Exercise Classes 6 Physical Chemistry 1 2021/2022

Exercise 19

In exercise 14 we looked at the hydrolysis of ATP and came to the conclusion that this reaction, which can be considered as the discharge of our biological battery, essentially is an irreversible reaction.
Here we will have a look at the charging of this energy battery and in particular at the efficiency of the process.
For that, we consider the efficiency of aerobic respiration in which, during complete combustion (to CO_2 and H_2O) of glucose ($C_6H_{12}O_6$), the energy is stored in ATP and that energy is then completely released during hydrolysis of ATP. Thus the main losses occur in the combustion of glucose.
Under biological standard conditions a fully oxidized glucose molecule results in approximately 38 ATP molecules.
The biological standard Gibbs free energy for the complete combustion of glucose is $\Delta_{comb}G^{\oplus}(\text{gluc}) = -2880$ kJ/mol at $T = 310$ K, whereas for the hydrolysis of ATP, according to

$$\text{ATP}(aq) + \text{H}_2\text{O}(l) \rightarrow \text{ADP}(aq) + \text{P}_i^-(aq) + \text{H}_3\text{O}^+(aq)$$

$\Delta_{hydr}G^{\oplus}(\text{ATP}) = -30$ kJ/mol at that temperature. We will approximate the activities of the dissolved substances by their molar concentrations (molarities).

a) Calculate the efficiency of aerobic respiration under biological standard conditions at $T = 310$ K under the assumption that the energy as a result of the combustion is completely stored in ATP and that the hydrolysis of ATP also proceeds without any loss.
Hint: At constant temperature and pressure ΔG is the maximum energy that a process can supply.

The circumstances in living cells deviate from the biological standard conditions.
The following physiological conditions are more realistic
$P_{CO_2} = 5.3 \cdot 10^{-2}$ bar, $P_{O_2} = 0.132$ bar, [glucose] $= 5.6 \cdot 10^{-2}$ mol/L,
[ATP] = [ADP] = [P_i^-]$= 1.0 \cdot 10^{-4}$ mol/L, pH = 7.4 and $T = 310$ K.

b) Calculate $\Delta_r G$ for the combustion of glucose in living cells.
Hint: first write out the corresponding chemical equation.

c) Calculate the efficiency of aerobic respiration in living cells.

d) Compare the efficiency of the previous part with that of an ideal diesel engine (a heat engine based on the Carnot cycle) that operates between the temperatures $T_h = 1923$ K and $T_c = 873$ K. Explain the striking difference.

Exercise 20

We consider a freezer. The deep-cold chamber is kept at $T_2 = 250$ K (-23 °C). The freezer is placed in an area with a temperature of $T_1 = 300$ K (27 °C), which we consider as the surroundings. The heat transport due to heat leakage from the outside into the chamber is $Q_2^{leak} = 10$ kJ/min. Consider the cooling process of the freezer to be performed by a Carnot-engine (working on a perfect gas) that operates between the two temperatures mentioned.
Choose the deep-cold chamber together with the Carnot engine as the system and assume that the temperature T_1 does not change due to the heat flows from and to the surroundings.
An overview of the heat transport between the chamber, the environment and the Carnot-engine is outlined in Figure 1.

a) Sketch the Carnot-cycle corresponding to Figure 1 in a (P, V)-diagram; indicate the direction of the process cycle.

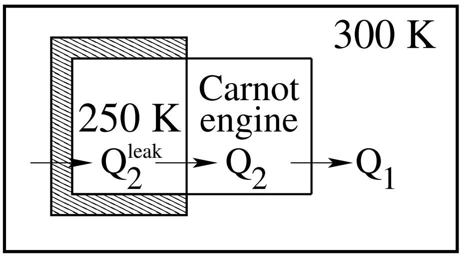

Figure 1: The heat flows in and around the freezer

b) Show that for a perfect-gas-Carnot-engine the net work on the adiabats is equal to zero. Verify that $W = -(Q_1 + Q_2)$, in which Q_1 and Q_2 represent the heat that is absorbed or supplied in the Carnot-cycle at T_1 and T_2.

c) Calculate the heat that is supplied to the surroundings. For this, use $\frac{Q_1}{Q_2} = -\frac{T_1}{T_2}$, which was derived during the lecture.

d) Calculate the work done on the system; also determine the sign of the work.

e) Calculate the efficiency of the Carnot-cycle as the quotient of the useful extracted heat and the work that is required for that. Explain the unexpected result.

f) What is the entropy change of the system and that of the environment as a consequence of the Carnot-process? Explain the answer with the second law of thermodynamics.

In such a freezer the Carnot-process is driven by a pump that compresses the gas. The pump is driven by an electrical motor. The expansion occurs by letting the gas expand spotaneously in a larger volume in the gas pipe. Finally, the adiabats are realized by thermally isolating the pipes in the right places (assume perfect isolation).
We define the efficiency of the freezer as the total efficiency η starting from the electrical outlet to the cooling process. Assume that the net efficiency of the freezer is 50 %.

g) Find an expression for the freezer efficiency in terms of the separate efficiencies that you can identify with the losses that play a role.

h) Calculate the electrical power that is taken up from the electrical outlet.

Exercise 21

A Carnot-cycle (Sadi Carnot, 1796-1832, France) is a special cyclic process. For this, a system is first expanded reversibly and isothermally, then expanded reversibly and adiabatically, after that compressed reversibly and isothermally and finally compressed reversibly and adiabatically to the original state.
A perfect gas goes through a Carnot-cycle in such a direction that net work is done on the environment. Sketch such a process, including the direction of the cyclic process in a

a) $P - V$ diagram; b) $P - T$ diagram; c) $T - S$ diagram;
d) $U - S$ diagram; e) $S - V$ diagram; f) $T - H$ diagram.

The exact shape of the 'curved' processes in these figures does not have to be determined.