Given 1 kg of water at 100°C and a very large (very very large) block of ice at 0°C. A reversible heat engine absorbs heat from the water and expels heat to the ice until work can no longer be extracted from the system. The heat capacity of water is 4.2 J/g·K. At the completion of the process:

a) What is the temperature of the water?
b) How much heat has been absorbed by the block of ice in the process?
c) How much ice has been melted (the heat of fusion of ice is 333 J/g)?
d) How much work has been done by the engine?

(A) Because the block of ice is very large, we can assume its temperature to be constant. In the process the temperature of water gradually decreases. When work can no longer be extracted from the system, the efficiency of the cycle is zero:

\[ e = 1 - \frac{T_{ice}}{T_{water}} = 0°C \]

\[ T_{water} = T_{ice} = 0°C \]
The heat absorbed by the block of ice can be calculated using eq. 4.3 (book) and eq. 4.5. Basically this is a heat engine where work is extracted while there is a temperature difference. So the total heat absorbed by the ice block is computed by integrating the following equation. Note that our variable is the temperature of the hot mass.

\[
e(T) = 1 - \frac{Q_{\text{ice}}}{Q_{\text{water}}} = 1 - \frac{T_{\text{ice}}}{T_{\text{water}}}
\]

\[
dQ_{\text{ice}} = \frac{T_{\text{ice}}}{T_{\text{water}}} dQ_{\text{water}} \rightarrow Q_{\text{ice}} = \int_{373K}^{273K} \frac{T_{\text{ice}}}{T} m_{\text{water}} C_{\text{water}} dT
\]

\[
Q_{\text{ice}} = 1 \text{kg} \times 2J/\text{Kg} \times 273K \times \ln \frac{273}{373} = -357.9 \text{KJ}
\]

The minus sign is just because the work was done by the water, but it is not relevant to this problem.
(C) The amount of melted ice is simple, now we just use the equation for latent heat of melting

\[ M_{\text{ice}} = \frac{Q_{\text{ice}}}{L} = \frac{357.9 \text{kJ}}{333 \text{J/g}} = 1.07 \text{kg} \]

(D) The work is straightforward: It is the difference between the heat available in the water and the heat transferred to the cold reservoir.

\[ W = Q_{\text{water}} - Q_{\text{ice}} = 1 \text{kg} \times 4.2 \text{J/kgK} \times 100 - 357.9 \text{kJ} = 62.1 \text{kJ} \]
2. 10 kg of water at 20°C is converted to ice at -10°C by being put in contact with a reservoir at -10°C. This process takes place at constant pressure and the heat capacities at constant pressure of water and ice are 4180 and 2090 J/kg·K respectively. The heat of fusion of ice is 3.34·10^5 J/kg.

(a) Calculate the heat absorbed by the cold reservoir.

(b) Calculate the change in entropy of the closed system "reservoir + water/ice".

The conversion consists of three processes: (1) water at 20°C --&gt; water at 0°C; (2) water at 0°C --&gt; ice at 0°C; (3) ice at 0°C --&gt; ice at -10°C:

(a) The heat absorbed by the cold reservoir is calculated in those three terms:

\[
\Delta Q_{reservoir} = MC_W \Delta T_w + ML + MC_i \Delta T_i =
\]

\[
= 10 kg \times (4180 \times 20 + 3.34 \cdot 10^5 + 2090 \times 10) J/kg = 4.385 \cdot 10^6 J
\]
(b) Calculate the change in entropy of the closed system “reservoir + water/ice”. Again this is equal to the sum of four different entropy changes, three due to the water entropy changes and one due to the reservoir entropy change: (1) entropy lose of water on cooling. (2) Entropy loss of water on freezing (3) entropy lose of ice on cooling. (4) Entropy gain by the reservoir.

(1) entropy lose of water on cooling.

\[ \Delta S_1 = \int_{293K}^{273K} \frac{M c_p^w dT}{T} = -2955 \text{J/K} \]

(2) Entropy loss of water on freezing

\[ \Delta S_2 = -\frac{M L_f}{T_f} = -12,234 \text{J/K} \]

(3) entropy lose of ice on cooling

\[ \Delta S_3 = \int_{273K}^{263K} \frac{M c_p^i dT}{T} = -780 \text{J/K} \]
(4) Entropy gain by the reservoir

$$\Delta S_4 = \frac{\Delta Q_{res}}{T_{res}} = \frac{4.385 \cdot 10^6 J}{263 K} = 16,673 J/K$$

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 = 704 J/K$$
3.- One mole of Nitrogen ($N_2$) has been compressed at $T_0=273$ K to the volume $V_0=1$ liter in an adiabatically insulated container. The critical parameters for $N_2$ are: $V_c = 3N_b = 0.12$ liter/mol, $T_c = (8/27)(a/k_B b) = 126$ K. The gas goes through the free expansion process ($Q = 0$, $W = 0$, and, thus, $U = 0$), in which the pressure drops down to the atmospheric pressure $P_{atm}=1$ bar. Assume that the gas obeys the van der Waals equation of state in the compressed state, and that it behaves as an ideal gas at the atmospheric pressure.

1.- Compute the $T$ change of the gas in the free expansion. This is easy, we need to find the $T$ initial (using vdW gas) and $T$ final (using ideal gas). You can derive an expression that depends in $T_c$ and $V_c$:

$$U_{vdW} = U_{ideal} - \frac{N^2 a}{V} = \frac{5}{2}RT - \frac{N^2 a}{V}$$

$$\frac{5}{2}RT_f = \frac{5}{2}RT_0 - \frac{N^2 a}{V_0}$$

$$T_f = T_0 - \frac{2}{5}\frac{N^2 a}{RV_0}$$

$$N^2 a = \frac{9}{8}RT_C V_C$$

$$T_f = T_0 - \frac{2}{5} \frac{9}{8} \frac{T_C V_C}{V_0} = 266.2K$$
2. Compute the change in entropy. Again as we know the initial and final T’s and initial and final v, and we also know how is the eq. for the entropy for the vdw case (we replace V by V-Nb in the ideal gas eq.), the result is easy.

\[ S_{vdW} = \frac{f}{2} R \ln T + R \ln (V - Nb) + f(N, m) \]

\[ \Delta S = \frac{5}{2} R \ln \frac{T_f}{T_0} + R \ln \left( \frac{V_f}{V_0 - Nb} \right) = \frac{5}{2} R \ln \frac{T_f}{T_0} + R \ln \left( \frac{V_f}{V_0 - V_C / 3} \right) \]

\[ T_f = T_0 - \frac{9}{20} \frac{T_C V_C}{V_0} = 266.2 \text{ K} \quad V_f = \frac{R T_f}{P_{atm}} = 2.2 \cdot 10^{-2} \text{ m}^3 \]

\[ \Delta S = \frac{5}{2} R \ln \frac{266.2}{273} + R \ln \left( \frac{2.2 \cdot 10^{-2}}{1 \cdot 10^{-3} - 0.04 \cdot 10^{-3}} \right) = -5.24 \cdot 10^{-1} + 26 \approx 25.5 \text{ J/K} \]
4.- For \( N_2 \), the vdW coefficients are \( N^2a = 0.138 \text{ kJ} \cdot \text{liter/mol}^2 \) and \( Nb = 0.0385 \text{ liter/mol} \). Evaluate the work of isothermal and reversible compression of \( N_2 \) (assuming it is a vdW gas) for \( n = 3 \text{ mol}, T = 310 \text{ K}, V_1 = 3.4 \text{ liter}, V_2 = 0.17 \text{ liter} \). Compare this value to that calculated for an ideal gas. Comment on why it is easier (or harder, depending on your result) to compress a vdW gas relative to an ideal gas under these conditions.

The work done on compression of the vdW gas:

\[
\Delta W = -\int_{V_i}^{V_f} PdV = -\int_{V_i}^{V_f} \left( \frac{Nk_B T}{V - Nb} - \frac{N^2 a}{V^2} \right) dV = -Nk_B T \ln \left( \frac{V_f - Nb}{V_i - Nb} \right) + N^2 a \left( \frac{1}{V_i} - \frac{1}{V_f} \right)
\]

\[
\Delta W = 9 \text{mol}^2 \cdot 0.138 \frac{\text{kJ} \cdot \text{l}}{\text{mol}^2} \left( \frac{1}{3.4 \text{l}} - \frac{1}{0.17 \text{l}} \right) - 3 \text{mol} \cdot 8.3 \frac{J}{K \cdot \text{mol}} \cdot 310K \ln \left( \frac{0.17l - 3 \text{mol} \cdot 0.0385 \text{l/mol}}{3.4l - 3 \text{mol} \cdot 0.0385 \text{l/mol}} \right)
\]

\[
= -6.94 \text{kJ} + 31.64 \text{kJ} = 24.7 \text{kJ}
\]

\[
\Delta W = -Nk_B T \ln \left( \frac{V_2}{V_1} \right) = -3 \text{mol} \cdot 8.3 \frac{J}{\text{mol} \cdot K} \cdot 310K \ln \left( \frac{0.17l}{3.4l} \right) = 23.12 \text{kJ}
\]
Depending on the interplay between the first and second terms, it’s either harder or easier to compress the vdW gas in comparison with an ideal gas. If both $V_1$ and $V_2 >> N_b$, the interactions between molecules are attractive, and $W_{vdW} < W_{ideal}$ However, as in this problem, if the final volume is comparable to $N_b$, the repulsive forces at short distances become more significant than the attractive forces at large distances (an increase of the second term overpowers the negative first term). Under these conditions, it is harder to compress the vdW gas rather than an ideal gas.
5.- Consider a Carnot cycle where the working substance is a van der Waals gas (1-2 and 3-4 are isotherms, 2-3 and 4-1 – adiabats). The temperatures of the hot and cold reservoirs are $T_H$ and $T_C$, respectively. Calculate the efficiency of this heat engine and compare it with that for the Carnot cycle with an ideal gas.
\[ e = \frac{\delta Q_H - \delta Q_C}{\delta Q_H} \]

Note: \( U \) state function (no integration needed), \( W \) is not, so integrations is needed.

1 – 2  isothermal expansion (at \( T_H \))  \[ \Delta U = \delta Q + \delta W \quad (\Delta U_{vdW})_T = N^2a \left( \frac{1}{V_i} - \frac{1}{V_f} \right) \]

\[ \delta W = -\int_{V_i}^{V_f} PdV = -\int_{V_i}^{V_f} \left( \frac{Nk_B T}{V-Nb} - \frac{N^2a}{V^2} \right) dV = -Nk_B T \ln \left( \frac{V_f-Nb}{V_i-Nb} \right) + N^2a \left( \frac{1}{V_i} - \frac{1}{V_f} \right) \]

\[ \delta Q_{1-2} = Nk_B T_H \ln \left( \frac{V_2-Nb}{V_1-Nb} \right) \]

Similarly,

\[ \delta Q_{3-4} = Nk_B T_C \ln \left( \frac{V_4-Nb}{V_3-Nb} \right) \]

\[ e = T_H \ln \left( \frac{V_2-Nb}{V_1-Nb} \right) - T_C \ln \left( \frac{V_3-Nb}{V_4-Nb} \right) \]
\[ S_{vdW} = \frac{f}{2} N k_B \ln T + N k_B \ln (V - N b) + \text{const} \]

\[ \Delta S_{vdW} = \frac{f}{2} N k_B \ln \frac{T_i}{T_f} + N k_B \ln \frac{V_f - N b}{V_i - N b} \]

Adiabatic process for a vdW gas:
\[ \frac{f}{2} N k_B \ln \frac{T_i}{T_f} + N k_B \ln \frac{V_f - N b}{V_i - N b} = 0 \]

\[ T_f^{f/2} (V - N b) = \text{const} \]
Using the same expression for e as in part I:

\[ e = \frac{T_H \ln \left( \frac{V_2 - Nb}{V_1 - Nb} \right) - T_c \ln \left( \frac{V_3 - Nb}{V_4 - Nb} \right)}{T_H \ln \left( \frac{V_2 - Nb}{V_1 -Nb} \right)} = \frac{T_H - T_c}{T_H} \]

Which is the same as for the ideal-gas Carnot Engine.