

Thermodynamics test 1

(duration : 2h)

any calculators allowed.

1 Cycles of an ideal gas (14 points)

(attached, page 2 a graph and page 3 two tables to complete, and return with your copy)

We consider a certain quantity of monoatomic gas, considered as ideal, for which $\bar{C}_V = 3R/2$ and $\bar{C}_p = 5R/2$ with $R = 8.314 \text{ Jmol}^{-1}\text{K}^{-1}$, arranged in a piston-cylinder system whose initial volume is $V_A = 37.4 \text{ L}$, under a pressure $P_A = 2.00 \text{ bar}$ and a temperature $T_A = 300.0 \text{ K}$. The gas is subjected to a cycle (labelled *cycle 1*) described by the following **reversible** processes :

- AB : isothermal compression until pressure $P_B = 4.00 \text{ bar}$
- BC : isobaric compression until the volume $V_C = 10.0 \text{ L}$
- CD : adiabatic expansion up to pressure $P_D = P_A/2$
- DE : isobaric expansion up to volume $V_E = V_A$
- EA : isochoric process to state A

All the steps of reasoning must be clearly justified.

1. Give the literal expressions and numerical values of V_B, T_C, V_D, T_D and T_E . The values of the different variables defining the states A, B, C, D and E will be presented in the table 1.
2. Represent the whole cycle on the Clapeyron's diagram (given in appendix). Is this cycle motor or receptor?
3. Give the literal expressions for the work W_i , the heat quantities Q_i , and the changes in internal energy ΔU_i exchanged between the gas and the surroundings during each process i . Calculate the numerical values (within a precision of 1 J) and present them in the table 2.
4. Calculate the sum of the amounts of heat and work exchanged during this cycle, and the total change in internal energy of the system. Add these values to the table. Comment.
5. Give the literal expressions for the entropy changes ΔS_i^e of the gas system for each process step and make numerical applications to a precision of 0.1 JK^{-1} . Interpret the values obtained.

A second cycle (labelled *cycle 2*) is defined by replacing the processes CD and DE with the processes CD' and D'E such that :

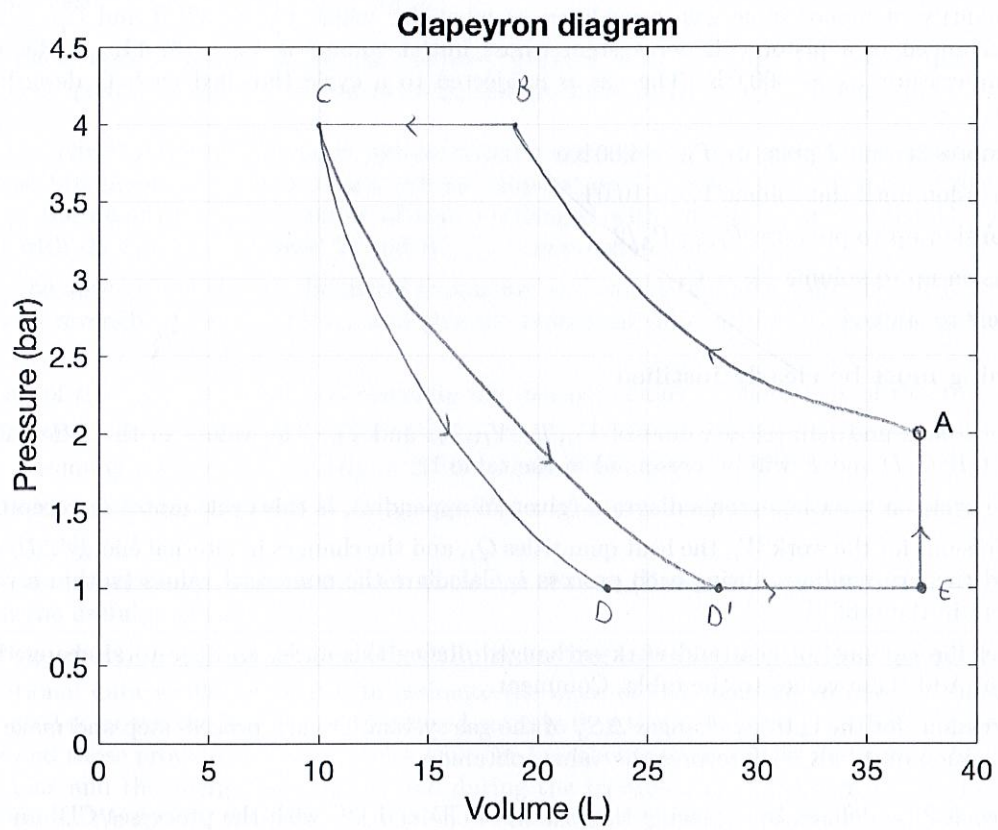
- CD' : **irreversible** adiabatic expansion, induced by an abrupt change in pressure from the pressure $P_{D'}$ ($P_{ext} = P_{D'}$ during the process,
 - D'E : **reversible** isobaric expansion up to the volume $V_E = V_A$.
6. Give the literal expressions and perform the numerical calculations of the volume $V_{D'}$ and the temperature $T_{D'}$ of the point D' (to report in Table 1 and represent the point on the graph of question (2)).
 7. Give the literal and numerical expressions for $Q_i, W_i, \Delta U_i$ for the processes CD' and D'E (report in table 2).
 8. Justifying the reasoning, rank the quantities :
 - $\Delta S_{\sigma}^{cycle 1}$ and $\Delta S_{\sigma}^{cycle 2}$
 - $\Delta S_e^{cycle 1}$ and $\Delta S_e^{cycle 2}$
 - $\Delta S_c^{cycle 1}$ and $\Delta S_c^{cycle 2}$

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Clapeyron's diagram for part I



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Table 1

State	T(K)	P(bar)	V(L)
A	300.0	2.00	37.4
B	300.0	4.00	18.7
C	160.4	4.00	10.0
D	92.2	1.00	23.0
E	150.0	1.00	37.4
D'	112.3	1.00	28.0

Table 2

Process	W(J)	Q(J)	$\Delta U(J)$	$\Delta S_{\sigma}(JK^{-1})$
AB	5187	-5187	0	-17.3
BC	3480	-8705	-5223	-39.0
CD	-2552	0	-2552	0
DE	-1440	3604	2162	30.3
EA	0	5612	5612	25.9
sum cycle ABCDEA.	4675	-4676	0	-0.7
CD'	-1800	0	-1800	
D'E	-940	2351	1410	

2 Freezer (6 points + 2 points bonus)

Technical characteristics of the freezer :

- Internal temperature, T_2 : -20°C
- Electrical power of the motor (which supplies the work to the refrigerant) : $P_{elec} = 200\text{ W}$
- Cooling capacity : $P_{2,real} = 12.5 \times 10^5\text{ Jh}^{-1}$ corresponding to the heat really extracted from the cold reservoir per unit of time

Thermodynamic data of water :

- thermal capacity : $c_{liq} = 4.18\text{ Jg}^{-1}\text{K}^{-1}$ $c_{sol} = 2.06\text{ Jg}^{-1}\text{K}^{-1}$
- Latent fusion heat of water at 0°C : $L = 334\text{ Jg}^{-1}$

Recall the reversible operation of a dithermal machine, working with two reservoirs at temperature T_1 and T_2 , and exchanging the heat quantities respectively equal to Q_1 and Q_2 must satisfy the condition : $Q_1/T_1 + Q_2/T_2 = 0$

1. After having defined the thermodynamic system noted σ , represent in a simplified way the thermodynamic diagram of the freezer functioning in a kitchen room whose temperature T_1 is constant and equal to 20°C . Put on the sketch the signs of the quantities Q_1 (quantity of heat exchanged with the hot source noted 1), Q_2 (quantity of heat exchanged with the cold source noted 2) and W_{comp} (compression work).
2. Specifying the approach, establish the literal expression and calculate numerically the coefficient of performance of the freezer in reversible process COP_{rev} and give the numerical value of the irreversible coefficient of performance COP_{irr} .
3. On the basis of these values, define and calculate the thermodynamic efficiency r_{th} of this freezer.
4. On the data sheet of the freezer, the mass of water that it can freeze per hour is not readable. Calculate this mass in $\text{kg} \cdot \text{h}^{-1}$ assuming the water is initially at 20°C and after freezing at -20°C .
5. What is the electricity consumption $W_{elec,1kg}$ (in Wh) to freeze 1 kilogram of water, assuming the efficiency of the compressor equal to 1?
6. Represent this transformation in the diagram of change of state (Pressure-Temperature) of water, on which you will indicate all the useful quantities.
7. Bonus - **This question can be answered without having solved the previous questions numerically**
 What additional data would be needed to estimate the mass of CO_2 emitted to freeze 1 kilogram of water if the electricity used to power the freezer were produced entirely by a thermal power plant burning methane (CH_4)? With these data and those provided in this exercise, give the literal expression of this amount of CO_2 . We will neglect the CO_2 emissions and the energy losses generated during the transport of the electricity and for the manufacture of the components. We specify that the combustion of one mole of methane generates one mole of CO_2 . The quantity of heat released by the combustion of one mole of methane is called Calorific Value and is noted PC (in $\text{J} \cdot \text{mol}^{-1}$).

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Exercise 1: We have $n = \frac{P_A V_A}{R T_A} = 3.00 \text{ mol}$

$$V_A = 37.4 \text{ L} ; P_A = 2.00 \text{ bar} ; T_A = 300.0 \text{ K}$$

AB: Isothermal compression until $P_B = 4.00 \text{ bar}$.

$$\text{Hence } T_B = T_A$$

$$T_B = \frac{P_B V_B}{nR} \quad T_A = \frac{P_A V_A}{nR}$$

$$\text{Since } T_A = T_B, P_B V_B = P_A V_A \Leftrightarrow V_B = \frac{P_A V_A}{P_B}$$

BC: isobaric compression until $V_C = 10.0 \text{ L}$

$$\text{Hence } P_B = P_C$$

$$P_B = \frac{nRT_B}{V_B} \quad P_C = \frac{nRT_C}{V_C}$$

$$\text{Since } P_B = P_C \Leftrightarrow \frac{T_B}{V_B} = \frac{T_C}{V_C} \Leftrightarrow T_C = T_B \frac{V_C}{V_B}$$

CD: adiabatic reversible expansion up to $P_D = \frac{P_A}{2}$

At state E: From process EA: $V_E = V_A$
From process DE: $P_E = P_D = \frac{P_A}{2}$

Process EA: isochoric process to state A:

$$V_A = \frac{nRT_A}{P_A} \quad ; \quad V_E = \frac{nRT_E}{P_E}$$

$$V_A = V_E \Leftrightarrow \frac{T_A}{P_A} = \frac{T_E}{P_E} \Leftrightarrow T_E = T_A \frac{P_E}{P_A} = \frac{T_A}{2} \quad \text{since } P_E = \frac{P_A}{2}$$

~~Process DE: isobaric expansion up to $V_E = V_A$~~

~~We have P_D~~

CD: adiabatic reversible compression up to $P_D = P_A / 2$

$$P_C V_C^\lambda = P_D V_D^\lambda \Leftrightarrow V_D = V_C \sqrt[\lambda]{\frac{P_C}{P_D}} \quad \text{with } \lambda = \frac{5}{3}$$

$$T_D = \frac{P_D V_D}{nR}$$

2. Since the work is positive the cycle is receptor.
(cycle goes in the trigonometric way)

$$3. W_{AB} = - \int P_{ext} dV = - \int \frac{nRT}{V} dV = -nRT_A \ln \left(\frac{V_B}{V_A} \right)$$

$$\Delta U_{AB} = n \bar{C}_V \Delta T = 0 \text{ J since } \Delta T = 0 \text{ K}$$

$$Q_{AB} = \Delta U_{AB} - W_{AB} = nRT \ln \left(\frac{V_B}{V_A} \right)$$

$$W_{BC} = -P_B (V_C - V_B) \quad \text{since it is isobaric}$$

$$\Delta U_{BC} = n \bar{C}_V \Delta T = n \bar{C}_V (T_C - T_B)$$

$$Q_{BC} = \Delta H_{BC} = n \bar{C}_P (T_C - T_B)$$

$$Q_{CD} = 0 \text{ J since it is adiabatic}$$

$$\Delta U_{CD} = n\bar{C}_V (T_D - T_C) = W \quad \text{since } Q = 0 \text{ J.}$$

$$W_{DE} = - \int P_{\text{ext}} dV = -P_D (V_E - V_D) \quad \text{since it is isobaric}$$

$$\Delta U_{DE} = n\bar{C}_V (T_E - T_D)$$

$$Q_{DE} = \Delta H = n\bar{C}_P (T_E - T_D)$$

$$W_{EA} = 0 \text{ J since it is isochoric}$$

$$\Delta U_{EA} = n\bar{C}_V (T_A - T_E)$$

$$Q_{EA} = \Delta U \quad \text{since } W_{EA} = 0 \text{ J}$$
$$= n\bar{C}_V (T_A - T_E)$$

4. We have $W > 0$ which confirms that the system receives energy we have $\Delta U = 0 \text{ J}$ which is normal since it is a state function and the fluid undergoes a cycle. We have $W + Q = \Delta U$ (almost because of the approximations)
- $\Leftrightarrow W = -Q \quad \text{since } \Delta U = 0 \text{ J}$

$$5. \Delta S_{\sigma}^{AB} = \frac{Q_{AB}}{T_A}$$

(We will not precise Q_{AB} since all the processes are irreversible)

$$\Delta S_{\sigma}^{BC} = \int \frac{\delta Q_{BC}}{T} = n\bar{C}_P \int \frac{dT}{T} = n\bar{C}_P \ln\left(\frac{T_C}{T_B}\right)$$

$$\Delta S_{\sigma}^{CD} = 0 \text{ J.K}^{-1} \text{ since } Q_{CD} = 0$$

$$\Delta S_{\sigma}^{DE} = \int \frac{\delta Q_{BC}}{T} = n\bar{C}_P \int \frac{dT}{T} = n\bar{C}_P \ln\left(\frac{T_E}{T_D}\right)$$

$$\Delta S_{\sigma}^{\text{EA}} = \int \frac{\delta Q_{\text{EA}}}{T} = n\bar{C}_v \int \frac{dT}{T} = n\bar{C}_v \ln\left(\frac{T_A}{T_E}\right)$$

When we have an adiabatic reversible process, $\Delta S_{\sigma} = 0 \text{ J}\cdot\text{K}^{-1}$

Otherwise when it is a compression, the system is more ordered hence ΔS_{σ} is negative. It refers to the processes AB, BC

Otherwise when there is an expansion the system is less ordered hence ΔS_{σ} is positive. It refers to the processes DE and EA.

Since it is a cycle, $\Delta S_{\sigma} = 0 \text{ J}\cdot\text{K}^{-1}$ (here $-0.1 \text{ J}\cdot\text{K}^{-1}$ because of the rounding errors)

6. Since CD' is adiabatic:

$$\Delta U_{\text{CD}'} = W_{\text{CD}'}$$

$$\Leftrightarrow n\bar{C}_v (T_{D'} - T_C) = -P_{D'} (V_{D'} - V_C)$$

$$\Leftrightarrow n\bar{C}_v T_{D'} + nRT_{D'} = n\bar{C}_v T_C + P_{D'} V_C$$

$$\Leftrightarrow T_{D'} = \frac{1}{n(\bar{C}_v + R)} (n\bar{C}_v T_C + P_{D'} V_C)$$

$$V_{D'} = \frac{nRT_{D'}}{P_{D'}}$$

7. $Q_{\text{CD}'} = 0 \text{ J}$ since it is adiabatic

$$\Delta U_{\text{CD}'} = W_{\text{CD}'} = n\bar{C}_v (T_{D'} - T_C)$$

$$\Delta U_{\text{D'E}} = n\bar{C}_v (T_E - T_{D'})$$

$$W_{\text{D'E}} = -P_{D'} (V_E - V_{D'}) \text{ since constant pressure}$$

$$Q_{\text{D'E}} = \Delta H = n\bar{C}_p (T_E - T_{D'}) \text{ since isobaric}$$

8. $\Delta S_{\sigma}^{\text{cycle 1}} = \Delta S_{\sigma}^{\text{cycle 2}} = 0 \text{ J}\cdot\text{K}$ since it is about a cycle and ΔS_{σ} is a state function.

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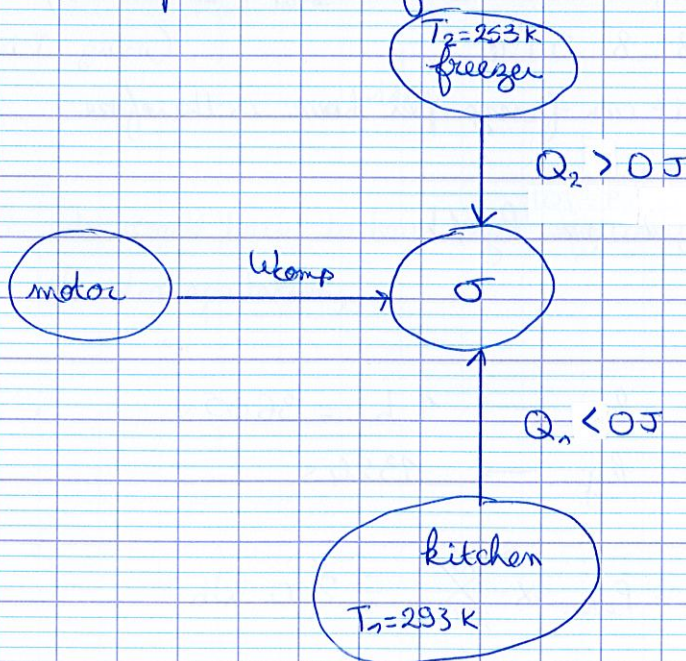
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$\Delta S_c^{\text{cycle 1}} = 0 < \Delta S_c^{\text{cycle 2}}$ since all the process are reversible in cycle 1 and not in cycle 2 and S_c is always non less than 0 J/K for a process that exists.

$\Delta S_e^{\text{cycle 1}} = 0 > \Delta S_e^{\text{cycle 2}}$ since $\Delta S_\sigma = \Delta S_c + \Delta S_e$

Exercise 2:

1. σ represents the fluid that will undergoes the cycles.



$$W_{\text{comp}} = P_{\text{elec}} \times \text{time}$$
$$Q_{2, \text{real}} = P_{\text{real}} \times \text{time}$$

$$2. \text{COP}_{\text{rev}} = \frac{Q_{2,\text{rev}}}{W_{\text{comp}}}$$

$$3. \eta_{\text{th}} = \frac{\text{COP}_{\text{irr}}}{\text{COP}_{\text{rev}}}$$

$$\text{COP}_{\text{irr}} = \frac{P_{2,\text{real}}}{W_{\text{comp}}} = 174\%$$

(use $W_{\text{comp}} = 2000 \times 3600 \text{ s}$ to be consistent with the unit of $P_{2,\text{real}}$)

$$\Delta U_{\text{cycle}} = 0 = Q_{1,\text{rev}} + Q_{2,\text{rev}} + W_{\text{comp}}$$

$$\frac{Q_1}{T_1} + \frac{Q_{2,\text{rev}}}{T_2} = 0 \Leftrightarrow Q_1 = -Q_{2,\text{rev}} \frac{T_1}{T_2}$$

$$\text{Hence } Q_{2,\text{rev}} \left(1 - \frac{T_1}{T_2}\right) = -W_{\text{comp}}$$

$$\Leftrightarrow Q_{2,\text{rev}} = \frac{W_{\text{comp}}}{\left(1 - \frac{T_1}{T_2}\right)}$$

$$\Leftrightarrow \text{COP}_{\text{rev}} = \frac{1}{\left(1 - \frac{T_1}{T_2}\right)} = 633\%$$

Comments: unlike the efficiency, the CoP is not given as a percentage. So:
 $\text{CoP}_{\text{irr}} = 1.74$
 $\text{CoP}_{\text{rev}} = 6.33$

$$3. \eta_{\text{th}} = \frac{\text{COP}_{\text{irr}}}{\text{COP}_{\text{rev}}} = 27\%$$

4. The heat needed to freeze 1g of water is:

$$Q_{\text{needed}} = \left(c_{\text{liq}} (273 - T_1) - L + c_{\text{solid}} (T_2 - 273) \right) \text{ J/g}$$

$$= -459 \text{ J/g} \quad (\text{using } T \text{ in K})$$

The mass it can freeze per hour is therefore

$$N = \frac{P_{2,\text{real}}}{|Q_{\text{needed}}|} = 2.72 \text{ kg/h}$$

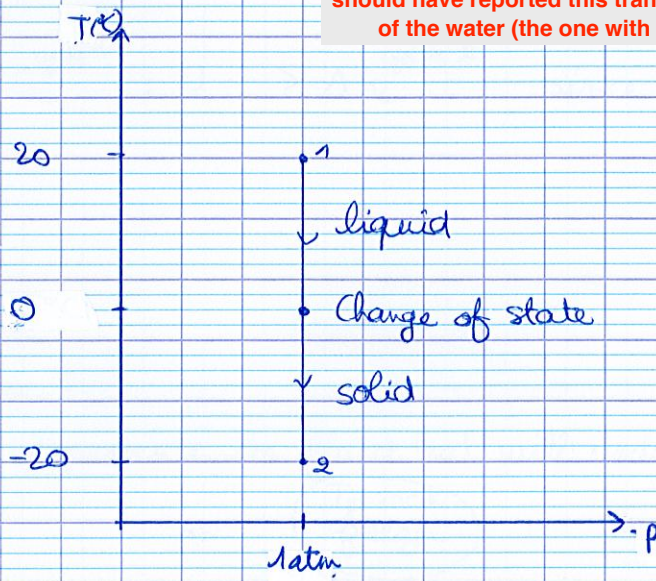
$$5. \quad \begin{array}{l} 2.72 \text{ kg} \rightarrow 1 \text{ h} = 3600 \text{ s} \\ 1 \text{ kg} \rightarrow 1324 \text{ s} \end{array}$$

$$W_{\text{elec. 1kg}} = P_{\text{elec.}} \times \dots$$

Comments: the electricity consumption to freeze 1kg of mass of water is given by the ration of the heat over the CoP irreversible. The heat is the one needed to bring 1kg of liquid water at 20°C to ice at -20°C.

$$Q_{\text{needed 1kg}} = -459 \text{ kJ}$$

6.



Comments: the transformation is correct. However the P,T diagram is usually done with T as x-axis and P as y-axis. You should have reported this transformation on the P,T diagram of the water (the one with the triple and critic point).

7. We would have to have the efficiency of the power plant, the motor, the transportation,

Comments: the transport efficiency is told to be negligible. By doing the energy chain needed to produce the electric power from methane combustion, you would have found that you need the alternator efficiency, the CO₂ molar mass and the methane calorific value.