General Physics II: Tutorial Material

Lecture 9 (Chapter 8 & Chapter 9, Entropy and thermal machines)

1) Follow-up question on problem 1.2 in Lecture exercise:
An isolated system of volume V_0 consists of two subsystems, labelled 1 and 2 separated by an impermeable (no particle flow) and moving diathermal (exchange of heat) wall of mass M and of negligible volume. Both subsystems contain ideal gas. Initially, both subsystems are at the temperature T_i. Subsystem 1 is in a state characterised by a volume V_{1i} and pressure P_{1i}. Likewise, subsystem 2 is characterised by a volume V_{2i} and pressure P_{2i}. When the system has reached equilibrium, the final temperature is equal to the initial temperature. We had already computed the number of moles n_1 and n_2, the final temperature T_f, the final volumes and final pressure P_f when the system has reached equilibrium. Now determine the entropy variation between the initial state and final equilibrium state. In particular show that for the specific case where $n_1 = n_2 = n$, the result implies an increase in entropy.

Solution: As we learned during the lecture, even though this process is irreversible, we can compute the entropy change as if the system underwent a reversible process (under closest conditions, i.e. an isothermal process). Thus, we consider that subsystem 1 and 2 undergo an isothermal process at $T = T_i = T_f$, which implies that their internal energy is constant, i.e. $dE_{int,1} = \frac{3}{2}n_1RdT = 0$ and $dE_{int,2} = \frac{3}{2}n_2RdT = 0$.

Thus, we can write :

$$\begin{aligned} dE_{int,1} &= -P_1dV_1 + TdS_1 = \frac{n_1RT}{V_1}dV_1 + TdS_1, \\ dE_{int,2} &= -P_2dV_2 + TdS_2 = \frac{n_2RT}{V_2}dV_2 + TdS_2. \end{aligned} \tag{1}$$

Solving these relations for dS and integrating these relations between the initial and final state, i and f, yields :

$$\Delta S_{1,if} = n_1R\log\left(\frac{V_{1f}}{V_{1i}}\right), \text{and}, \Delta S_{2,if} = n_2R\log\left(\frac{V_{2f}}{V_{2i}}\right). \tag{2}$$

In the particular case of $n_1 = n_2 = n$, and thus, $V_{1f} = V_{2f} = \frac{V_0}{2}$ (see exercise tutorial 3), we have $V_{2i} = V_0 - V_{i1}$. Thus, the total entropy variation is given by :

$$\begin{aligned} \Delta S_{if} = \Delta S_{1,if} + \Delta S_{2,if} &= nR\log\left(\frac{V_{1f}}{V_{1i}}\right) + nR\log\left(\frac{V_{2f}}{V_{2i}}\right) \\ &= -nR\log\left(\frac{V_{1i}V_{2i}}{V_{1f}V_{2f}}\right) = -nR\log\left(4\frac{V_{1i}}{V_0}\left(1-\frac{V_{1i}}{V_0}\right)\right) \end{aligned} \tag{3}$$

where $0 < \frac{V_{1i}}{V_0} < 1$. The argument of the logarithm is unity when $\frac{V_{1i}}{V_0} = \frac{1}{2}$ and then the entropy variation vanishes, i.e. $\Delta S_{if} = 0$. This means that in this particular case nothing happens as the initial state is already the equilibrium state. For all other values of $\frac{V_{1i}}{V_0}$, the argument of the logarithm is found between 0 and 1, hence the entropy variation is positive.

2) Entropy production by heat transfer: An isolated system consists of two subsystems labelled 1 and 2, analysed in Chapter 8.5 ("stationary heat transfer between two blocks"). Using the second law, show that in a stationary state, when $T_1 > T_2$, the entropy production dS_{prod} of the whole system is positive when heat flows across these two subsystems despite the fact that the entropy production within individual subsystems is constant (as net heat flow in each subsystem is 0), i.e. $dS_{prod,1} = dS_{prod,2} = 0$.

Solution:
Recall that the entropy production rate of the system cannot be simply obtained by adding the entropy production in each subsystem. The system is in a stationary state, which implies that the overall change of entropy (with time) vanishes : $dS = 0$. Thus, according to the definition of entropy, the change in entropy production is equal to the opposite of the change of entropy due to heat exchange with the environment : $dS_{prod} = -dS_{env.}$.
The entropy change due to environment is the sum of the entropy inflow from the environment into the subsystem 1, $\frac{dQ_{01}}{T_1}$ and the entropy outflow $-\frac{dQ_{02}}{T_2}$ from subsystem 2 to the environment (where the negative sign indicates a loss of entropy).
Thus, we have :

$$dS_{prod} = \frac{dQ_{02}}{T_2} - \frac{dQ_{01}}{T_1}. \tag{4}$$

Since $T_1 > T_2$, heat flows from subsystem 1 to subsystem 2 and thus, $dQ_{12} > 0$. We have established in Chapter 8.5 that $dQ_{01} = dQ_{12} = dQ_{20}$ for a stationary heat flow, and thus :

$$dS_{prod} = \left(\frac{1}{T_2} - \frac{1}{T_1}\right) dQ_{12} > 0. \tag{5}$$

3) An n-mole ideal gas with a volume V_1 expands adiabatically ($Q = 0$) into the vacuum (free expansion) and its volume becomes V_2. Is this process a reversible process? Show that the entropy change is positive, i.e. $\Delta S > 0$. Is this result paradoxical? How can we explain this?

Solution:
First we note that one simple definition of reversibility is that the process can be reversed by switching the signs of Q and W. The free expansion can only be reversed if we apply work to compress the gas isothermally. Thus, the free expansion is not reversible. More technically, the free expansion of the gas into vacuum is not a reversible process since it cannot be controlled to proceed through a succession of many infinitesimally small quasi-statistical paths. Thus, the entropy change cannot be obtained by

$$\Delta S_{env} = \int \frac{dQ_{reverse}}{T} \tag{6}$$

On the other hand, the final state is well defined: Since it is an adiabatic process, $Q = 0$. The pressure of the vacuum is zero, thus no work is done during the expansion and $W = 0$. It follows that

$$\Delta E_{int} = Q - W = 0 \tag{7}$$

Thus, no change in the temperature during the expansion: Thus the final state has the same temperature, T, as the initial state with a volume V_2.

Since the entropy difference between the two states does not depend on the path, ΔS_{system}, calculated between the initial and final states with a reversible isothermal expansion of volume $V_1 \to V_2$, is a valid approximation for ΔS for the free expansion process. Therefore, we can use the previous solution with $T_1 = T_2$. It follows that

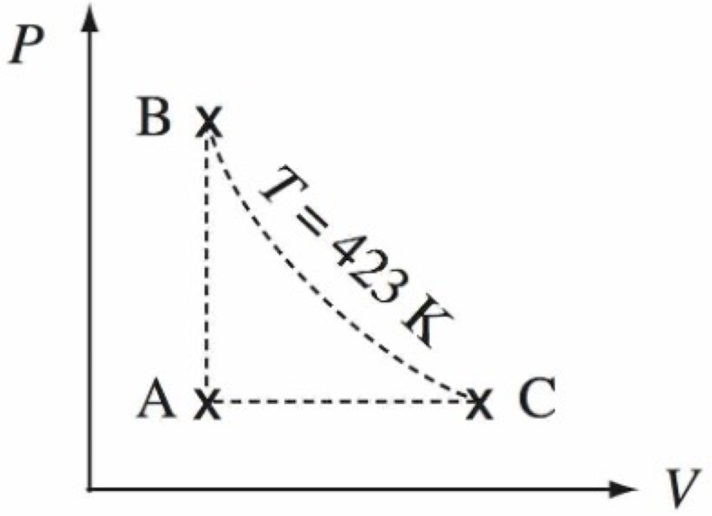
$$\Delta S_{system} = nR\ \log \frac{V_2}{V_1} \tag{8}$$

for the entropy change in the system.

Since $V_1 < V_2$, we have $\Delta S_{system} > 0$, increase of the entropy (production) in the system.

From a usual expression of $\Delta S_{env} = Q/T$, one wants to conclude $\Delta S_{system} = 0$ for the free expansion – but this is the case only for $\Delta S_{system} = \Delta S_{env}$ (i.e., a reversible process, where the entropy change is entirely due to heat exchange with the environment). Instead, the total entropy change is given by $\Delta S_{system} = \Delta S_{env} + \Delta S_{prod}$, meaning in the free expansion process entropy is produced within the system.

4) The figure below shows the P-V diagram of a heat engine with 1 mol of a diatomic molecule ideal gas. At point A, it is at STP (273 K and 1 atm). Points B and C are on the isothermal line at T = 423 K. The process A-B is with a constant volume and A-C with a constant pressure.



a) Obtain the volume, pressure and temperature for the state B and C.

b) Which is the path to generate the work, A-B-C or A-C-B, and why?

c) What is the efficiency, ϵ, of the engine where $\epsilon = \frac{W}{Q_{in}}$?

d) Show that total heat minus total work is zero.

Solution to a:
The initial state A is given by :

$$A: \; T = 273K, P = 1.013 \times 10^5 \frac{N}{m^2}, V = \frac{nRT}{P} = 2.24 \times 10^{-2} m^3. \tag{9}$$

The temperature of the state B is given as T=423 K, and it is on the isovolumetric line with A, we have $V_A = V_B$ and :

$$B: \; T = 423K, P = \frac{nRT}{V} = 1.57 \times 10^5 \frac{N}{m^2}, V = 2.24 \times 10^{-2} m^3. \tag{10}$$

The state C is on the isobaric line with A, i.e. $P_C = P_A$, and on the isothermal line with B, i.e. $T_C = T_B$, thus we have :

$$C: \; T = 423K, P = 1.013 \times 10^5 \frac{N}{m^2}, V = \frac{nRT}{P} = 3.47 \times 10^{-2} m^3. \tag{11}$$

Solution to b:

By noting that no work is done in A→B or B→A, since they are isovolumetric processes, the work done for the cycle A→B→C→A is given by the area below B-C minus the area below A-C on the V-P diagram, which is positive. The work done for the cycle A→C→B→A is given by the area below A-C minus the area below B-C, which is negative. Therefore A→B→C→A is the cycle, which generates the work.

Solution to c:
The work done in the isothermal path, B→C, is given by :

$$\begin{aligned} W_{B\to C} &= nRT\ln\left(\frac{V_C}{V_B}\right) \\ &= 1mol \times 8.314\frac{J}{mol.K} \times 423K \times \ln\left(\frac{3.47\times 10^{-2}}{2.24\times 10^{-2}}\right) = 1539J, \end{aligned} \tag{12}$$

and C→A :

$$\begin{aligned} W_{C\to A} &= P_A(V_A - V_C) \\ &= 1.013\times 10^5\frac{N}{m^2} \times (2.24 - 3.47)\times 10^{-2}m^3 = -1246J. \end{aligned} \tag{13}$$

Therefore the total work, i.e. net-work done, is :

$$W = W_{B\to C} + W_{C\to A} = 1539J - 1246J = 293J. \tag{14}$$

For the heat, processes with positive heat are A→B and B→C. Using the molar specific heat under constant volume is given by $C_V = \frac{n_f}{2}R$, where the number of degrees of freedom, $n_f = 5$ for a diatomic molecule, the heat for A→B is given as :

$$Q_{A\to B} = nC_V\Delta T = 1mol \times \frac{5}{2} \times 8.314\frac{J}{mol.k} \times (423 - 273)K = 3118J. \tag{15}$$

No change in the internal energy is generated in B→C, thus

$$Q_{B\to C} = W_{B\to C} = 1539J, \tag{16}$$

making to total positive heat into the system to be :

$$Q_{in} = Q_{A\to B} + Q_{B\to C} = 4657J. \tag{17}$$

Thus the efficiency of the engine is given by :

$$\epsilon = \frac{W}{Q_{in}} = 0.063, \tag{18}$$

i.e. about 6%.

Solution to d:
Using the molar specific heat under constant pressure, $C_P = C_V + R$, the heat for C→A is given by :

$$Q_{C\to A} = nC_P\Delta T = 1mol \times \frac{7}{2} \times 8.314\frac{J}{mol.k} \times (273 - 423)K = -4365J. \tag{19}$$

Therefore, the sum of the total heat and work is given by :

$$Q_{A\to B} + Q_{B\to C} + Q_{C\to A} - W_{B\to C} - W_{C\to A} = 0J, \tag{20}$$

within the rounding error.

5) We consider now a similar heat engine starting from A as defined above, but the B-C path is done adiabatically. The temperature of B is kept at T = 423 K and on the isovolumetric line with A. The state C remains on the isobaric line with A.

a) Obtain the volume, pressure and temperature of C.

b) Calculate the efficiency.

Solution to a):
The states A and B are given as before :

$$A: \; T = 273K, \; P = 1.013 \times 10^5 \frac{N}{m^2}, \; V = \frac{nRT}{P} = 2.24 \times 10^{-2} m^3, \tag{21}$$

and :

$$B: \; T = 423K, \; P = 1.57 \times 10^5 \frac{N}{m^2}, \; V = 2.24 \times 10^{-2} m^3. \tag{22}$$

The state C is still on the isobaric line with A, i.e. $P_C = P_A$, but now on the adiabatic line with B, i.e. $V_C^\gamma P_C = V_B^\gamma P_B$. By recalling that $V_A = V_B$, we obtain :

$$V_C = V_B \left(\frac{P_B}{P_C}\right)^{\frac{1}{\gamma}} = V_A \left(\frac{P_B}{P_A}\right)^{\frac{1}{\gamma}}, \tag{23}$$

and :

$$T_C = \frac{P_C V_C}{nR} = \frac{P_A V_A}{nR} \left(\frac{P_B}{P_A}\right)^{\frac{1}{\gamma}} \tag{24}$$

For the diatomic ideal gas, we have $C_V = \frac{5}{2}R$ and $C_P = C_V + R = \frac{7}{2}R$, leading to :

$$\frac{1}{\gamma} = \frac{C_V}{C_P} = 0.714 \tag{25}$$

i.e.

$$C: \; T = 373.2K, \; P = 1.013 \times 10^5 \frac{N}{m^2}, \; V = 3.063 \times 10^{-2} m^3. \tag{26}$$

Solution to b):
As for the previous engine, no work for A→B and for C→A :

$$W_{C\to A} = P_A(V_A - V_C) = 1.013 \times 10^5 \frac{N}{m^2} \times (2.24 - 3.06) \times 10^{-2} m^3 = -830J. \tag{27}$$

For the work in B→C, using the adiabatic relation, $V^\gamma P = const = V_B^\gamma P_B$, it follows that :

$$\begin{aligned} W_{B\to C} &= \int_B^C P dV = V_B^\gamma P_B \int_B^C V^{-\gamma} dV = \frac{V_B^\gamma P_B}{1-\gamma} V^{1-\gamma}\Big|_{V_B}^{V_C} \\ &= \frac{V_B^\gamma P_B}{1-\gamma}(V_C^{1-\gamma} - V_B^{1-\gamma}) \end{aligned} \tag{28}$$

and $1 - \gamma = -0.4$ giving $W_{B\to C} = 1034J$. The total work is then :

$$W = W_{B\to C} + W_{C\to A} = 204J. \tag{29}$$

For the heat, $Q_{A\to B} = 3118J$ is unchanged from the previous case, but no heat in B→C since it is an adiabatic process. Therefore, total positive heat is $Q_{in} = Q_{A\to B} = 3118J$ and efficiency :

$$\epsilon = \frac{W}{Q_{in}} = 0.065. \tag{30}$$