

Problem Set 3

Thermodynamics and Climate Change

MOSTEC 2021

Solutions

1. **Concept questions:** Answer the following with a brief explanation.

- (a) For a system undergoing a reversible *process*: (i) Can there be a total positive change in entropy? (ii) Can there be a total negative change in entropy? (iii) Answer parts (i) and (ii) if instead the system is undergoing an *irreversible* process.

In general, the entropy of a *process* can increase or decrease depending on how the state changes. For example, for a solid undergoing a reversible heat transfer, the change in entropy is simply $mc \ln T_2/T_1$, so if $T_2 > T_1$ then the change is positive and if $T_2 < T_1$ the change is negative. Same thing goes for an irreversible process. Entropy may be generated but that may be offset by the change in entropy due to change in state. In general, the Second Law of Thermodynamics does not place any constraints on the change in entropy for a process. The big caveat here though is that for an irreversible process, the net entropy in the *Universe* must increase. So while the entropy of our control volume may decrease, the entropy outside the control volume certainly will increase. Therefore, (i) yes, (ii) yes, (iii) depends on our CV.

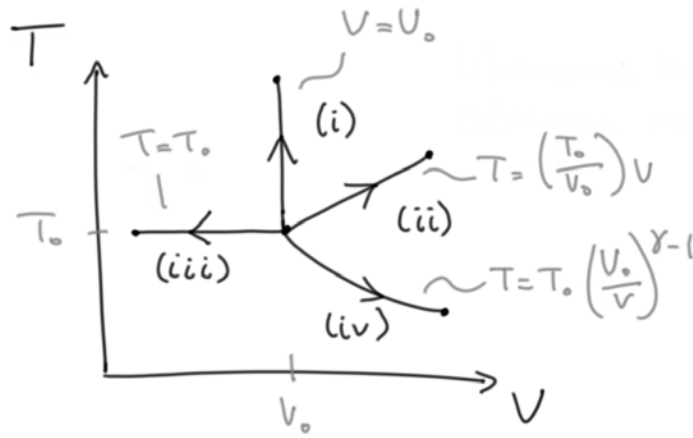


Figure 1: Different processes on T - V diagram for Problem 1. (i) isochoric heating, (ii) isobaric heating, (iii) isothermal compression, and (iv) adiabatic expansion.

- (b) For a system undergoing a reversible *cycle*: (i) Can there be a total positive change in entropy? (ii) Can there be a total negative change in entropy? (iii) Answer parts (i) and (ii) if instead the system is undergoing an *irreversible* cycle.

This is where the Second Law comes into play. The Second Law tells us that

$$\Delta S_{cycle} = \oint \frac{dQ}{T} \geq 0 \quad (1)$$

where $\Delta S_{cycle} = 0$ only for reversible cycles. Again we need to be careful about control volumes but for just our system in general, (i) no, (ii) no, (iii) yes (guaranteed) and no.

- (c) On a T - V diagram (V on x-axis and T on y-axis), sketch the following curves for an ideal gas, each starting from the same initial temperature and volume: (i) Isochoric heating, (ii) isobaric heating, (iii) isothermal compression, (iv) adiabatic expansion

(i) Isochoric heating: $V = \text{constant}$, $T > T_0$

(ii) Isobaric heating: $P = \text{constant}$, $T = \left(\frac{T_0}{V_0}\right) V$

(iii) Isothermal compression: $T = \text{constant}$, $V < V_0$

(iv) Adiabatic expansion: $TV^{\gamma-1} = \text{constant}$, $T = T_0 \left(\frac{V_0}{V}\right)^{\gamma-1}$. For an ideal diatomic gas, $\gamma = 1.4$ and in general is > 1 , so the exponent will be positive and likely < 1 .

See Fig. 1 for these processes plotted on T - V diagram.

- (d) Air conditioners and heat pumps are engines in reverse and can have a COP > 1 (i.e. more heat can be transferred than work is put in). How is this possible?

Thermal energy is being transferred from a colder thermal reservoir to a hotter one, which requires work. The physics are consistent because heat is being transferred and not generated, more heat can be transferred than work is put in.

- (e) Describe generally how to have (i) a reversible process that expands a gas from V_1 to V_2 , (ii) an irreversible process that does the same. Where does the irreversibility come from?

(i) To be reversible, a process must occur slowly such that there is no dissipation and that the system is always in mechanical and thermal equilibrium with the environment. Also any heat transfer that occurs cannot be across a temperature difference. The thermal reservoir must always be at the same temperature as the system boundary over which the heat transfer occurs. (ii) The opposite of all these. Irreversibility comes from diffusive and dissipative processes.

- (f) For each of the following scenarios, state whether or not the Second Law is violated and why: (i) A thermodynamic cycle in which net heat is transferred from a cold object to a hotter object. (ii) A system in communication with only one thermal reservoir and that does work. (iii) A reversible process in which a gas expands isothermally and adiabatically. (iv) Heat flowing from a cold object to a hotter object without any work being done. (v) An irreversible cycle in which the net entropy generated is negative. (vi) A reversible cycle in which the net entropy generated is negative.

(i) Does not violate the Second Law if done using a reversible heat pump. (ii) Does not violate for a single process as we saw with the reversible isothermal heating process. The Second Law places limitations on the net work done for a cycle, and we know that for a system in thermal communication with only one thermal reservoir, $W_{net} \leq 0$. (iii) This is a bit of trick question since this is not possible

unless the number of moles of gas changes over the course of the expansion, which might cause dissipation but does not necessarily violate the Second Law. (iv) Violation. (v) Violation. (vi) Also violation. At best can generate 0 entropy.

2. **Entropy of a Perfect Gas:** We know that the change in entropy for a perfect gas is given by

$$\Delta s = s_2 - s_1 = c_v \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1} \quad (2)$$

Show that this expression is equivalent to:

(a)

$$\Delta s = c_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1} \quad (3)$$

While we could re-derive this equations from the differential forms of the First and Second Laws, the easiest way to solve these problems is to apply the Ideal Gas Law and manipulate the given equation algebraically, taking into account our relationship between c_p and c_v for an ideal gas:

$$\Delta s = c_v \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1} \quad (4)$$

$$= c_v \ln \frac{T_2}{T_1} + R \ln \frac{T_2/P_2}{T_1/P_1} \quad (5)$$

$$= c_v \ln \frac{T_2}{T_1} + R \left[\ln \frac{T_2}{T_1} + \ln \frac{P_1}{P_2} \right] \quad (6)$$

$$= (c_v + R) \ln \frac{T_2}{T_1} + R \ln \frac{P_1}{P_2} \quad (7)$$

$$= \boxed{c_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}} \quad (8)$$

(b)

$$\Delta s = c_p \ln \frac{V_2}{V_1} + c_v \ln \frac{P_2}{P_1} \quad (9)$$

This time, we will start with the expression in part (a) and substitute in the Ideal Gas Law to get T in terms of V :

$$\Delta s = c_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1} \quad (10)$$

$$= c_p \ln \frac{V_2 P_2}{V_1 P_1} - R \ln \frac{P_2}{P_1} \quad (11)$$

$$= c_p \left[\ln \frac{V_2}{V_1} + \ln \frac{P_2}{P_1} \right] - R \ln \frac{P_2}{P_1} \quad (12)$$

$$= c_p \ln \frac{V_2}{V_1} + (c_p - R) \ln \frac{P_2}{P_1} \quad (13)$$

$$= \boxed{c_p \ln \frac{V_2}{V_1} + c_v \ln \frac{P_2}{P_1}} \quad (14)$$

3. **Carnot Solar-Powered Heat Pump:** As the Earth warms, efficient cooling systems are becoming ever more important so as to not compound the problem and create a positive feedback loop between energy usage and carbon emissions driving that energy usage. We want to design a simple solar-powered heat pump based on the ideal reversible Carnot Cycle that can keep a house cool in the summer. Our house can be represented by a thermal reservoir at $T_L = 20^\circ\text{C}$ and the outside by a thermal reservoir at $T_H = 35^\circ\text{C}$.

In our system, as shown in Fig. 2 we have a solar panel powering a small electric motor driving an *isentropic* (reversible and adiabatic) compressor. Our working fluid is assumed to be an ideal gas. From states $1 \rightarrow 2$ in this Reverse Carnot Cycle, our gas flows smoothly past our cold reservoir (house) absorbing thermal energy isothermally at T_L . Then from states $2 \rightarrow 3$ the gas is compressed isentropically, bringing its temperature to T_H . From states $3 \rightarrow 4$, heat is rejected isothermally at T_H to the environment. Finally, from states $4 \rightarrow 1$, the gas expands isentropically, doing some work and bringing the gas back to T_L . The work done in this expansion is used to partially drive the compressor, though some additional solar energy will be needed. Assume the working fluid is air, modeled as a perfect gas with a specific heat at constant volume, $c_v = 718 \text{ J/kg-K}$, and a molar mass of 28.97 g/mol . For this problem, $P_1 = 10 \text{ bar}$ and $P_2 = 1 \text{ bar}$.

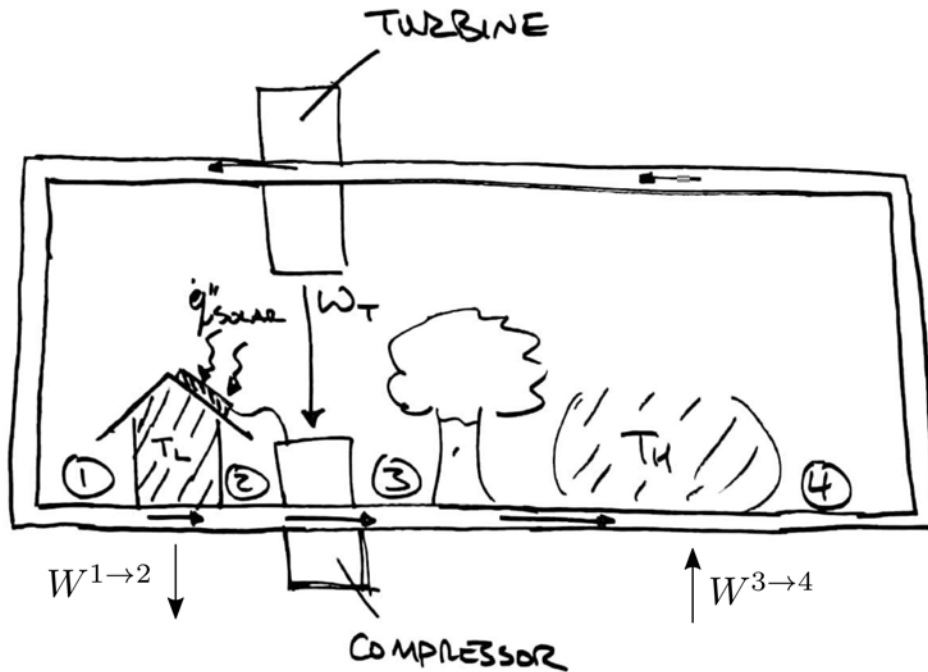


Figure 2: Solar-powered Carnot heat pump for Problem 3.

- (a) Sketch this cycle on a P - V diagram. Clearly label states 1-4 and sketch the curves between them. Be sure to include arrows on the curves to show direction of processes.

See Fig. 3.

- (b) For each process, what is the total work and heat transfer to/from the gas per unit mass?

For this problem we will imagine tracking a packet of air of unit mass flowing around this cycle undergoing heat and work transfer. Our control volume will be drawn around this unit mass and changes shape and size to encapsulate it at all times. Going around the loop, we can write the First and Second Law where relevant for each process:

1 \rightarrow 2 (Isothermal Heating):

First Law:

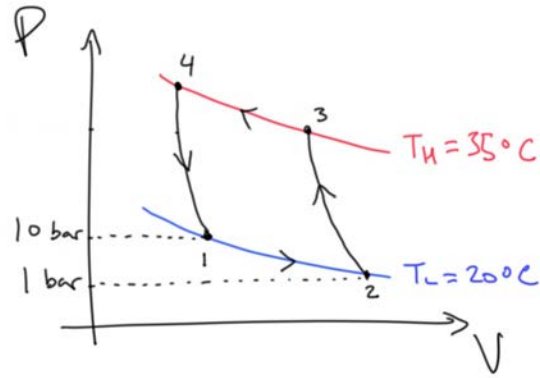


Figure 3: P - V diagram for Problem 3, Part a.

$$U_2 - U_1 = Q^{1 \rightarrow 2} - W^{1 \rightarrow 2} \quad (15)$$

$$\Rightarrow W^{1 \rightarrow 2} = Q^{1 \rightarrow 2} \quad (16)$$

Second Law:

$$S_2 - S_1 = \frac{Q^{1 \rightarrow 2}}{T_L} + \Delta S_{gen} \quad (17)$$

$$\Rightarrow Q^{1 \rightarrow 2} = mT_L(s_2 - s_1) \quad (18)$$

$$= mT_L \left(c_p \ln \frac{T_2}{T_1} - \tilde{R} \ln \frac{P_2}{P_1} \right) \quad (19)$$

$$= -mT_L \tilde{R} \ln \frac{P_2}{P_1} \quad (20)$$

and thus

$$w^{1 \rightarrow 2} = -T_L \tilde{R} \ln \frac{P_2}{P_1} \quad (21)$$

$$= -(20 + 273.15) \frac{8.314 \text{ J/mol-K}}{28.97 \text{ e-3 kg/mol}} \ln \frac{10}{1} \quad (22)$$

$$= \boxed{-194 \text{ kJ/kg}} \quad (23)$$

and $q^{1\rightarrow 2} = w^{1\rightarrow 2}$.

2 → 3 (Adiabatic Compression):

First Law:

$$U_3 - U_2 = \cancel{Q^{2\rightarrow 3}} - W^{2\rightarrow 3} \quad (24)$$

$$\Rightarrow w^{2\rightarrow 3} = u_3 - u_2 \quad (25)$$

$$= c_v(T_H - T_L) \quad (26)$$

$$= 718 \text{ J/kg-K}(35 - 20) \quad (27)$$

$$= \boxed{10.8 \text{ kJ/kg}} \quad (28)$$

and $q^{2\rightarrow 3} = 0$.

3 → 4 (Isothermal Heat Rejection):

First Law:

$$\cancel{U_4 - U_3} = Q^{3\rightarrow 4} - W^{3\rightarrow 4} \quad (29)$$

$$\Rightarrow W^{3\rightarrow 4} = Q^{3\rightarrow 4} \quad (30)$$

Second Law:

$$S_4 - S_3 = \frac{Q^{3\rightarrow 4}}{T_L} + \cancel{\Delta S_{gen}} \quad (31)$$

$$\Rightarrow Q^{3\rightarrow 4} = mT_L(s_4 - s_3) \quad (32)$$

$$= mT_L \left(c_p \ln \frac{T_4}{T_3} - \tilde{R} \ln \frac{P_4}{P_3} \right) \quad (33)$$

$$= -mT_L \tilde{R} \ln \frac{P_4}{P_3} \quad (34)$$

Now we can determine P_3 and P_4 from the fact that the pressures of P_3/P_2 and P_4/P_1 must be equal since both processes are adiabatic expansion/compression operating between the same two temperatures, T_H and T_L . Thus

$$\frac{P_3}{P_2} = \frac{P_4}{P_1} \quad (35)$$

$$\Rightarrow \frac{P_4}{P_3} = \frac{P_1}{P_2} \quad (36)$$

and so

$$w^{3 \rightarrow 4} = -T_H \tilde{R} \ln \frac{P_4}{P_3} \quad (37)$$

$$= T_H \tilde{R} \ln \frac{P_2}{P_1} \quad (38)$$

$$= (35 + 273.15) \frac{8.314 \text{ J/mol-K}}{28.97 \text{ e-3 kg/mol}} \ln \frac{10}{1} \quad (39)$$

$$= \boxed{204 \text{ kJ/kg}} \quad (40)$$

and $q^{3 \rightarrow 4} = w^{3 \rightarrow 4}$.

4 → 1 (Adiabatic Expansion):

Finally, since this process operates between the same temperatures as 2 → 3 and is also adiabatic, we know that the work done must be equal in magnitude and opposite in sign. Thus

$$w^{4 \rightarrow 1} = \boxed{-10.8 \text{ kJ/kg}} \quad (41)$$

and $q^{4 \rightarrow 1} = 0$.

- (c) If 500 W of heat consistently during the day is being added to the house, what mass flow rate is needed for our system to keep the house at a constant temperature?

The cooling process is done between states 1 and 2, so we want $\dot{Q}^{1 \rightarrow 2} = 500 \text{ W}$.

$$\dot{Q}^{1 \rightarrow 2} = \dot{m}q^{1 \rightarrow 2} = 500 \text{ W} \quad (42)$$

$$\Rightarrow \dot{m} = \frac{500 \text{ W}}{q^{1 \rightarrow 2}} \quad (43)$$

$$= \frac{500 \text{ W}}{194 \text{ kJ/kg}} \quad (44)$$

$$= \boxed{2.6 \text{ g/s}} \quad (45)$$

- (d) If we want to minimize the amount of working fluid used, should it have a high or low heat capacity? Why?

In this problem it actually does not matter. Important design factor is the pressure difference between states 1 and 2 and the temperature at which this heat transfer occurs.

- (e) The real system will not be perfectly reversible. Identify a few sources of irreversibility and explain how we can help reduce entropy generation for the real system.

Heat transfer across finite temperature difference, isentropic inefficiencies in the compressor and turbine due to friction and other dissipation, heat loss in the pipe carrying the gas, mixing and turbulence inside the pipes, etc.

4. **Exploring Entropy:** (Coding) Using the nasaPoly library, what is the change in entropy for the gas per mole in the following cases for carbon dioxide? Assume imperfect gas (i.e. $c_p = c_p(T)$). Start by copying the Google Colab template [here](#).

- (a) An expansion that brings the gas temperature from 600 to 400 K with an accompanying pressure drop from 10 to 1 bar.
- (b) A compression that brings the gas from a specific volume of 4 to 2 m^3/mol with an accompanying temperature rise of 300 to 700 K.
- (c) Isobaric heat transfer at 1 bar raising the gas temperature from 600 to 900 K.

See Google Colab Solutions [here](#).

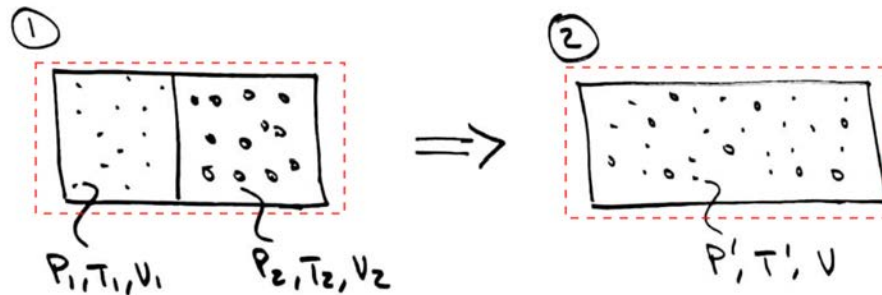


Figure 4: Mixing of argon and nitrogen gas for Problem 5.

5. **(Challenge) Non-Isothermal Gas Mixing:** (Coding) As shown in Fig. 4, we have two gases that are mixed non-isothermally. In state 1, we have 2 kg of nitrogen gas (N_2) at an initial temperature of 400 K and pressure of 5 bar and 1 kg of carbon dioxide gas at an initial temperature of 600 K and pressure of 10 bar. They are separated by an adiabatic membrane at first. Suddenly, this membrane vanishes and the system proceeds to state 2 with the gases evenly mixed throughout the total volume. Throughout this process, there is no heat or work exchanged with environment.

- (a) What volumes do the gases initially occupy in state 1?
- (b) What is the final temperature and pressure of the gas mixture at equilibrium in state 2?
Hint: You will need to solve this part iteratively in code to find a value of temperature that satisfies one of your equations.
- (c) What is the entropy generated in this process?
- (d) What would be the minimum work required to separate these gases isothermally at 300 K?

See [Google Colab Solutions here](#).

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