{\partial P}{\partial T} \right)_V. \]
It is said that the internal energy of a gas is volume-independent under constant temperature:

$$\left(\frac{\partial E}{\partial V}\right)_T = 0.$$  \hspace{1cm} (DH6.19)

Thus, (DH6.18) implies

$$0 = T \left(\frac{\partial S}{\partial V}\right)_T - P = T \left(\frac{\partial P}{\partial T}\right)_V - P.$$  \hspace{1cm} (DH6.20)

$PV = \phi(T)$ implies

$$V \left(\frac{\partial P}{\partial T}\right)_V = \phi'(T).$$  \hspace{1cm} (DH6.21)

Therefore, multiplying $V$ to (DH6.20) gives us

$$T \phi'(T) = \phi(T) \Rightarrow d\phi/\phi = dT/T.$$  \hspace{1cm} (DH6.22)

That is, $\phi \propto T$.

4 [Mixing diatomic and monatomic gases]

Assume that the system is, as a whole, adiabatic. Initially, the left-hand half (volume $V$) contains one mole of a monatomic ideal gas A (red) ($C_V = 3R/2$) at temperature $T$ and the right-hand half (volume $V$) contains one mole of diatomic ideal gas B (green) ($C_V = 5R/2$) at temperature $2T$. After the separating wall is removed, eventually, the system reaches a new uniform equilibrium state as illustrated in Fig. DH6.3.

(1) Find the final temperature $T_F$ and pressure $P_F$.
(2) What is the entropy increase? You need not get the numerical answer but may keep $R$ as a symbol.

![Figure DH6.3: The mixing process.](image)

Soln.

(1) Since the internal energy must be conserved:

$$E = \frac{3}{2}RT + \frac{5}{2}R \times 2T = \frac{13}{2}RT = \left(\frac{3}{2}R + \frac{5}{2}R\right)T_F = 4RT_F.$$  \hspace{1cm} (DH6.23)

Thus, $T_F = (13/8)T$. As to the pressure, mixture or not does not matter; what matters is the total number of particles; there are two moles. Thus the final pressure must satisfy

$$P_F(2V) = 2RT_F = \frac{13}{4}RT.$$  \hspace{1cm} (DH6.24)

That is, $P_F = 13RT/8V$.  

4
To find the entropy change we must find a quasistatic process that can connect the initial and the final states. To this end, we invent a process illustrated in Fig. DH6.4

Superposition of the expanded states is adiabatic and reversible, so there is no entropy change in the final step. All the changes are during expansions.

For the red arrow the volume of the red gas is changed from $V$ to $2V$ and the temperature $T$ to $T_F = 13T/8$, that is, the internal energy is from $(3/2)RT$ to $(3/2)R \times 13T/8$. Therefore,
\[
\Delta S_{\text{red}} = \frac{3}{2} R \log \frac{13}{8} + R \log 2. \quad (\text{DH6.25})
\]

For the green arrow the volume of the green gas is changed from $V$ to $2V$ and the temperature $2T$ to $13T/8$, that is, the internal energy is from $(5/2)R(2T)$ to $(5/2)R \times 13T/8$. Therefore,
\[
\Delta S_{\text{green}} = \frac{5}{2} R \log \frac{13}{16} + R \log 2. \quad (\text{DH6.26})
\]

The total entropy change is thus
\[
\Delta S = \frac{3}{2} R \log \frac{13}{8} + \frac{5}{2} R \log \frac{13}{16} + R \log 4. \quad (\text{DH6.27})
\]