**Chapter 20, six more example problems:**

**(20.28)** Make tea with 0.250 kg of 85.0 °C water and let it cool to 20.0 °C before drinking it.

(a) \[ \Delta S_{\text{water}} = \int_{85.0 \, ^\circ \text{C}}^{20.0 \, ^\circ \text{C}} \frac{\sigma Q}{T} = \int_{358 \, K}^{293 \, K} \frac{m_{\text{water}} \, dT}{T} \]
\[ = 0.250 \, \text{kg} \times 4190 \, \text{J/kg} \cdot \text{K} \times \ln (293 \, \text{K} / 358 \, \text{K}) = -209.9 \, \text{J/K}. \]

[Note: When heat flows out of (or into) a system, its entropy must always decrease (or increase). This is why we get a negative answer here.]

(b) Cooling process is isothermal for the air in the kitchen. Find \( \Delta S_{\text{air}} \).

We first calculate the heat output of water. It is equal to:

\[ -\int_{85.0 \, ^\circ \text{C}}^{293 \, K} mc_{\text{water}} \, dT = -0.250 \, \text{kg} \times 4190 \, \text{J/kg} \cdot \text{K} \times (293 \, \text{K} - 358 \, \text{K}) = +68087.5 \, \text{J}. \]

This is just heat input of air. And it should be positive. Since air temperature is essentially always at 293 K, we have:

\[ \Delta S_{\text{air}} = 68087.5 \, \text{J} / 293 \, \text{K} = 232.4 \, \text{J/K}. \]

Total entropy change of (water + air) is +22.5 J/K. It is positive as expected, since for a non-equilibrium system to reach equilibrium, which is an irreversible process, the total change of entropy of the universe must increase.

**(20.34)** A box separated into two parts of equal volume \( V \). Left side contains 500 molecules of N\(_2\). Right side contains 100 molecules of O\(_2\). Two gases are at the same \( T \). Partition punctured. Equilibrium eventually attained. Assume that each gas made free expansion into the larger volume \( 2V \), with \( T \) not changed.

(a) On average, each side will now have 250 N\(_2\) molecules and 50 O\(_2\) molecules.

(b) \[ \Delta S = 500 \, k_B \ln (2V/V) + 100 \, k_B \ln (2V/V) = 600 \times 1.381 \times 10^{-23} \, \text{J/K} \times \ln 2 \]
\[ = 5.74 \times 10^{-21} \, \text{J/K}. \]

[Note: (i) This answer is very small because 600 molecules is only a tiny amount of Material. It is way less than a mole. The answer would not be so small if a good fraction of a mole of material or more is involved. (ii) The original formula is \( \Delta S = nR \ln (V_f / V_i) \), but \( nR \) is the same as \( Nk_B \).]

(c) To get the same distribution of molecules before the partition is punctured, \( \text{viz.} \), 500 N\(_2\) molecules on the left side and 100 O\(_2\) molecules on the right side, the probability would be \( (1/2)^{500} \times (1/2)^{100} = 10^{-600} \log (1/2) = 10^{-0.618} = 0.241 \times 10^{-180}. \]

[Note: (i) This is an extremely small number. If you do it with a calculator, you would have just gotten zero! (ii) We get it because each molecule has the probability of (1/2) to choose a side. (iii) If the left-side volume is twice as big as the right-side volume, then the probability for a molecule to be on the left side would be (2/3), and the probability for a molecule to be on the right side would be (1/3). How would you have to change the above answer? (iv) In the final simplification to get our answer given above, we have used \( 10^{a+b} = 10^a \times 10^b \), and here \( a = -180 \), and \( b = -0.618. \) Note how difficult it is to get three significant digits in this extremely small number for the sought probability.]
(20.36) Baloon. Volume \( V = 2.40 \, \text{L} \). Number of moles of air \( n = 0.100 \, \text{mol} \). Left to drift in the temporary uninhibited and depressurized Space Station. Sun light through a porthole explodes the balloon, causing free expansion of the air in the balloon into the empty station of volume 425 \( \text{m}^3 \). Calculate \( \Delta S \).

This is an adiabatic free expansion problem. This is not the same as an adiabatic process. The latter is a quasi-equilibrium or quasi-static process, whereas the former is a non-equilibrium process. For a non-equilibrium process, you can not use \( \text{d}S = \text{d}Q / T \). In fact, in this problem, \( \text{d}Q = 0 \), but \( \Delta S = \int \text{d}S > 0 \). [In general, for a non-equilibrium process, \( \text{d}S > \text{d}Q / T \).]

In the book and notes, it has been shown that for an adiabatic free expansion,
\[
\Delta S = nR \ln \left( \frac{V_f}{V_i} \right),
\]
which gives:
\[
\Delta S = 0.100 \, \text{mol} \times 8.314 \, \text{J/mol} \cdot \text{K} \times \ln \left( \frac{425 \, \text{m}^3}{2.40 \times 10^{-3} \, \text{m}^3} \right) = 10.05 \, \text{J/K}.
\]
Strictly speaking, \( V_f = 425 \, \text{m}^3 + 2.40 \times 10^{-3} \, \text{m}^3 \). But the second part is so small in relation to the first part that we can simply neglect this second part in calculating \( V_f \).

(20.38) Carnot engine uses 2 mol of CO\(_2\). Treat as ideal. Maximum temperature 527 \( ^\circ \text{C} \). Maximum pressure 5.00 atm. Heat input 400 J per cycle. Want 300 J useful work (per cycle).

(a) Want to find \( T_C \). \( e = W / Q_H = 300 \, \text{J} / 400 \, \text{J} = 0.75 \) (or 75 \%). But since this is a Carnot cycle, it must be equal to \( 1 - T_C / T_H = 1 - T_C / (527 + 273) \). Hence \( T_C = 0.25 \times 800 \, \text{K} = 200 \, \text{K}, \) or \( -73 \, ^\circ \text{C} \).

(b) To melt 10.0 kg block of ice at 0.0 \( ^\circ \text{C} \), we need \( 10.0 \, \text{kg} \times 334 \times 10^3 \, \text{J/kg} = 3.34 \times 10^6 \, \text{J} \) of heat. Dividing it by the 100 J of heat rejected by the engine per cycle, we need \( 3.34 \times 10^4 \) cycles. But this heat is rejected to a \( -73 \, ^\circ \text{C} \) cold reservoir. It couldn’t melt ice at 0.0 \( ^\circ \text{C} \), or else the engine efficiency will have to be much lower, since we would have to change \( T_C \) from 200 K to 273 K, giving a new \( e \) of \( 1 - 273 \, \text{K} / 800 \, \text{K} = 65.88 \% \). Then with 400 J heat input per cycle, the ejected heat per cycle would have to be 136.5 J, and the work output per cycle would have to be 263.5 J, instead of the original 300 J. Thus this problem is poorly made, and is a contradiction. [Note: We have used the generally true equation for any engine, viz., \( Q_H = |Q_C| + W \), which is the same as \( Q = Q_H + Q_C = W \) because \( \Delta U = 0 \) for any cycle. \( Q_C \) is by definition negative for a heat engine, so \( Q_C = -|Q_C| \). \( Q_H \) and \( W \) are by definition positive for a heat engine. ]
Heat engine. 0.350 mol diatomic gas. Cycle shown.

Process 1→2 is at constant volume. Process 2→3 is adiabatic. Process 3→1 is a constant pressure of 1.00 atm. $\gamma = 1.40$ for the gas.

(a) $p_1 = 1.00$ atm (given). $T_1 = 300$ K (given).

$$V_1 = \frac{nRT_1}{p_1} = \frac{0.350 \text{ mol} \times 0.0821 \text{ atm-L/mol-K} \times 300 \text{ K}}{1.00 \text{ atm}} = 8.62 \text{ L}.$$ 

$$p_2 = p_1 \times (T_2/T_1) = 2 \text{ atm}.$$ 

$$p_3 = p_1 = 1.00 \text{ atm}. \quad T_3 = 492 \text{ K} (\text{given}).$$

$$V_3 = V_2 \times (p_2/p_3)^{1/\gamma} = 14.1 \text{ L}.$$ 

**Double check:** We should have $V_3/V_1 = T_3/T_1$. Indeed, we find that both sides give 1.64 to three significant digits. (Note that here all numbers are calculated to three significant digits only.)

(b) $Q_{1\rightarrow 2} = nC_V \Delta T = 0.350 \text{ mol} \times (5/2) \times 0.0821 \text{ atm-L/mol-K} \times 300 \text{ K} = 21.6 \text{ atm-L}.$

$W_{1\rightarrow 2} = 0$. $\Delta U_{1\rightarrow 2} = Q_{1\rightarrow 2} = 21.6 \text{ atm-L}.$

$Q_{2\rightarrow 3} = 0$ (because it is an adiabatic process).

$\Delta U_{2\rightarrow 3} = -7.85 \text{ atm-L}.$ $W_{2\rightarrow 3} = (p_2V_2 - p_3V_3) / (\gamma - 1) = 7.85 \text{ atm-L}.$

$Q_{3\rightarrow 1} = nC_P \Delta T = 0.350 \text{ mol} \times (7/2) \times 0.0821 \text{ atm-L/mol-K} \times (-192 \text{ K}) = -19.3 \text{ atm-L}.$

$W_{3\rightarrow 1} = 1.00 \text{ atm} \times (8.62 \text{ L} - 14.1 \text{ L}) = -5.48 \text{ atm-L}.$

**Double check:** (i) $Q = \Delta U + W$ should be true in each process. We have used it in the first two processes. So we check it against the third process:

$$\Delta U_{3\rightarrow 1} + W_{3\rightarrow 1} = (-13.8 \text{ atm-L}) + (-5.48 \text{ atm-L}) = -19.3 \text{ atm-L} = Q_{3\rightarrow 1}. \quad \text{OK.}$$

(ii) $\Delta U$ for the whole cycle should be zero. That is, we should have $\Delta U_{1\rightarrow 2} + \Delta U_{2\rightarrow 3} + \Delta U_{3\rightarrow 1} = 0$. Indeed, we get $21.6 \text{ atm-L} + (-7.85 \text{ atm-L}) + (-13.8 \text{ atm-L}) = -0.05 \text{ atm-L}$, which is beyond the accuracy of our calculation. So it is essentially zero.

(c) $W_{\text{cycle}} = W_{1\rightarrow 2} + W_{2\rightarrow 3} + W_{3\rightarrow 1} = 0 + 7.85 \text{ atm-L} + (-5.48 \text{ atm-L}) = 2.37 \text{ atm-L}.$

(d) $Q_H = Q_{1\rightarrow 2} = 21.6 \text{ atm-L}$.

(e) $e = W_{\text{cycle}} / Q_H = 2.37 \text{ atm-L} / 21.6 \text{ atm-L} = 0.110 = 11.0 \%$. A Carnot cycle running between the same minimum and maximum temperatures of this heat engine would have the efficiency $e_{\text{Carnot}} = 1 - T_1/T_2 = 1 - 300/600 = 50 \%$.

Thus we see that the $e$ of this heat engine is far less than the ideal maximum.
(20.46) Cycle $1 \to 2 \to 3 \to 4 \to 1$. $n$ moles of diatomic gas. Calculate thermal efficiency $e$.

$W = W_{2 \to 3} + W_{4 \to 1}$

$W_{2 \to 3} = 2p_0 \times (2V_0 - V_0) = 2p_0V_0$.

$W_{4 \to 1} = p_0 \times (V_0 - 2V_0) = -p_0V_0$.

$W = p_0V_0$ (which is just the area enclosed by the cycle, with height in N/m$^2$, and width in m$^3$. The product of these units is J, as it should be.)

Next, we need to find $Q_H = Q_{1 \to 2} + Q_{2 \to 3}$ (because these $Q$’s are positive, whereas $Q_{3 \to 4}$ and $Q_{4 \to 1}$ are both negative, so the magnitude of their sum is $Q_C$).

The process $1 \to 2$ is an isochoric process (i.e., at constant $V$). So $Q_{1 \to 2} = nC_V\Delta T = n \times (5/2) R (T_2 - T_1) = (5/2) (2p_0 \times V_0 - p_0 \times V_0) = (5/2) p_0V_0$.

The process $2 \to 3$ is an isobaric process (i.e., at constant $p$). So $Q_{2 \to 3} = nC_p\Delta T = n \times (7/2) R (T_3 - T_2) = (7/2) (2p_0 \times 2V_0 - 2p_0 \times V_0) = 7p_0V_0$.

Hence $Q_H = (19/2) p_0V_0$.

We thus find $e = W / Q_H = 2/19 = 10.53\%$.

[Note that we have used the fact that for a diatomic ideal gas near room temperature, we have $C_V = (5/2) R$, and $C_p = (7/2) R$, so that $\gamma \equiv C_p / C_V = 7/5 = 1.4$ .]