Problem 12: Metal Nanoclusters

Nanometer-sized metal clusters have different properties than the bulk materials. To investigate the electrochemical behaviour of silver nanoclusters, the following electrochemical cells are considered:
(on the right-hand side: half-cell with the higher potential)

(I) Ag(s)/ AgCl (saturated) // Ag^+ (aq, c = 0.01 mol L^{-1})/ Ag(s) $U_1 = 0.170$ V

(II) Pt/ Ag_n(s, nanoclusters), Ag^+ (aq, c = 0.01 mol L^{-1}) // AgCl (saturated)/ Ag(s)
a) $U_2 = 0.430$ V for Ag_{10} nanoclusters
b) $U_3 = 1.030$ V for Ag_5 nanoclusters

12.1 Calculate the solubility product of AgCl.

Ag_5- and Ag_{10}-nanoclusters consist of metallic silver but nevertheless have standard potentials different from the potential of metallic bulk silver.

12.2 Calculate the standard potentials of the Ag_5 and Ag_{10} nanoclusters.

12.3 Explain the change in standard potential of silver nanoclusters with particle sizes ranging from very small clusters to bulk silver.

12.4 What happens if you put

a) the Ag_{10} clusters and – in a second experiment – the Ag_5 clusters , into an aqueous solution of pH = 13 ?

b) the Ag_{10} clusters and – in a second experiment – the Ag_5 into an aqueous solution of pH = 5

c) both clusters together into an aqueous solution having a pH of 7 with $c(Cu^{2+}) = 0.001$ mol L^{-1} and $c(Ag^+) = 1\cdot10^{-10}$ mol L^{-1} ? Calculate.
What happens if the reaction proceeds (qualitatively)?

$E^0(Ag/Ag^+) = 0.800$ V
$E^0(Cu/Cu^{2+}) = 0.345$ V
T= 298.15 K

Problem 13: Absorption of Light by Molecules

Absorption of light by molecules is the first step of all photochemical reactions. The Beer - Lambert law relates the absorbance *A* of a solution containing an absorbing species of molar concentration *c* with the optical path length *d*:

$A = \log\frac{P_0}{P} = \varepsilon cd$ ε is the molar absorptivity (also called extinction coefficient).

Light can be considered as a stream of photons, each carrying an energy of $E = h\frac{c}{\lambda}$;

h is Planck's constant, λ is the wavelength and *c* the speed of light .

A solution with a dye concentration of $c = 4 \cdot 10^{-6}$ mol L^{-1} has a molar absorptivity of $\varepsilon = 1.5 \cdot 10^5$ mol^{-1} L cm^{-1}. It is illuminated with green laser light at a wavelength of 514.5 nm and with a power of $P_0 = 10$ nW.

13.1 What is the percentage of light that is absorbed by the sample after a path length of 1 μm?

13.2 Calculate the number of photons per second absorbed by the sample.

The absorption cross section of a molecule is the effective area that captures all incoming photons under low illumination conditions (like an idealized solar cell that would capture all light photons hitting its surface). At room temperature, this corresponds roughly to the molecular area exposed to the light beam. If you calculate it from the molar absorptivity, imagine that all molecules interacting with the light are arranged periodically in a plane perpendicular to the incoming light beam.

13.3 What area is occupied by each molecule?

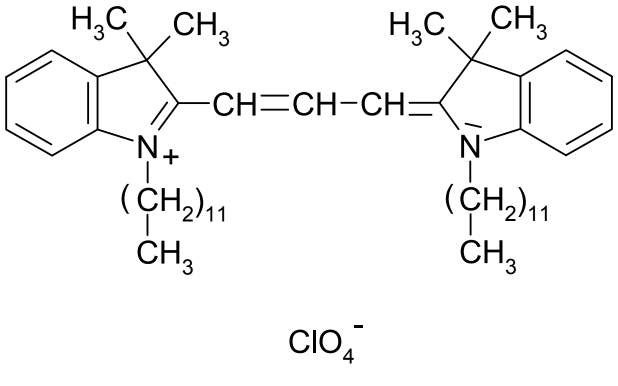
13.4 Calculate the molecular absorption cross section in units of Å ^{2}.

A crucial photochemical reaction for life on our planet is photosynthesis, which converts the absorbed light energy into chemical energy. One photon of 680 nm is necessary to produce one molecule of ATP. Under physiological conditions, the reaction requires an energy of 59 kJ per mol of ATP.

13.5 What is the energy efficiency of photosynthesis?

Problem 14: Observing Single Molecules

Since pioneering work in the early 1990s, the areas of single molecule detection and microscopy have exploded and expanded from chemistry and physics into life sciences. Great progress came about with the demonstration of room-temperature imaging (with a near-field scanning optical microscope) of the carbocyanine dye 1,1'-didodecyl-3,3,3',3'-tetramethylindo-carbocyanine perchlorate (diIC$_{12}$). In this experiment, dye molecules are spread on a sample surface and localized according to their fluorescence signals. The structure of diIC$_{12}$ is shown below.



14.1 Indicate which part of the diIC$_{12}$ molecule is responsible for its fluorescence. Mark the correct answer.

- ***(1) The benzene rings***
- ***(2) The dodecyl side chains***
- ***(3) The four methyl groups at the heterocyclic rings***
- ***(4) The C-N chain connecting the two benzene rings***
- ***(5) The perchlorate ion***

The surface densities of the molecules have to be sufficiently low, if you want to observe them as individual fluorescent spots under a microscope. No more than 10 molecules per µm^2 on the sample surface is a good value.
10 µL of a solution of diIC$_{12}$ in methanol are deposited on a very clean glass cover slide. The drop covers a circular area having a diameter of 4 mm.

14.2 Calculate the molar concentration of the solution necessary to obtain the value of 10 molecules per µm^2. (For this calculation we assume that the transfer of the dye molecules from solution to the sample surface by evaporation of the solvent is homogeneous on the whole wetted area.)

The sample is illuminated with the 543.5 nm-line of a green He-Ne laser. The excitation power is adjusted so that the illuminated area (100 nm in diameter) is hit by $3 \cdot 10^{10}$ photons per second.

14.3 What is the excitation power that has been used?

The absorption cross section is an important parameter for the calculation of the expected fluorescence signal from a single molecule. It may be regarded as the effective area of the molecule that captures all incoming photons. At room temperature, this value corresponds approximately to the size of the dye molecule.

14.4 An illuminated diIC$_{12}$ molecule absorbs $2.3 \cdot 10^5$ photons per second under the described conditions. Calculate the absorption cross section of the diIC$_{12}$ molecule in Å^2 (It can be assumed that the 100 nm diameter area is uniformly illuminated).

The fluorescence quantum yield, i.e. the average number of fluorescence photons created for each absorbed photon, is 0.7 for diIC$_{12}$ (7 fluorescence photons are created for every 10 absorbed photons). The collection efficiency of the generated fluorescence photons by the experimental setup (including filters to suppress remaining excitation light) is 20%, and the photon detection efficiency of the highly sensitive photodetector is 55% over the range of the molecular fluorescence.

14.5 How many fluorescence photons will actually be detected on average by the photodetector during a 10 ms acquisition window if one diIC$_{12}$ molecule is located in the illuminated area?

The fluorescence image is constructed by raster scanning the illuminated area across the sample surface.

14.6 What diameter do you expect for the fluorescence spot corresponding to one single dye molecule? Mark the correct answer.

(1) One pixel
(2) 543.5 nm
(3) 100 nm
(4) 200 nm
(5) Approximately 1 µm

Problem 15: Infrared Spectroscopy of Tetrahedral Molecules

Fig. 1: IR spectrum of CF_4 , intensity vs. wavenumber $\tilde{\nu}$ in cm^{-1}

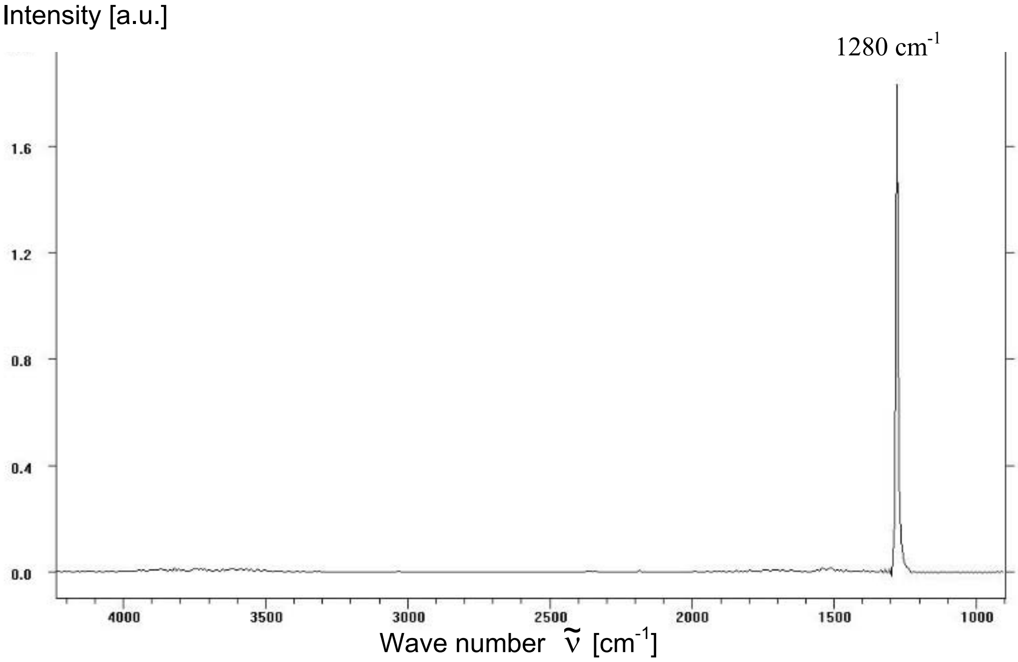
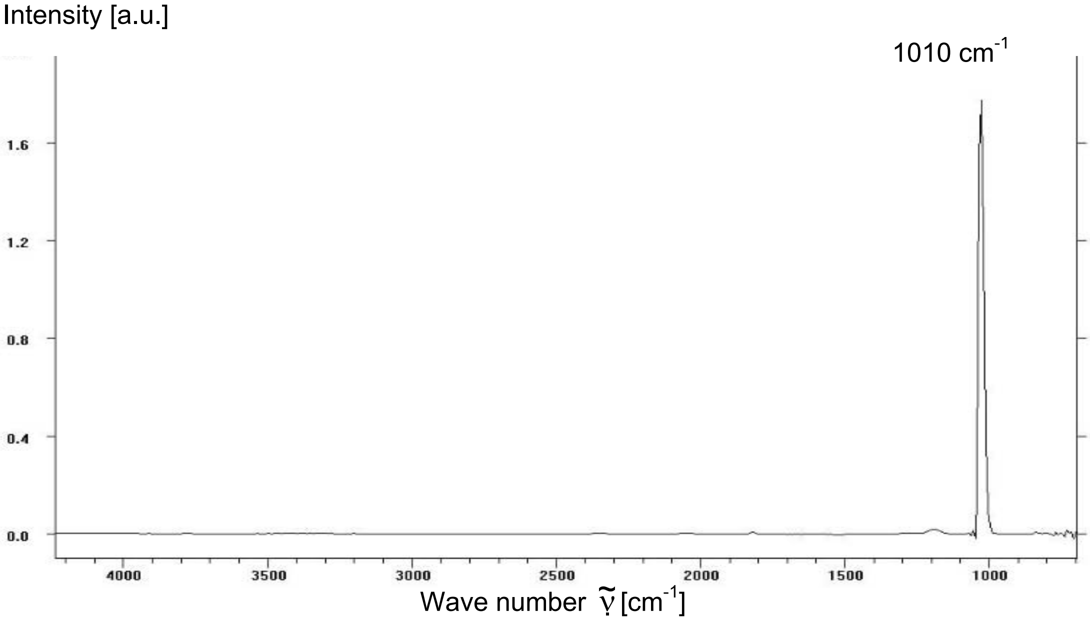


Fig. 2: IR spectrum of SiF_4 , intensity vs. wavenumber $\tilde{\nu}$ in cm^{-1}



The IR spectrum indicates vibrations that depend on the force constant *k* of the bonds that keep the atoms together and the so-called reduced mass μ .

The reduced mass for the highest frequency vibration in a XY_4 molecule is given by

$\mu = \dfrac{3m_X * m_Y}{3m_X + 4m_Y}$ and the vibrational frequency ν is given by $2\pi\nu = \sqrt{\dfrac{k}{\mu}}$.

15.1 Calculate the force constant of CF_4 and SiF_4 and compare their relative strengths with each other.

The heats of formation of CF_4 and SiF_4 are -1222 $kJmol^{-1}$ and -1615 $kJmol^{-1}$.

15.2 What kind of relation is there between them and the force constants of vibration that you have calculated?

The enthalpies of vaporization of carbon and silicon are 717 $kJmol^{-1}$ and 439 $kJmol^{-1}$.

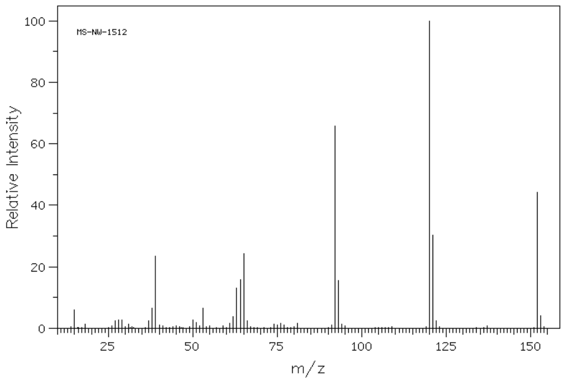
15.3 Take these values into account and comment on the relation between the heat of formation of the gases and the vibrational frequencies again.

Problem 16: Spectroscopy in Bioorganic Chemistry

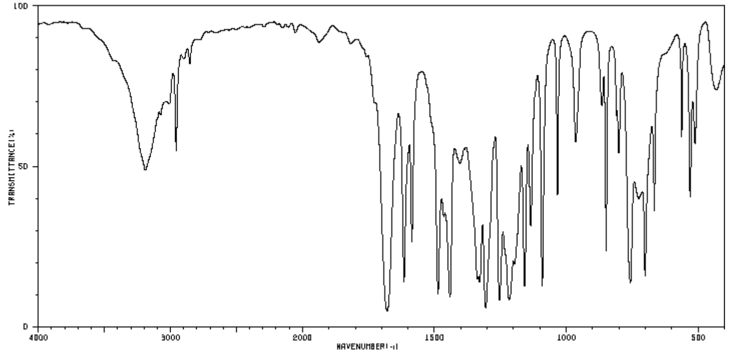
It is well known that strawberries help to reduce minor headaches. The substance **A** that is responsible for this effect is also used as an aroma substance in bubble gums. However, it does not taste like strawberries!

5.00 g of substance **A** yield 2.37 g of water and 6.24 L of carbon dioxide (at 303.7 K and 106.3 kPa). In addition, the infrared (IR), the mass (MS), the ^{1}H-NMR, and the ^{13}C-NMR spectra of the substance have been recorded:

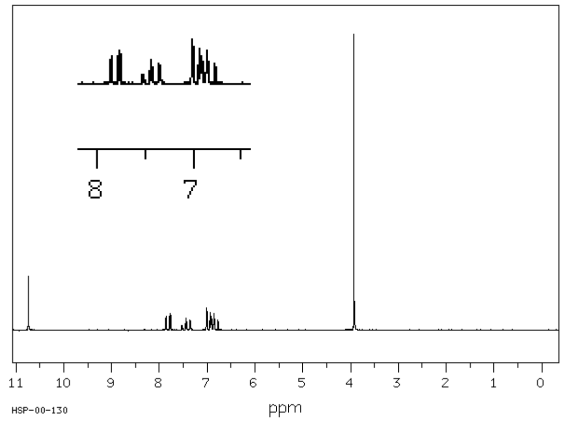
MS spectrum



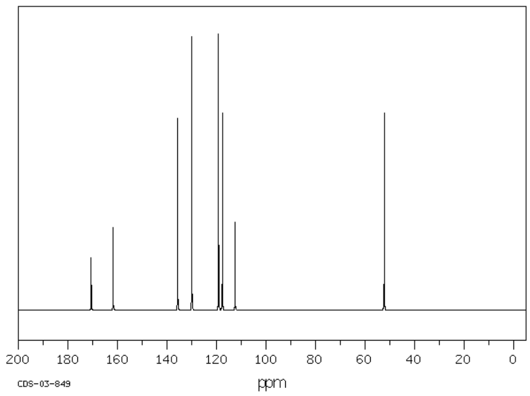
IR spectrum



^{1}H-NMR spectrum



^{13}C-NMR spectrum



16.1 Determine the molecular weight of the substance from the MS spectrum.

16.2 Determine the molecular formula of the substance from the elementary analysis.

16.3 Suggest one fragment B (molecular formula and structure(s)) for the signals at m/z=39 in the MS spectrum. Suggest a probable fragment C (molecular formula and structure(s)) for m/z=65 that contains B.

16.4 The two groups of signals around 3200 cm^{-1} and 1700 cm^{-1} in the IR spectrum are typical of a total of four structural features. Give information about the structures of these four functional groups. What additional information can be given, if the substance contains an –OH group?

Table of IR absorptions:

<table>
<tr><th></th><th>3800</th><th></th><th>3400</th><th></th><th>3000</th><th></th><th>2600</th><th></th><th>2200</th><th></th><th>1800</th><th>group</th></tr>
<tr><td></td><td>v</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td>O−H (free)</td></tr>
<tr><td></td><td></td><td colspan="2">v</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td>O−H (hydrogen bond)</td></tr>
<tr><td></td><td></td><td></td><td></td><td colspan="3">v</td><td></td><td></td><td></td><td></td><td></td><td>O−H (intramolecular h. bond)</td></tr>
<tr><td></td><td></td><td></td><td>s</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td>C−H in C≡C−H</td></tr>
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<tr><td></td><td></td><td></td><td></td><td>w</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td>C−H in C÷C−H</td></tr>
<tr><td></td><td></td><td></td><td></td><td></td><td>s</td><td></td><td></td><td></td><td></td><td></td><td></td><td>C−H (alkanes)</td></tr>
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<tr><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td>m</td><td></td><td>C=C=C</td></tr>
<tr><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td>w</td><td>C=C</td></tr>
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<tr><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td>s</td><td>C=O</td></tr>
</table>

The interatomic bond that absorbs the light is bold. The intensities correspond to strong (s), medium (m), weak (w) and varying intensity (v). An aromatic bond is marked by "÷".

16.5 Assign the total of six signals at 4.0 ppm, 6.5 – 8.0 ppm, and 10.8 ppm in the ^{1}H-NMR spectrum to moieties that you expect in the unknown substance (consider 16.3 and 16.4).

Simplified table of ^{13}C-NMR chemical shifts:

C=O	C÷C, C=C	C≡C			O−C	CH, CH_2, CH_3
200 ppm 180 170	160 150 140 130 120 110	100 90	80	70	60 50	40 30 20 10

An aromatic bond is marked a "÷".

16.6 Assign the signals at 52 ppm, 170 ppm, and 110 – 165 ppm in the ^{13}C-NMR spectrum to moieties that you expect in the unknown substance (consider 16.3 and 16.4).

Simplified table of ^{1}H-NMR chemical shifts:

OH, COOH, CHO		C÷CH	C=CH	OCH_x	CH	CH_2	CH_3
12 ppm 10	9	8 7 6	5	4	3	2	1

An aromatic bond is marked by "÷".

A very simple rule helps to understand NMR spectra: The chemical shift increases with decreasing electron density at the nuclei. This is the reason why you may estimate relative chemical shift values from I- and M- effects.

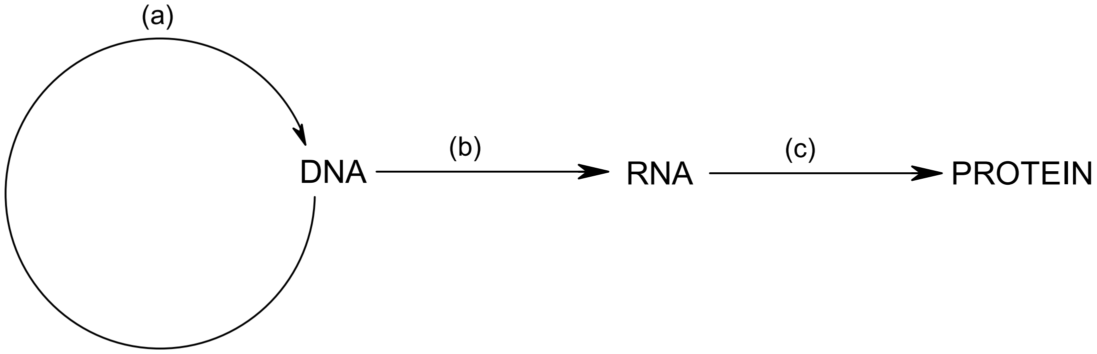
You will have to combine the chemical shift information with your knowledge about I- and M-effects to make distinctions between potential isomers. You may also consider the fine splitting of the signals at 6.8, 6.9,7.5, and 7.8 ppm in the ^{1}H-NMR spectrum and the –O–H band in the IR spectrum.

16.7 Suggest <u>one</u> molecular structure for the unknown substance. Assign the resonances at 6.8, 6.9, 7.5, and 7.8 ppm in the ^{1}H-NMR spectrum and the signals at 52 and 161 ppm in the ^{13}C-NMR spectrum to individual atoms in your solution structure. According to your solution, suggest fragments that explain the signals at m/z=92 and m/z=120 in the MS spectrum. Write down the structural feature that is responsible for the low wave number of the –O–H band.

16.8 The substance A is related to a drug widely used against headaches. Write down the chemical structure of this drug.

Problem 17: DNA, RNA, Proteins

The “central dogma of Molecular Biology“ describes the transfer of genetic information from DNA via RNA to protein:



(a): replication (b): transcription (c): translation

The chemical structures of the biopolymers DNA, RNA and proteins enable them to play such important roles for all forms of life. Fifty years ago, in 1953, James Watson and Francis Crick published a structure of DNA in the journal “Nature” which involves specific interactions between nucleobases in complementary strands.

17.1 Draw the line-bond structure of the nucleotide 2’-deoxyadenosine 5’-monophosphate (dAMP, disodium salt) and of the bases cytosine, guanine, and thymine. Indicate the correct hydrogen bonds between the nucleobases as they occur in the Watson-Crick double strand.

17.2 How does the composition of RNA differ from that of DNA, and how does that affect the chemical stability of the molecule?

Proteins are probably the most versatile biomolecules, with immensely varying properties that are determined by their amino-acid sequence.

17.3 Write down three general functions of proteins.

17.4 Draw a reaction scheme with line-bond structures that shows how two amino acids combine to form a dipeptide. What conformation does the peptide bond usually adopt?
Which high-molecular weight particle catalyses the formation of peptide bonds in human cells during translation?

17.5 Draw the stereochemical formula of the tripeptide L-Ser − L-Va − L-Gly indicating the charges at the isoelectric point.

Problem 18: Fatty acid degradation

Grizzly bears love eating fish. Since the rivers are frozen in winter, they have to build up body fat in autumn which they burn during hibernation.

18.1 Draw a typical triglyceride and name its building blocks. Mark centres of chirality.

The reaction cascade specific to fatty acid degradation is called "β-oxidation". It takes place in the mitochondria of the bear's cells. In each cycle of β-oxidation an acetyl group is split off the fatty acid and two different reaction partners A,B are reduced.

18.2 Write down the complete names and the commonly used abbreviations of the molecules A and B.
Draw the line bond structures of the reactive moieties of these molecules in the oxidized and reduced forms.

The acetyl group is further oxidized in a second reaction cycle, which takes place in the matrix of the mitochondrion.

18.3 What is the name of this reaction cycle?
Which oxidation product is released from the cycle? What are the reduced products?

The reduced products A and B are reoxidized to build up adenosine triphosphate (ATP) in a third cascade of reactions, called the respiratory chain, at the inner mitochondrial membrane.

18.4 What is the oxidation product of the respiratory chain?
How is the free energy stored at the inner mitochondrial membrane independently of chemical bonds, and how is it used for the synthesis of ATP?

18.5 Write down the molecular formula of the overall oxidation reaction of a fatty acid in these three reaction cascades.
What roles do A and B play in these reaction cascades?