Solutions Exercise Classes 6 Physical Chemistry 1 2021/2022

Exercise 19

a) Per mole of oxidized glucose 38 mol ATP is formed. If we assume that the energy delivered by the combustion is fully stored in ATP and also completely released during hydrolysis, we find for the efficiency under biological standard conditions ($\Delta G|_{P,T} = W'_{\text{max}}$, the maximal non-volume work)

$$\eta^{\oplus} = \frac{\text{delivered energy}}{\text{energy input}} = \frac{38\Delta_{hydr}G^{\oplus}(\text{ATP})}{\Delta_{comb}G^{\oplus}(\text{gluc})} = \frac{38 \cdot (-30)\ \text{kJ/mol}}{-2880\ \text{kJ/mol}} = 0.40 \quad \text{or} \quad \eta = 40\ \%.$$

b) The complete combustion reaction for glucose is

$$C_6H_{12}O_6(\text{s}) + 6O_2(\text{g}) \rightarrow 6CO_2(\text{g}) + 6H_2O(\text{l}).$$

Under the given conditions the reaction Gibbs free energy for combustion of glucose is

$$\Delta_{comb}G(\text{gluc}) = \Delta_r G^{\oplus} + RT\ln Q.$$

N.B. Q is now the reaction quotient defined with respect to the biological standard conditions and thus has a different value than when Q is defined with respect to thermodynamic standard conditions.
If we assume that the water is present abundantly, so low concentrations of the solutes, we can assume that $a_{H_2O} = 1$ and we find for the reaction quotient ($P^{\oplus} = P^{\ominus} = 1$ bar)

$$Q = \frac{\left(\frac{P_{CO_2}}{P^{\ominus}}\right)^6}{\frac{[\text{gluc}]}{c^{\ominus}}\left(\frac{P_{O_2}}{P^{\ominus}}\right)^6} = \frac{\left(5.3 \cdot 10^{-2}\right)^6}{5.6 \cdot 10^{-2}\,(0.132)^6} = 0.0747, \quad \text{such that}$$

$$\Delta_{comb}G(\text{gluc}) = -2880 \cdot 10^3 + 8.314 \cdot 310 \ln 0.0747\ \text{kJ/mol} = -2887\ \text{kJ/mol}.$$

This value does not deviate much from the reaction energy under standard conditions.

c) The reaction Gibbs free energy for the hydrolysis of ATP under physiological conditions becomes

$$\Delta_{hydr}G(\text{ATP}) = \Delta_r G^{\oplus} + RT\ln Q, \quad \text{in which}$$

Q now has to be expressed with respect to the biological standard, or (we assume again that the activities can be replaced by molar concentrations)

$$Q = \frac{\frac{[ADP]}{[ADP]^{\oplus}}\frac{[P_i]}{[P_i]^{\oplus}}\frac{[H_3O^+]}{[H_3O^+]^{\oplus}}}{\frac{[ATP]}{[ATP]^{\oplus}}} = \frac{\frac{1\cdot 10^{-4}}{1}\frac{1\cdot 10^{-4}}{1}\frac{10^{-7.4}}{10^{-7.0}}}{\frac{1\cdot 10^{-4}}{1}} = 10^{-4.4}, \quad \text{such that}$$

$$\Delta_{hydr}G(\text{ATP}) = -30 \cdot 10^3 + 8.314 \cdot 310 \cdot \ln\left(10^{-4.4}\right) = -56\ \text{kJ/mol}.$$

The efficiency for physiological conditions thus becomes

$$\eta = \frac{38 \cdot (-56)\ \text{kJ/mol}}{-2887\ \text{kJ/mol}} = 0.74 \quad \text{or} \quad \eta = 74\ \%.$$

d) The efficiency of an ideal (reversible) heat engine at the given temperatures is given by

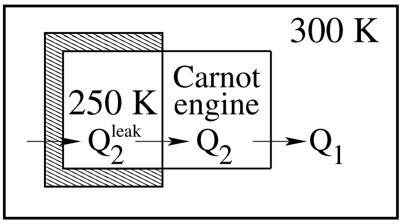
$$\eta = 1 - \frac{T_c}{T_h} = 1 - \frac{873}{1923} = 0.55 \quad \text{or} \quad \eta = 55\ \%.$$

The efficiency of the biological process is therefore significantly higher than that of an ideal diesel engine. The important difference is that for a diesel engine the heat must be transformed into

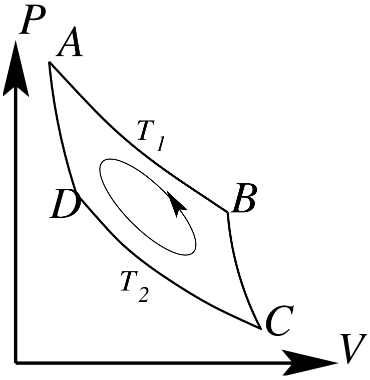
(mechanical) work. The second law of thermodynamics tells us that this is never completely possible, unless the temperatures T_h and T_c are infinitely far apart.
The biological process transforms heat in the form of $\Delta_r G$ directly into chemical energy in ATP, at the same temperature. Nevertheless, the second law of thermodynamics also plays a role there. The entropy of the starting material (glucose) and of the ATP will be different; that difference is already taken into account in the different Gibbs free energies for the combustion of glucose and for the hydrolysis of ATP. The transformation of the stored energy into mechanical energy, for example during a muscle contraction, will again lower the efficiency due to losses.

Exercise 20

a) We assume that the temperature in the deep-cold chamber remains constant. The constant leakage heat then flows from the surroundings into the system and is absorbed at the low temperature isotherm of the Carnot-engine at $T_2 = 250$ K. So $Q_2 = |Q_2^{leak}| > 0$.
The Carnot-engine drops a larger amount of heat Q_1 per minute in the surroundings at the higher temperature T_1, so $Q_1 < 0$.
We can determine the cycle direction by realizing that the Carnot-engine must release net heat ($Q = Q_1 + Q_2 < 0$) to cool the chamber. For a circular process it holds that $\Delta U = 0$ such that $W = -Q > 0$. So we have to do work on the system to keep the chamber at temperature T_2.



(a) The heat flow in and around the freezer



(b) The corresponding Carnot-cycle; $T_1 = 300$ K and $T_2 = 250$ K

b) $Q = 0$ for the adiabats AD and CB, such that there $\Delta U = W$. For a perfect gas the internal energy is only dependent on T; e.g. $U = \frac{3}{2}nRT$ for an *atomic* perfect gas and, more general, $U = C_V T$ for a molecular perfect gas, with C_V independent of T, P and V. [1] Thus ΔU and therefore W is only determined by the initial and final temperatures. $W_{AD} = U(T_D) - U(T_A) = C_V(T_2 - T_1)$ and $W_{CB} = C_V(T_1 - T_2)$, such that $W_{AD} + W_{CB} = 0$. In other words, the net work for the two adiabats is equal to zero.
Thus the total work W of the Carnot-cycle is only determined by the isotherms. Since for the total circular process $\Delta U = 0$ applies, the work is given by $W = -Q = -(Q_1 + Q_2)$

c) For a Carnot-engine it is derived that (Atkins Justification 3A.1):

$$\frac{Q_1}{Q_2} = -\frac{T_1}{T_2}$$

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[1] This might seem confusing. We defined two types of heat capacities: $C_V \equiv \left(\frac{\partial U}{\partial T}\right)_V$ and $C_P \equiv \left(\frac{\partial H}{\partial T}\right)_P$. As for perfect gases U is (linearly) dependent on T and the same holds for $H \equiv U + PV = U + nRT$, both C_V and C_P are independent of T, P and V and $C_P = C_V + nR$. So, for perfect gases we can use C_V to determine $U(T)$ and C_P to determine $H(T)$ for any process whether or not at constant V or P.

For the Carnot-engine we found in a) $Q_2 = Q_2^{leak} = 10$kJ/min, such that
$Q_1 = -\frac{300}{250} 10 \cdot 10^3 = -12$ kJ/min.

d) According to b) the work per minute is $W = -(Q_1 + Q_2) = -(-12 + 10) \cdot 10^3 = 2$ kJ/min.
This is positive work, done on the Carnot-engine as part of the system. This net amount of work will have to be delivered during the compression and expansion of the gas.

e) For this question the choice for the definition of efficiency is important.
The Carnot-process has a limited efficiency due to the second law of thermodynamics. The second law (according to Clausius) states that it is impossible to (as only result) withdraw an amount of heat from a reservoir and completely transfer it to a reservoir with a higher temperature, without doing work. For the Carnot-cycle of the freezer this is expressed in the work being done which ensures that more heat is dropped in the environment at T_1 than is absorbed at T_2. The difference is equal to the work. The efficiency of the Carnot-cycle in a freezer is the quotient of the useful (withdrawn) heat and the work that is required for that $\eta_{Carnot} = \frac{|Q_2|}{|W|} = \frac{10 \cdot 10^3}{2 \cdot 10^3} = 5$, or 500 %. This is more than 100 %! This appears strange, but apparently it does not take a lot of energy (work) to transport a certain amount of heat to a higher temperature. However, the fact is that the larger the temperature difference, the more energy it costs to transport the heat, since (use again $\frac{Q_1}{Q_2} = -\frac{T_1}{T_2}$)

$$\eta_{Carnot} = \frac{|Q_2|}{|W|} = \frac{|Q_2|}{|Q_1| - |Q_2|} = \frac{1}{\frac{|Q_1|}{|Q_2|} - 1} = \frac{1}{\frac{T_1}{T_2} - 1},$$

such that for $T_1 > 2T_2$ we find $\eta_{Carnot} < 1$.
Note the difference compared with the reverse engine, which has an efficiency $\eta_{heatengine} = \frac{|W|}{|Q_1|} < 1$.
For the freezer we could even use the heat that is dumped at T_1 and now is considered to be lost, for other useful purposes.
In the Carnot-cycle no energy is lost since $W = -(Q_1 + Q_2)$.

f) 1. The deep-cold chamber
First we establish that there is no net heat flow in or out of the system (the chamber) ($Q_2^{leak} = -Q_2$), such that $\Delta S = 0$ for the system.
2. The Carnot engine
S is a state function, so for any cyclic process $\oint \mathrm{d}S_{Carnot} = 0$.
We also find this result by looking at the four process steps. The entire Carnot-process (as second system) is reversible or $Q^{rev} = Q$ for all steps.
For the adiabates $Q = 0$ such that also there $\Delta S = 0$.
For the isotherms: $\Delta S_{Carnot,in} = \frac{Q_2}{T_2} = \frac{10 \cdot 10^3}{250} = 40$ J/Kmin, or an entropy increase, which is compensated by $\Delta S_{Carnot,out} = \frac{Q_1}{T_1} = \frac{-12 \cdot 10^3}{300} = -40$ J/Kmin.
So $\Delta S_{Carnot} = \oint \mathrm{d}S_{Carnot} = 0$, as for any cyclic process, whether it is run reversibly or irreversibly.
3. The surroundings
The surroundings absorb heat at T_1 as a consequence of the work done, such that $\Delta S_{sur,in} = \frac{Q^{sur}}{T_1} = \frac{-Q_1}{T_1} = \frac{12 \cdot 10^3}{300} = 40$ J/Kmin. However, at the same time heat is absorbed from the surroundings Q_{leak} and transferred to the Carnot-engine without losses. This heat absorption also occurs at T_1, such that $\Delta S_{sur,out} = \frac{Q^{sur,leak}}{T_1} = \frac{-Q_2}{T_1} = \frac{-10 \cdot 10^3}{300} = -33.3$ J/Kmin. So the net change in entropy is $\Delta S_{sur} = 6.7$ J/Kmin.
4. Total
The total entropy change $\Delta S_{tot} = \Delta S + \Delta S_{Carnot} + \Delta S_{sur} = 6.7$ J/Kmin, which is positive and therefore the process runs spontaneously. This is the case because we added the Carnot cycle as an engine with the work W as a kind of fuel. Without the Carnot engine the only change in S would be the result of Q_{leak}, heating up the chamber until $T_2 = T_1$. The supplied work is required to have the freezer running.

g) Firstly, the efficiency is determined by the Carnot-process, see e), if we assume that the cooling process proceeds reversibly. Besides that, there are losses that are not related to the (ideal) Carnot-process, such as heat leakage at imperfect adiabats, the friction in the pump and electrical losses in the electrical motor driving the pump. If the cooling power of the Carnot-engine is regulated with a thermometer then the heat leakage can be compensated exactly, such that a constant temperature is maintained in the freezing chamber. We can denote the efficiency as a consequence of the friction in the pump and the electrical losses with $\eta_{pump} = \frac{|W|}{|W_{pump}|}$, in which W_{pump} represents the electrical work that is used in the pump motor. The total efficiency then becomes

$$\eta = \frac{|Q_2|}{|W_{pump}|} = \frac{|Q_2|}{|W|} \cdot \frac{|W|}{|W_{pump}|} = \eta_{Carnot}\eta_{pump}.$$

h) For an efficiency of 50 % $\eta = 0.5$. The loss is $|Q_2| = 10$ kJ/min. such that the electrical power the freezer consumes is determined by

$$P = \frac{|W_{pump}|}{\Delta t} = \frac{|Q_2|}{\eta \Delta t} = \frac{10 \cdot 10^3 \text{ J}}{0.5 \cdot 60 \text{ s}} = 333 \text{ Watt}.$$

Exercise 21

First we construct the $P - V$ diagram (see diagram (a)). The isotherms obey $P = \frac{nRT}{V}$ (perfect gas) and thus have the form of the function $P(V) = \frac{constant}{V}$. The exact shape of the adiabats ($\mathrm{d}Q = 0$) is more difficult to determine. For those interested we explain below, as an example, that the slope of the adiabat BC becomes less negative for increasing V_C. [2] For the $P - T$ diagram we find analogously $\frac{P_B}{P_C} = \left(\frac{T_1}{T_2}\right)^{c_v+1}$, with increasing slope in the direction of T_1 according to $\frac{\mathrm{d}P_B}{\mathrm{d}T_1} = P_C \left(\frac{1}{T_2}\right)^{c_v+1} (c_v+1)T_1^{c_v}$. We find the shape of the curved isotherms in the $S - V$ diagram as follows. For the isotherms $\mathrm{d}T = 0$ and thus for our perfect gas $\mathrm{d}U = 0$, or $T\mathrm{d}S - P\mathrm{d}V = 0$. So the slope of those isotherms in the $S - V$ diagram becomes $\frac{\mathrm{d}S}{\mathrm{d}V} = \frac{P}{T} = \frac{nRT}{VT} = \frac{nR}{V}$. So the slope becomes smaller with increasing V. The slope in the $T - H$ diagram is $C_P = C_V + nR = nR(c_v + 1)$.

To determine the direction of the cyclic process we consider the following. $W = W_{AB} + W_{BC} + W_{CD} + W_{DA}$. For the direction indicated in the $P-V$ diagram (all processes are reversible) $W_{AB} = -\int_A^B P\mathrm{d}V < 0$ and equal to minus the area under the curve AB. Analogously $W_{BC} < 0$, $W_{CD} > 0$ and $W_{DA} > 0$. Thus the total work is the closed curve line integral $W = -\oint_{ABCDA} P\mathrm{d}V$, or the area of the enclosed figure $ABCDA$ and with the above inequalities $W < 0$, such that the indicated process direction indeed is in agreement with the a process doing net work on the environment. The process directions for the other diagrams also follow from these considerations.

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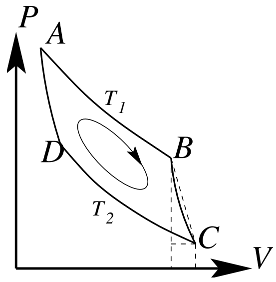
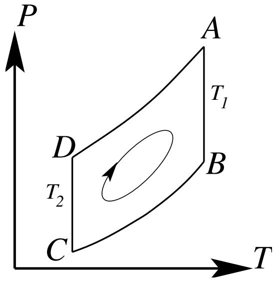
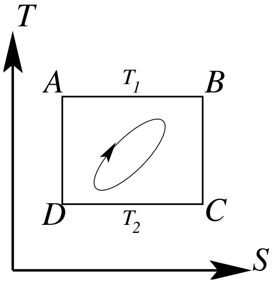
[2] Explanation of the shape of BC in the $P - V$ diagram. Adiabatic and reversible, so $\mathrm{d}U = -P\mathrm{d}V$. Perfect gas, so $\frac{3}{2}nR\mathrm{d}T = -nRT\frac{\mathrm{d}V}{V}$, or $\frac{C_V}{nR}\int \frac{\mathrm{d}T}{T} = -\int \frac{\mathrm{d}V}{V}$, such that $\frac{C_V}{nR} \ln \frac{T_2}{T_1} = -\ln \frac{V_C}{V_B}$. Defining $c_v \equiv \frac{C_V}{nR}$ this results in $\frac{V_B}{V_C} = \left(\frac{T_2}{T_1}\right)^{c_v} = \left(\frac{P_C V_C}{nR}\frac{nR}{P_B V_B}\right)^{c_v}$, such that $\frac{P_C}{P_B} = \left(\frac{V_B}{V_C}\right)^{\frac{c_v+1}{c_v}}$. For the chosen point B we find $\frac{\mathrm{d}P_C}{\mathrm{d}V_C} = -P_B V_B^{\frac{c_v+1}{c_v}} \frac{c_v+1}{c_v} \left(\frac{1}{V_C}\right)^{\frac{c_v+1}{c_v}+1}$. As $c_v \geq \frac{3}{2}$, the slope of the adiabat becomes less negative for increasing V_C.



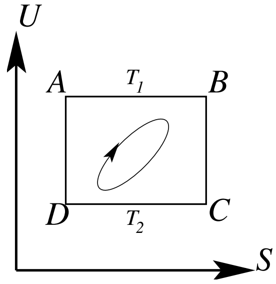
(c) $A \to B$: V increases; P decreases $B \to C$: V increases; P decreases



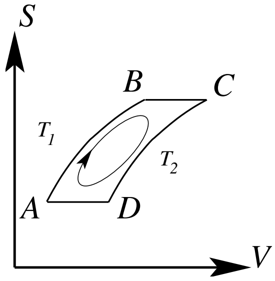
(d) $A \to B$: T constant;P decreases $B \to C$: T decreases; P decreases



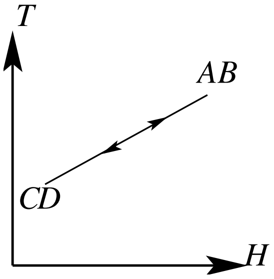
(e) $A \to B$: T constant;S increases $B \to C$: S constant; T decreases



(f) $A \to B$: U constant;S increases $B \to C$: S constant; U decreases



(g) $A \to B$: V increases; S increases $B \to C$: S constant; V increases



(h) $A \to B$: T const.; H const. $B \to C$: T decreases; H decreases