CHEMISTRY: ART, SCIENCE, FUN

THEORETICAL EXAMINATION

SOLUTION and GRADING SCHEME

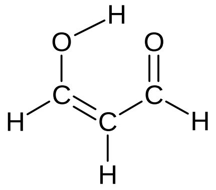
JULY 20, 2007
MOSCOW, RUSSIA

Official English version

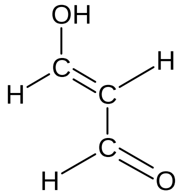
Problem 1. Proton tunneling

1.1.1 *The structures of propanedial and two of its isomers*

O=CH–CH$_2$–CH=O 1 mark



1 mark



1 mark

3 marks maximum

1.1.2

Acidic hydrogen atom is in CH$_2$ (in enol forms acidic hydrogen is in OH).

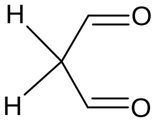
1 mark

Acidity of CH$_2$ group is caused by the stability of carbanion due to conjugation with two carbonyl groups. The first answer is correct.

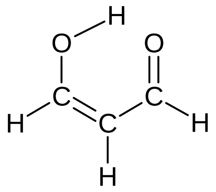
2 marks

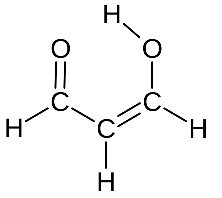
3 marks maximum

1.2.1 The distance between two minima on the energy curve is 0.06 nm. In a purely aldehyde form



such distance between two possible positions of proton is impossible. Tunneling takes place only in enol Z-form:





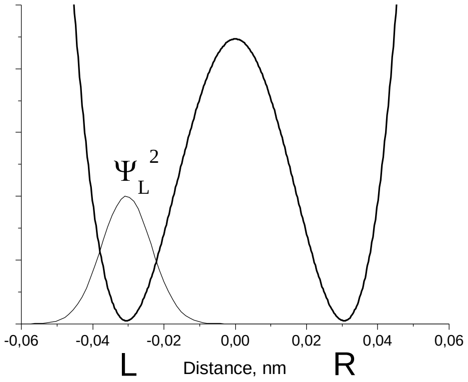
1 mark for each structure

2 marks maximum

1.3.1 *Expressions and plots of probability density*

(a) $\Psi^2(x,0) = \frac{1}{2}\left[\Psi_L^2(x)+\Psi_R^2(x)+\Psi_L^2(x)-\Psi_R^2(x)\right] = \Psi_L^2(x)$ 1 mark

The probability density is concentrated in the left well:

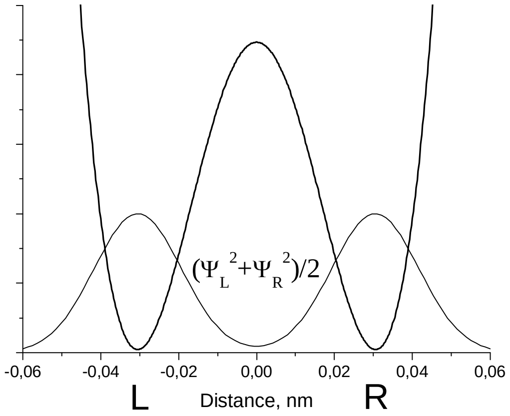


0.5 marks

(b) In the middle of the time interval

$$\Psi^2\left(x,\frac{\pi}{2\omega}\right) = \frac{1}{2}\left[\Psi_L^2(x)+\Psi_R^2(x)\right]$$ 1 mark

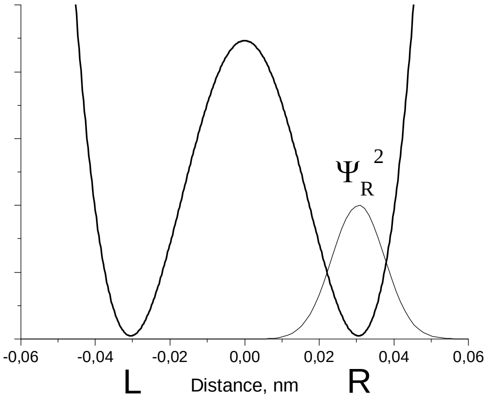
The probability density has a symmetric form, a proton is delocalized between two wells:



0.5 marks

(c) $$\Psi^2\left(x,\frac{\pi}{\omega}\right) = \frac{1}{2}\left[\Psi_L^2(x)+\Psi_R^2(x)-\Psi_L^2(x)+\Psi_R^2(x)\right] = \Psi_R^2(x)$$ 1 mark

The probability density is concentrated in the right well:



0.5 marks

<u>4.5 marks maximum</u>

1.3.2 *The probability of finding the proton in the left well* is 1/2, because probability function is symmetric, and both wells are identical.

2 marks

1.3.3 *The time of transfer* from one well to another is $t = \pi / \omega$.

$$t = \frac{3.14}{6.48 \cdot 10^{11}} = 4.85 \cdot 10^{-12}\ \text{s.}$$ 2 marks

The proton velocity:

$$V = \frac{0.06 \cdot 10^{-9}}{4.85 \cdot 10^{-12}} = 12\ \text{m/s.}$$ 2 marks

4 marks maximum

1.3.4

The uncertainty of proton position is approximately equal to half of the distance between minima, that is 0.03 nm (0.06 nm will be also accepted).

1 mark

The minimal uncertainty of velocity can be obtained from the uncertainty relation:

$$\Delta V = \frac{\hbar}{2m\Delta x} = \frac{1.055 \cdot 10^{-34}}{2 \cdot \frac{0.001}{6.02 \cdot 10^{23}} \cdot 0.03 \cdot 10^{-9}} \approx 1000\ \text{m/s.}$$ 3 marks

Comparing this uncertainty with the velocity 12 m/s we see that the notion of proton velocity during transfer from one well to another is senseless. Therefore, proton tunneling is a purely quantum phenomenon and cannot be described in classical terms. *The second conclusion is correct.*

2 marks

6 marks maximum

Problem 2. Nanochemistry

2.1.1

The Gibbs energy and the equilibrium constant of reaction (1)

$$\Delta_r G^0_{500}(1) = \Delta G^0_{f,500}(\text{CoO,s}) - \Delta G^0_{f,500}(\text{H}_2\text{O,g}) = -198.4 + 219.1 = 20.7\ \text{kJ/mol}$$ 0.5 marks

$$K = e^{-\frac{\Delta_r G^0_{500}(1)}{RT}} = e^{-\frac{20700}{8.314\cdot 500}} = 6.88\cdot 10^{-3}$$ 0.5 marks

1 mark maximum

2.1.2

The standard Gibbs energy of the reaction (1) with the spherical cobalt nanoparticles of radius r_a is

$$\Delta_r G^\circ_{500}(1,r_a) = G^0_{bulk,500}(\text{CoO,s}) + G^0_{500}(\text{H}_2\text{,g}) - G^0_{500}(\text{H}_2\text{O,g}) - G^0_{sph}(\text{Co}) =$$

$$= G^0_{500}(\text{CoO,s}) + G^0_{500}(\text{H}_2\text{,g}) - G^0_{500}(\text{H}_2\text{O,gas}) - \left(G^0_{500}(\text{Co,s}) + \frac{2\sigma_{\text{Co-gas}}V(\text{Co})}{r_a}\right) =$$

$$= \Delta_r G^\circ_{500}(1) - \frac{2\sigma_{\text{Co-gas}}V(\text{Co})}{r_a};$$

$$V(\text{Co}) = \frac{M_{\text{Co}}}{\rho(\text{Co})} = \frac{10^{-6}\cdot 59.0}{8.90} = 6.6\cdot 10^{-6}\ \frac{\text{m}^3}{\text{mol}};$$

for spherical particles with $r_a = 10^{-8}$, 10^{-9} m one gets, respectively

$$\frac{2\sigma_{\text{Co-gas}}V(\text{Co})}{r_a} = 210 \text{ and } 2100 \text{ J/mol.}$$

$\Delta_r G^\circ_{500}(1,r_a)$ is equal to 20.5 (a), and 18.6 (b) kJ/mol, respectively.

The equilibrium constant is calculated from the equation

$$K(1,r_a) = \exp\left(-\frac{\Delta_r G^\circ_{500}(1,r_a)}{RT}\right);$$

$K(1,r_a) = 7.22\times 10^{-3};\quad r_a = 10^{-8}$ m $\qquad$ $K(1,r_a) = 11.4\times 10^{-3};\quad r_a = 10^{-9}$ m

2 marks maximum

2.2.1

The standard Gibbs energy for reaction (1) involving nanoparticles of cobalt is

$$\Delta_r G^\circ_{500}(1, r_a) = \Delta_r G^\circ_{500}(1) - \frac{2\sigma_{\text{Co-gas}}}{r_a} V(\text{Co})$$

$\Delta_r G^\circ_{500}(1)$ is 20.7 kJ/mol. For spherical cobalt particles with r_a = 1 nm $\Delta_r G^\circ_{500}(1, r_a)$ is 18.6 kJ/mol. Solid cobalt oxide can be formed spontaneously when Gibbs energy of reaction (1) is negative. The inequality for bulk cobalt is:

$$\Delta_r G(1) = \Delta_r G^\circ_{500}(1) + RT \ln\left(\frac{p(\text{H}_2)}{p(\text{H}_2\text{O})}\right) = \Delta_r G^\circ_{500}(1) - RT \ln\left(\frac{p(\text{H}_2\text{O})}{p(\text{H}_2)}\right) \le 0$$

and for spherical cobalt nanoparticles with r_a = 1 nm:

$$\Delta_r G(1, r_a) = \Delta_r G^\circ_{500}(1, r_a) + RT \ln\left(\frac{p(\text{H}_2)}{p(\text{H}_2\text{O})}\right) = \Delta_r G^\circ_{500}(1) - \frac{2\sigma_{\text{Co-gas}}}{r_a} V(\text{Co}) - RT \ln\left(\frac{p(\text{H}_2\text{O})}{p(\text{H}_2)}\right) \le 0$$

$\Delta_r G^\circ_{500}(1)$ is 20.7 kJ/mol. For spherical cobalt particles with r_a = 1 nm $\Delta_r G^\circ_{500}(1, r_a)$ is 18.6 kJ/mol.

The minimum ratios $\dfrac{p(\text{H}_2\text{O})}{p(\text{H}_2)}$ are 145.6 (a) and 87.7 (b), respectively.

The hydrogen pressure is

$$1\text{bar} \cdot 0.0015 = 1.5 \cdot 10^{-3}\ \text{bar}$$

The minimum pressures of water are
$1.5 \cdot 10^{-3} \cdot 145.6 = 0.218$ bar (a) and $1.5 \cdot 10^{-3} \cdot 87.7 = 0.132$ bar (b), for the bulk cobalt and for nanoparticles, respectively.

H_2O%(bulk Co) = 21.8% *H_2O%*(nanoparticles with $r_a = 1 \cdot 10^{-9}$ m) = 13.2%.
We assume that bulk cobalt oxide is formed.

4 marks maximum

2.2.2

For the spontaneous oxidation

$$\Delta_r G(1, r_a) = \Delta_r G^\circ_{500}(1) - \frac{2\sigma_{\text{Co-gas}}}{r_a} V(\text{Co}) - RT \ln\left(\frac{p(\text{H}_2\text{O})}{p(\text{H}_2)}\right) \le 0$$

and

$$\Delta_r G^\circ_{500}(1) - \frac{2\sigma_{\text{Co-gas}}}{r_a} V(\text{Co}) \le RT \ln\left(\frac{p(\text{H}_2\text{O})}{p(\text{H}_2)}\right)$$

The left hand side of the last inequality becomes more positive with the increase of r_a. At certain point the inequality will be disturbed and the spontaneous oxidation will not take place. So, to protect cobalt nanoparticles from the spontaneous oxidation in this case one has to lengthen the radius r_a. The answer (a) is correct.

2 marks maximum

2.3.1

The equation for the standard molar Gibbs function of CoO (external layer) reads:

$$G^0_{sph}(\text{CoO}, r_b) = G_{bulk}(\text{CoO}) + \frac{2\sigma_{\text{CoO-gas}}}{r_b} V(\text{CoO}) = G^\circ(\text{CoO,s}) + \frac{2\sigma_{\text{CoO-gas}}}{r_b} V(\text{CoO})$$

1 mark

2.3.2

The equation for the standard molar Gibbs function of Co (internal layer) reads:

$$G^0_{\text{sph}}(\text{Co},r_a,r_b) = G_{\text{bulk}}(\text{Co}) + V(\text{Co})\left(\frac{2\sigma_{\text{CoO-gas}}}{r_b} + \frac{2\sigma_{\text{CoO-Co}}}{r_a}\right) =$$

$$= G^\circ(\text{Co,s}) + V\left(\text{Co}\right)\left(\frac{2\sigma_{\text{CoO-gas}}}{r_b} + \frac{2\sigma_{\text{CoO-Co}}}{r_a}\right)$$

The expression in brackets gives the additional pressure in the internal layer (see the Hint).

<u>5 marks maximum</u>

2.3.3

The standard Gibbs energy for reaction (1) with the double-layered nanoparticles is

$$\Delta_r G^0(1,r_a,r_b) = G^0_{sph}(\text{CoO},r_b) + G^\circ(\text{H}_2, gas) - G^\circ(\text{H}_2\text{O,gas}) - G^0_{sph}(Co,r_a,r_b) =$$

$$= G^\circ(\text{CoO,s}) + G^\circ(\text{H}_2, gas) - G^\circ(\text{H}_2\text{O,gas}) - G^\circ(\text{Co,s}) +$$

$$+ \frac{2\sigma_{\text{CoO-gas}}}{r_b} V(\text{CoO}) - 2V(\text{Co})\left(\frac{\sigma_{\text{CoO-gas}}}{r_b} + \frac{\sigma_{\text{CoO-Co}}}{r_a}\right) =$$

$$= \Delta_r G^\circ(1) + \frac{2\sigma_{\text{CoO-gas}}}{r_b}\big(V(\text{CoO}) - V(\text{Co})\big) - \frac{2\sigma_{\text{CoO-Co}}}{r_a} V(\text{Co})$$

<u>2 marks maximum</u>

2.3.4.

Under the assumptions made

$$\Delta_r G^\circ(1,r_a,r_b) = \Delta_r G^0(1,r_0) = \Delta_r G^\circ(1) + \frac{2\sigma_{\text{CoO-gas}}}{r_b}\big(V(\text{CoO}) - V(\text{Co})\big) - \frac{2\sigma_{\text{CoO-Co}}}{r_a} V(\text{Co}) =$$

$$= \Delta_r G^\circ(1) + \frac{2\sigma_{\text{CoO-gas}}}{r_0}\left(V(\text{CoO}) - \frac{3}{2}V(\text{Co})\right)$$

The term in brackets in the right-hand side is positive

$$\left(V(\text{CoO}) - \frac{3}{2}V(\text{Co})\right) = 6.56\cdot 10^{-6}\ \text{m}^3$$

$\Delta_r G^0(1,r_0)$ is directly proportional to $\left(\frac{1}{r_0}\right)$. The plot (a) is correct.

<u>3 marks maximum</u>

2.3.5.

The spontaneous forward reaction (1) is possible, when $\Delta_r G(1,r_0) \leq 0$, and

$$\Delta_r G^0(1) + \frac{2\sigma_{\text{CoO-gas}}}{r_0}\left(V(\text{CoO}) - \frac{3}{2}V(\text{Co})\right) \leq RT\ln\frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2}}$$

The term in brackets in the left-hand side is positive. The left hand side of the inequality becomes more positive with the decrease of r_0. At certain point the inequality will be violated and the spontaneous oxidation will not take place.

In order to protect nanoparticles from oxidation in this case one has to shorten the radius r_0.

The answer (b) is correct.

2 marks maximum

Problem 3. Unstable reaction

3.1.1 The overall reaction equation

$$B + D \rightarrow P$$ 1 mark

The kinetic equation for X

$$\frac{d[X]}{dt} = k_1[B][X]^2 - k_2[D][X]$$ 1 mark

<u>2 marks maximum</u>

3.1.2 Under the steady-state conditions

$$\frac{d[P]}{dt} = k_2[D][X] = k_1[B][X]^2,$$

whence

$$[X] = \frac{k_2[D]}{k_1[B]}$$

$$\frac{d[P]}{dt} = \frac{k_2^{\,2}[D]^2}{k_1[B]}$$ 3 marks

The reaction order is 2 with respect to D, –1 with respect to B; the overall order is 1

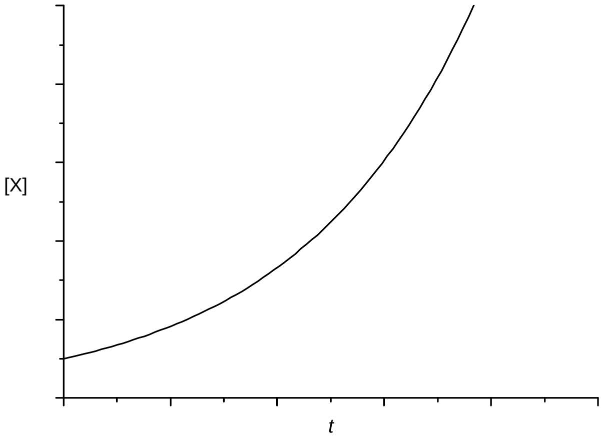
0.5 marks for each correct order

<u>4.5 marks maximum</u>

3.2.1 In an open system the initial reaction rate is:

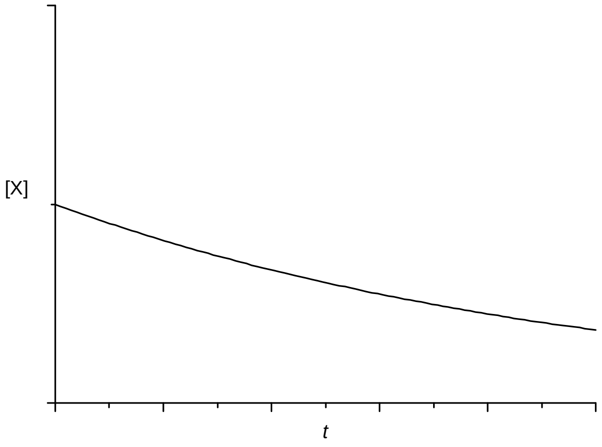
$$\frac{d[X]}{dt} = [B][X]\left(k_1[X] - k_2\right)$$

1) If $[X]_0 > k_2/k_1$, then $d[X]/dt > 0$ at any time, and the concentration of X monotonically increases:



2 marks

2) If $[X]_0 < k_2/k_1$, then $d[X]/dt < 0$ at any time, and the concentration of X monotonically decreases:



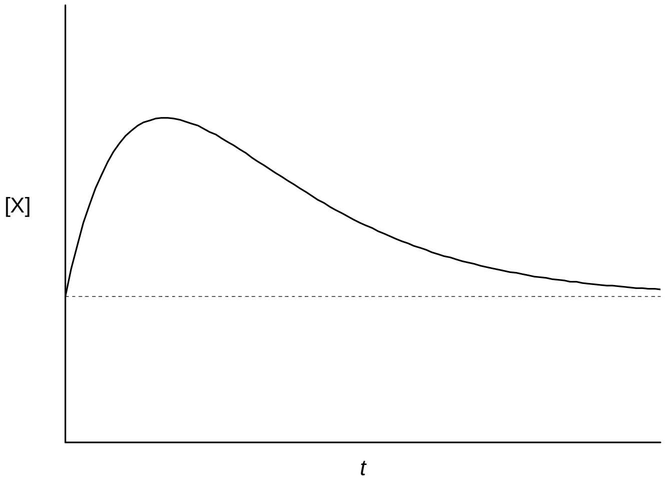
2 marks

4 marks maximum

3.2.2 In a closed system the initial reaction rate is:

$$\left.\frac{d[\mathrm{X}]}{dt}\right|_{t=0} = k_1[\mathrm{B}]_0[\mathrm{X}]_0^2 - k_2[\mathrm{D}]_0[\mathrm{X}]_0 = [\mathrm{B}]_0[\mathrm{X}]_0\left(k_1[\mathrm{X}]_0 - k_2\right) > 0$$

Hence, at the beginning of the reaction [X] increases but it cannot increase infinitely and finally goes to its initial value, because the second reaction is irreversible:



2 marks for maximum

1 mark for the asymptotic value

3 marks maximum

3.3.1 X – $C_2H_6O_2$, Y – C_2H_4O, P – C_2H_6O. Dots denote O_2 and H_2O.

$$C_2H_6 + C_2H_6O_2 + O_2 \rightarrow 2C_2H_6O_2$$
$$C_2H_6O_2 + C_2H_4O \rightarrow 2C_2H_4O + H_2O$$
$$C_2H_6 + C_2H_4O + H_2O \rightarrow 2C_2H_6O$$

0.5 marks for each unknown substance (X, Y, P, three blanks)

3 marks maximum

3.4.1 At the highest possible temperature the rate constants are equal:

$$A_1 \exp\left(-\frac{E_{A,1}}{RT}\right) = A_2 \exp\left(-\frac{E_{A,2}}{RT}\right)$$

$$T = \frac{E_{A,2} - E_{A,1}}{R \ln \frac{A_2}{A_1}} = 354 \text{ K}$$

1 mark for the calculation
2 marks for the correct answer
3 marks maximum

Problem 4. Determination of water by Fischer titration

4.1. *Equation:*

$I_2 + SO_2 + 2\ H_2O + 4\ Py = 2\ PyHI + (PyH)_2SO_4$ 1 mark

(0.75 marks for not accounting for the formation of Py salts)

4.2.1. *T is equal to:*

$M(Na_2C_4H_4O_6 \cdot 2H_2O) = 230.05$ $2M(H_2O) = 36.04$

$m(H_2O) = 1.3520 \cdot 36.04 / 230.05 = 0.2118$ g = 211.8 mg

1 mark for the formula

$T = 211.8 / 12.20 = 17.36$ mg/mL

$T = 17.36$ *mg/mL*

0.25 marks for the correct result (within 2 digits)

<u>1.25 marks maximum</u>

4.2.2. *T is equal to:*

Your work:

Volume of iodine spent for 10 mL of pure $CH_3OH = 2.20 \cdot 10.00 / 25.00 = 0.88$ mL

0.5 marks for the correct formula of pure methanol titration)

$T = 21.537 \bullet 0.01 \bullet 10^3 / (22.70 – 0.88) = 9.87$ mg/mL

More exactly

10.00 mL of the solution contains $(1000-21.5) \times 10.00 / 1000 = 9.785$ mL of methanol

Volume of iodine spent for 9,785 mL of pure $CH_3OH = 2.20 \cdot 9{,}785 / 25.00 = 0.86$ mL

$T = 21.537 \bullet 0.01 \bullet 10^3 / (22.70 – 0.86) = 9.86$ mg/mL

1 mark for the formula of water titration, only 0.5 marks without subtracting 0.88

$T = 9.87$ *mg/mL* 0.25 marks for the correct result

<u>1.75 marks maximum</u>

4.2.3. *T is equal to:*

Your work:

<u>**Approach 1**</u>.

Let 1 mL of CH_3OH contain x mg H_2O, then 1 mL of **A** contains ((1.000 – 0.006)·x + 5.624) mg H_2O.

$$\begin{cases} 15.00\cdot T = 22.45\cdot(0.994\cdot x + 5.624) \text{ – 1st titration,} \\ 10.00\cdot T = 25.00\cdot x + 10.79\cdot(0.994\cdot x + 5.624) \text{ – 2nd titration.} \end{cases}$$

Hence, $x = 1.13$ mg/mL, $T = 10.09$ *mg/mL* (10.10 without taking into account 0.994 factor)

<u>**Approach 2**</u>.

Let y mL of **B** be spent for the titration of water, contained in 1 mL of CH_3OH.

Then $T = \dfrac{22.45\cdot 5.624}{15.00 - 22.45\cdot 0.994\cdot y}$ (1st titration) = $\dfrac{10.79\cdot 5.624}{10.00 - 25.00y - 10.79y}$ (2nd titration).

Hence, $y = 0.1116$ and $T = 10.10$ mg/mL

$T = 10.09$ *mg/mL* (10.10 without taking into account 0.994 factor)

2 marks for the correct formulas (with or without taking into account 0.994 factor) and 0.25 marks for the correct result (10.10 or 10.09)

<u>2.25 marks maximum</u>

4.3. *Equation(s):*

$CaO + SO_2 = CaSO_3$
$2CaO + 2I_2 = CaI_2 + Ca(OI)_2$
$6CaO + 6I_2 = 5CaI_2 + Ca(IO_3)_2$

(Instead of CaO, $Ca(OH)_2$ may be written.)

1 mark for ANY correct equation

<u>1 mark maximum</u>

4.4.1 *Equation(s):*

$Fe_2(SO_4)_3 + 2HI = 2FeSO_4 + \mathbf{I_2} + H_2SO_4$ 1 mark

$Fe_2(SO_4)_3 + \mathbf{H_2O} + SO_2 + CH_3OH = 2FeSO_4 + CH_3OHSO_3 + H_2SO_4$
1 mark

(or in ionic form)

<u>2 marks maximum</u>

4.4.2. *Equation:*

$Fe_2(SO_4)_3 \cdot xH_2O$ + **$(x - 1)$**I_2 **+** xSO_2 + xCH_3OH = $2FeSO_4$ + xCH_3OHSO_3 + H_2SO_4 + $2(x - 1)HI$ 1 mark

4.4.3. *The composition of the crystallohydrate is:*

Your work:

$M(Fe_2(SO_4)_3 \cdot xH_2O) = 399.9 + 18.02x$

$m_{H2O}\,(g) = \dfrac{0.6387 \cdot 18.02x}{(399.9 + 18.02x)}$; 1 mark

$m_{H2O}\,(g) = 10.59(mL) \times 15.46(mg/mL) \times 0.001(g/mg) \times \dfrac{x}{x-1}$

1 mark

→

$0.1637 \cdot (399.9 + 18.02x) = 11.51x - 11.51$;

$x = 8.994$

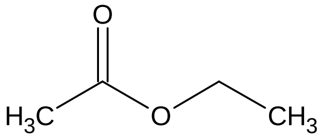
Formula: $Fe_2(SO_4)_3 \cdot 9\ H_2O$ $x = 9$

0.25 marks (for correct answer)

2.25 marks maximum

Problem 5. A mysterious mixture (organic hide-and-seek game)

5.1.1 *Structure of product* ***D***



Ethyl acetate, ethyl ethanoate

Any structural formula or any shorter versions ($CH_3COOC_2H_5$) including the adopted shortcuts for organic radicals (Me, Et, Ac), or systematic IUPAC name – 5 marks

5.1.2 *Which class of organic compounds does* ***D*** *belong to? Check the appropriate box.*
Note! *Only one checkmark is allowed. Several checkmarks will lead to 0 mark for this question.*

ketones	ethers	acetals	esters	alcohols	aldehydes	glycols
☐	☐	☐	☑	☐	☐	☐

The only correct answer is ester – 5 marks

5.1.3 *The expected yield of* ***D***

Your work:
Statement that the reaction is an equilibrium without any further actions – 1 mark
Answer to quantitative question: lower than 85% - 2 marks

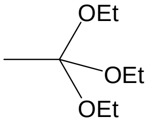
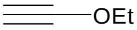
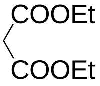
Qualitative estimation of yield can be done assuming that the reaction is at equilibrium, and that the equilibrium constant is supposed to not vary with temperature and composition of the reaction mixtures.

$$K = \frac{[\mathrm{AcOEt}][\mathrm{H_2O}]}{[\mathrm{AcOH}][\mathrm{EtOH}]} = \frac{(0.85)^2}{0.15 \cdot 1.15} = 4.2$$

Calculation of yield using this constant in 1:1 mixture gives 67%

yield = 67%
maximum – 10 marks, if the yield is computed within 67±1% error limits

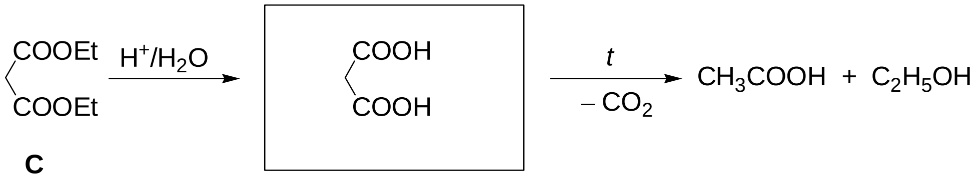
5.2.1 *The structures of* ***A***, ***B***, *and* ***C***.

 $CH_3C(OEt)_3$ triethyl orthoacetate, 1,1,1-triethoxyethane	 HC≡COEt ethoxyacetylene, ethynylethyl ether	 $CH_2(COOEt)_2$ diethyl malonate
A	***B***	***C***

Each structure represented by structural formula or unambiguous linear notation – 10 marks
Systematic name given in place of structure – 5 marks

5.2.2 *Draw in the boxes intermediate compounds formed during the acidic hydrolysis of* ***C***, *and basic hydrolysis of* ***B***.

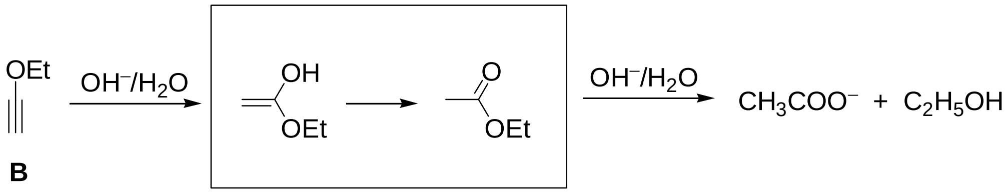
a) Malonic acid is formed as intermediate in the hydrolysis of diethyl malonate – 5 marks



C

Also accepted will be monoethyl malonate – 2 marks
maximum 5 marks

b) Hydrolysis of ethoxyacetylene starts from the addition of hydroxide to the triple bond to give unstable enolic form of ethylacetate, into which it immediately is transformed

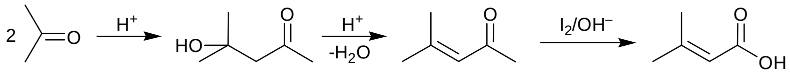


B

Indication of any of keto- or enol forms of ethylacetate – 5 marks
Hydrolysis of strong ether bond to give hydroxyacetylene, or any forms coming along this path (ketene, diketene) is impossible and is not allowed – 0 marks
Maximum for a) and b) together – 10 marks

5.3.1 *The structure of senecioic acid*

From acetone alone the synthesis includes aldol condensation, dehydration, with subsequent iodoform reaction
3 marks



Senecioic acid structure alone – 4 marks, with scheme - maximum 10 marks

5.3.2 *The structure of* ***E****.*

Iodoform, triiodomethane, CHI_3 – 5 marks

Problem 6. Silicates as the base of the Earth crust

6.1.1

$SiO_3^{2-} + 2CO_2 + 2H_2O =$ "H_2SiO_3"$\downarrow$ (Silica acid gel) $+2HCO_3^-$ or
$SiO_2(OH)_2^{2-}+2CO_2+H_2O=$"$H_2SiO_3$"$\downarrow+2HCO_3^-$ or
$SiO_3^{2-} + CO_2 + H_2O =$ "H_2SiO_3"$\downarrow + CO_3^{2-}$

3 marks maximum
2 marks if silicic acid is written in any form
1 mark if the reaction contains carbonate (or bicarbonate) ions with silicic acid missing

6.1.2

a) protonation of ortho-silicate ions leading to the formation of Si-OH groups
$SiO_4^{4-} + H_2O = [SiO_3(OH)]^{3-} + OH^-$ or
$SiO_4^{4-} + H^+ = [SiO_3(OH)]^{3-}$ or
$[SiO_2(OH)_2]^{2-} + H^+ = [SiO(OH)_3]^-$ Yes ☒ No ☐

b) formation of hydrated $[SiO_4(H_2O)_2]^{4-}$ anions
$SiO_4^{4-} + 2H_2O = [SiO_4(H_2O)_2]^{4-}$
Yes ☐ No ☒

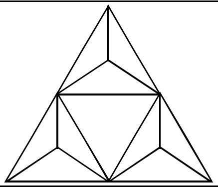
c) polycondensation of ortho-silicate ions leading to the formation of Si-O-Si bonds
$2\ SiO_4^{4-} + H_2O = [O_3Si\text{-}O\text{-}SiO_3]^{6-} + 2\ OH^-$ or
$2\ SiO_4^{4-} + 2H^+ = [O_3Si\text{-}O\text{-}SiO_3]^{6-} + H_2O$ or
$2SiO_2(OH)_2^{2-} + H_2O = [O\text{-}Si(OH)_2\text{-}O\text{-}Si(OH)_2\text{-}O]^{2-} + 2\ OH^-$ Yes ☒ No ☐

9 marks maximum
2 marks for each correct reaction
1 mark for each correct choice of check-boxes

6.2.1 n= 6 (assuming oxidation numbers of silicon (+4) and oxygen (-2), or taking into account its structure and the charge of orthosilicate ion (-4))
2 marks maximum
1 mark penalty for miscalculation

6.2.2 $Si_3O_9 \equiv 3\ [SiO_4] - 3\ O$, i.e. there are 3 oxygen atoms bridging adjacent tetrahedra
2 points maximum
1 point penalty for miscalculation

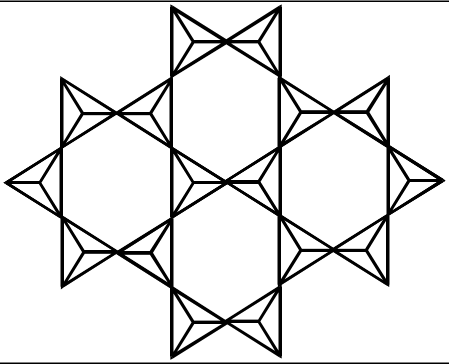
6.2.3



3 marks maximum

6.2.4

Calculations:
m=4 (assuming oxidation numbers of silicon (+4) and oxygen (-2), or taking into account its structure and the charge of orthosilicate ion (-4))
$Si_4O_{10} \equiv 4[SiO_4] - 6O$, i.e. the formula of the tetrahedron is now $SiO_{2.5}$, which is possible if 1 O atom belongs to this tetrahedron and the other three are shared between 2 tetrahedra (their contribution =3/2). This is possible if the tetrahedra are set on a plane and joined together through all apexes of their bases.



<u>10 marks maximum</u>

2 marks for charge determination

3 marks for determination of the number of oxygen bridges

5 marks for the correct structure

1 mark penalty if 6 to 15 tetrahedra shown, the connection being correct

3 marks penalty if less than 6 tetrahedra shown (i.e. it is not clear that polyhedra form layer)

4 marks penalty for connection via apexes, but in 3D network

4 marks penalty for connection via apexes, but in 1D chain

0 mark of 5 for any other structure

6.3.1

pH = 4

$$Cu(H_2O)_4^{2+} + H_2O = Cu(OH)(H_2O)_3^{+} + H_3O^{+},$$

$$[H^+] \approx (c\,K_a^{I})^{1/2} = 1\cdot10^{-4}\text{ M},\ pH = -\log[H^+] = 4$$

<u>5 marks maximum</u>

1 mark penalty for miscalculation

2 marks penalty for wrong expression of $[H^+]$ via K_a^I

2 marks penalty if there are some errors in definition of pH (e.g. using ln instead of lg)

3 marks penalty if the hydrolysis reaction is wrong

6.3.2

$CuSO_4 + Na_2SiO_3 + 2H_2O = Cu(OH)_2\downarrow + \text{“}H_2SiO_3\text{”}\downarrow + Na_2SO_4$

or $2CuSO_4 + Na_2SiO_3 + 2H_2O = (CuOH)_2SO_4\downarrow + \text{“}H_2SiO_3\text{”}\downarrow + Na_2SO_4$

This (or those) reaction(s) (apart from formation of copper silicate) can be deduced from the fact that the reaction describes mutual (self-amplifying) hydrolysis. It comes from the previous parts of the task: pH of LGL is greater than 7 (see questions **6.2**), and pH of copper sulfate solution is less than 7 (see **6.3.1**).

<u>3 marks maximum</u>

2 marks if reaction coefficients are wrong

1 mark if only one of two principal precipitates shown ($Cu(OH)_2\downarrow$ or “H_2SiO_3”↓)

Problem 7. Atherosclerosis and intermediates of cholesterol biosynthesis

7.1.1 E2-E4 catalyze one and the same (and only one) reaction type. The only reaction which can be carried out three times in a row is monophosphorylation (all the rest reaction types are not consistent with either initial or final products). This is also supported by presence of pyrophosphate residue in IPP and liberation of inorganic products (including inorganic phosphate) upon spontaneous decomposition of **X1**.

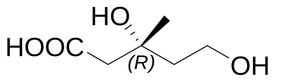
X is a monocarboxylic acid composed of atoms of three elements: carbon, hydrogen and oxygen. It can contain neither sulfur which is found in CoA nor phosphorus which is introduced into intermediates on the pathway from HMG-CoA towards IPP or present in CoA. Thus, **E1** catalyzes non-hydrolytic removal of CoA from HMG-CoA and is not involved in phosphorylation. Since water is not a substrate in this reaction, liberation of CoA must be conjugated with another reaction which affects the carboxylic group esterified in HMG-CoA. The only possible variant is its 4 electron reduction towards hydroxyl group. **E1** can not catalyze dehydration because of optical activity of **X** (removal of water leads to the loss of sole chiral center). Decarboxylation is excluded, since **X**, being an acid, must contain a carboxylic group. Oxidation of tertiary hydroxyl group in HMG-CoA according to β-oxidation mechanism is impossible. Further evidence comes from the fact that the carboxylic group initially involved in thioester bond formation is present as the residue of hydroxyl group in IPP. So:

E1 *4, 5*

E3 *6*

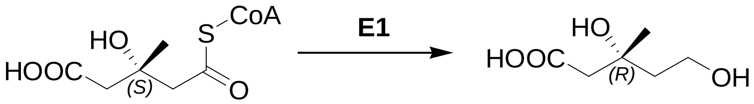
12 marks maximum
E1: 9 marks if 2 variants are given and both are correct.
4 marks if only one variant is given and it is correct
4 marks if two correct and one incorrect variants are given
0 mark if one correct and any number of incorrect variants are given
0 mark if more than three variants are given.
E3: 3 marks if only correct variant is given. Otherwise 0 mark

7.1.2 Based on the reaction types catalyzed by **E1** and configuration of HMG-CoA stereocenter, the structure of **X** is:



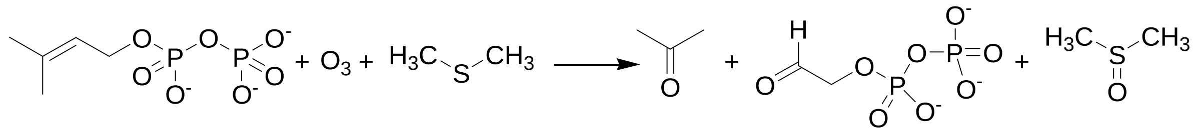
X, mevalonic acid

Note the absolute configuration of the chiral center is changed as a result of HMG-CoA metabolism into mevalonic acid due to alteration of substituents priority.



12 marks maximum
8 marks for correct structural formula
4 marks for correct stereochemistry (only in case both the structure is correct and R-isomer is indicated; otherwise 0 mark).
No penalty for incorrect stereochemistry or absence of stereochemical information

7.2.1 Reaction equation for reductive ozonolysis



5 marks maximum

4.5 marks for correct products (1.5 marks each), incorrect structures not penalized

0.5 mark for correct equation coefficients

7.2.2 DAP molecule contains only one carbon atom which can be involved in the formation of C–C bond during **Y** biosynthesis. Irrespective of the way this molecule is incorporated in **Y**, ozonolysis of this fragment will lead to dimethyl ketone (acetone). (See DAP ozonolysis reaction in **7.2.1**). Thus, acetone can be unambiguously attributed to **Y1**, since it contains 3 carbon atoms (**Y2** and **Y3** contain 5 and 4 carbon atoms, respectively). Taking into account the ratio between ozonolysis products, we have:

$$n_Y(C)= 2*n_{Y1}(C)+4* n_{Y2}(C)+ n_{Y3}(C)= 2*3 + 4*5 + 4 = 30$$

Y is an acyclic molecule, thus DAP residues can be found only at its ends. **Y** has only two ends, since IPP contains only two elongation sites (at least three such sites are needed to get a branched molecule). Since reductive ozonolysis of one **Y** molecule produces two acetone molecules, **Y** contains 30 carbon atoms.

To determine the number of hydrogen atoms double bonds in **Y** should be counted. Formation of each double bond reduces by 2 the number of hydrogen atoms in the coupling product as compared to the sum of atoms of starting substances. The ratio of **Y** to the sum of its ozonolysis products is 1:7 (2+4+1), which corresponds to 6 double bonds in **Y**. Then, by using the general formula for alkanes we have:

$$n(H)= 2*n_Y(C)+2–2*n_{C=C}=30*2 + 2 - 6*2 = 50$$

Y (squalene) formula – $C_{30}H_{50}$.

Number of carbon atoms 30	Work: $n_Y(C)= 2*n_{Y1}(C)+4*n_{Y2}(C)+ n_{Y3}(C)= 2*3 + 4*5 + 4 = 30$
Number of hydrogen atoms 50	Work: $n(H)= 2*n_Y(C)+2–2*n_{C=C}=30*2 + 2 - 6*2 = 50$
Gross formula of **Y** $C_{30}H_{50}$	

12 marks maximum

8 marks for correct justification of molecular formula

4 marks for correct molecular formula

7.2.3 IPP and DAP are structural isomers containing 5 carbon atoms each. Since all carbon atoms of these substances are found in **Y**, one can calculate the total quantity of IPP and DAP molecules needed to synthesize **Y**:

$$n(IPP\&DAP)= n_Y(C)/5=30/5=6$$

The number of DAP molecules was determined earlier and is equal to 2. Then, 4 molecules of IPP are needed.

$n(IPP\&DAP)= n_Y(C)/5=30/5=6$

Number of DAP molecules 2

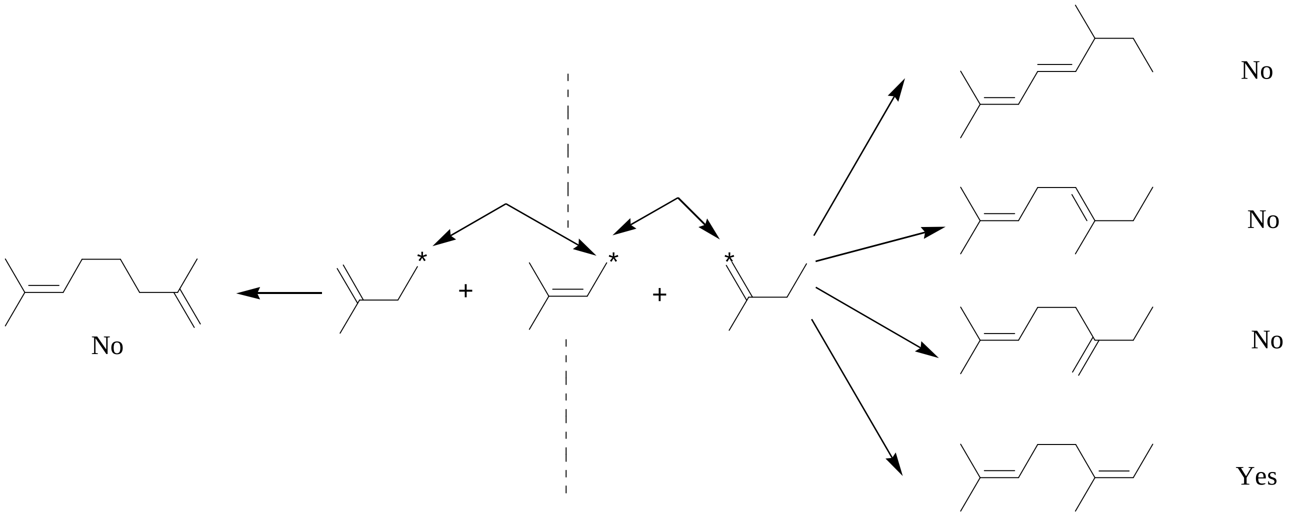
Number of IPP molecules 4

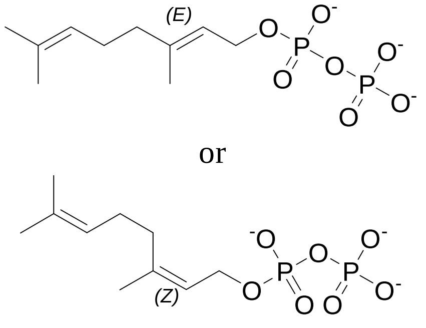
7 marks maximum

3.5 marks for calculation of the total number of DAP and IPP molecules

3.5 marks for correct individual numbers of DAP and IPP molecules

7.2.4 All possible combinations that do not alter hydrocarbon skeleton are given below (pyrophosphate fragments not shown). Two groups of products differing in carbon atoms involved in coupling reaction are separated by the dashed line. IPP fragments should be attached to DAP so that ozonolysis of the product leads to **Y2** containing 5 carbon atoms. Only one variant is possible if stereochemistry is not taken into consideration and two variants with stereochemical details





The upper isomer is geranyl pyrophosphate

8.5 marks maximum

8.5 marks for correct structure

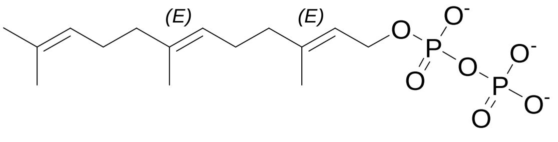
No penalty for stereochemistry, any correct structure is accepted

2.5 marks if ozonolysis of the product leads to acetone, but does not lead to the compound with 5 carbon atoms

2.5 marks if ozonolysis of the product leads to the compound with 5 carbon atoms, but does not lead to acetone

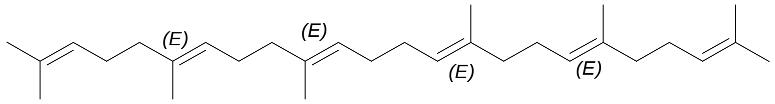
0 mark for any other variant

7.2.5 It is seen from the coupling reaction (Scheme 2) that **Y4** contains 15 carbon atoms or 1 DAP and 2 IPP fragments, the latter being attached to the former consecutively. It is important to note that **Y3** can not be found in two hydrocarbon residues originating for **Y4,** since **Y3** is formed as a result of ozonolysis in a molar ratio of 1:1 to **Y**. Thus, geranyl phosphate is the intermediate on the way to **Y** (all double bonds in *trans* configuration). Attachment of the next IPP fragment to geranyl phosphate leads to the product giving 1 molecule of **Y1** and 2 molecules of **Y2** upon its ozonolysis. Thus, **Y4** structure with stereochemical details:



Y4, farnesyl pyrophosphate

Combining two hydrocarbon fragments of **Y4** and taking into account that the double bond between them is being reduced we get the following structure of **Y**:



Y, squalene

16 marks maximum
9 marks for farnesyl pyrophosphate (6.5 marks for correct structural formula and 2.5 marks for correct stereochemistry)
7 marks for squalene (5 marks for correct structural formula and 2 marks for correct stereochemistry)
2.5 marks penalty for unreduced double bond in squalene

Problem 8. ATRP allows new polymers

8.1.1 *Expressions for the rates of ATRP elementary stages: activation (v_{act}), deactivation (v_{deact}), propagation (v_p) and termination (v_t)*

$v_{act} = k_{act}\cdot[\text{R-Hal}]\cdot[\text{CuHal(Ligand)}_k]$	2 marks
$v_{deact} = k_{deact}\cdot[\text{R}^\cdot]\cdot[\text{CuHal}_2\text{(Ligand)}_k]$	2 marks
$v_p = k_p\cdot[\text{R}^\cdot]\cdot[\text{M}]$	2 marks
$v_t = 2k_t\cdot[\text{R}^\cdot]^2$	2 marks (no penalty for missing 2)
	8 marks maximum

8.1.2 *Comparison of rates of ATRP elementary stages*

Since all the chains grow with equal rate, the process proceeds as living polymerization. Living radical polymerization is possible only if concentration of active radicals is low to prevent chain transfer and termination. So:

$$v_{deact} >> v_{act}$$

The portion of active radicals must be small, so the equilibrium is shifted towards dormant species.

$$v_{deact} >> v_p$$

Propagation rate should be much slower than that of deactivation to make chains propagate with equal rate.

$$v_{deact} >> v_t$$

Termination does not occur since the total number of polymer chains is equal to a certain constant number – number of initiator molecules.

$v_{deact} >> v_{act}$	3 marks
$v_{deact} >> v_p$	3 marks
$v_{deact} >> v_t$	3 marks
	9 marks maximum

8.2.1 *Calculation of mass (m) of the obtained polymer.*

1st variant

$[M] = [M]_0\exp(-k_P[R\cdot]t)$ or $n(MMA) = n_0(MMA)\exp(-k_P[R\cdot]t)$ 1 mark

Quantity of MMA monomer remaining after polymerization during 1400 s is

$31.0\cdot\exp(-1616\cdot 1.76\cdot 10^{-7}\cdot 1400) = 20.8$ mmol. 2 marks

Quantity of monomer consumed during polymerization: 31-20.8=10.2 mmol 1 mark

Mass of the obtained polymer is $m = \Delta n(MMA)\cdot M(MMA) = (10.2/1000)\cdot 100.1 = 1.03\,\text{g}$ 1 mark

2nd variant

$[M] = [M]_0\exp(-k_P[R\cdot]t)$ or $n(MMA) = n_0(MMA)\exp(-k_P[R\cdot]t)$ 1 mark

Quantity of MMA monomer consumed during 1400 seconds of polymerization is

$\Delta n(MMA) = n_0(MMA)(1-\exp(-k_p\cdot[R^\bullet]\cdot t)) = 31.0\cdot(1-1616\cdot 1.76\cdot 10^{-7}\cdot 1400) = 10.2\,\text{mmol}$

3 marks

Mass of the obtained polymer is $m = \Delta n(MMA)\cdot M(MMA) = (10.2/1000)\cdot 100.1 = 1.03\,\text{g}$ 1 mark

3rd variant

$\ln\left(\dfrac{[M]}{[M]_0}\right) = -k_P[R\cdot]t = -1616\cdot 1.76\cdot 10^{-7}\cdot 1400 = -0.398$ 1 mark

$\dfrac{[M]}{[M]_0} = e^{-0.398} = 0.672$ 1 mark

$\dfrac{[M]}{[M]_0} = \dfrac{n(MMA)}{n_0(MMA)}$

$n(MMA) = 0.672\cdot n_0(MMA) = 20.8$ mmol 1 mark

Quantity of monomer consumed during polymerization is 31-20.8=10.2 mmol 1 mark

Mass of the obtained polymer is $m = \Delta n(MMA)\cdot M(MMA) = (10.2/1000)\cdot 100.1 = 1.03\,\text{g}$ 1 mark

m = 1.03 g 5 marks maximum

8.2.2 *Calculation of degree of polymerization (DP) of the obtained polymer.*

The number of growing chains is equal to the number of TsCl molecules (0.12 mmol) 2 marks

At the first stage, 7.3 mmol of MMA was consumed (0.73/100.1).

The total quantity of monomers at the beginning of the 2nd stage is 23.7 + 23.7 = 47.4 mmol.

2 marks

Since the monomers have the same reactivity, they will be involved in polymerization with the same rate.

Quantity of monomers consumed during the second stage is

$\Delta n = n_0(1-\exp(-k_P[R\cdot]t)) = 47.4(1-\exp(-1616\cdot 1.76\cdot 10^{-7}\cdot 1295)) = 14.6$ mmol. 4 marks

Totally 7.3+14.6 = 21.9 mmol of monomers was polymerized during two stages. 2 marks

DP = 21.9/0.12 = 182.5 1 mark

DP = *182-183 (all answers within this range are credited)* 11 marks maximum

8.2.3 *Structure of the obtained polymer.*

The product of polymerization is a block copolymer because it was obtained by sequential polymerization on living chains.

The first block is built of MMA units solely. The DP is 7.3/0.12 = 60.8 ≈ 61 monomer units.

The second block is obtained by copolymerization of two competing monomers with the same reactivity. So, it is a statistical copolymer. Fractions of A and B in the 2nd block are equal because their concentrations in the reaction mixture at the beginning of the 2nd stage were equal. The DP of the 2nd block is 183-61 = 122 monomer units (121 is also correct if the total DP in **8.2.2** is 182).

Ts-A_{61}-block-(A-stat-B)$_{61}$-Cl or Ts-A_{61}-block-(A_{61}-stat-B_{61})-Cl

14 marks maximum

4 marks for block copolymer with blocks A and co-AB

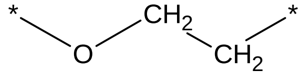
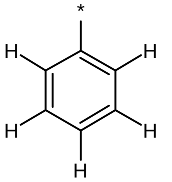
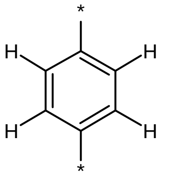
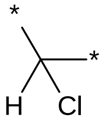
4 marks for an indication of the statistic character of the 2nd block

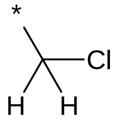
1 mark for equal fractions of A and B in the 2nd block

2 marks for correct DPs of each block

1 mark for indication of terminal groups

8.3.1 *Assignment of NMR signals to substructures given in the Answer Sheet.*

	a, b, g 3x1.5 marks
	c 2 marks
	d 2 marks
	e 4 marks

	f 4 marks

16.5 marks maximum

8.3.2 *Determination of molar fractions of units C and D and molecular weights of P1 and P2.*

Intensity of multiplets b and g is 40.2, so intensity per 1 proton is 40.2/4/58=0.173 for both copolymer spectra 2 marks

Intensity of multiplet c is 13.0, which is equivalent to 13.0/0.173=75 protons. Taking into account that each styrene ring has 5 aromatic protons, DP of styrene block is 75/5=**15.** 2 marks

Molar fraction of styrene units in P1 is 15/(15+58) = **20.5%** 1 mark

Intensity of multiplet d is 10.4, which is equivalent to 10.4/0.173=60 protons. Since each monomer unit of *p*-chloromethylstyrene has 4 protons, DP of PCS is 60/4=15. 2 marks

Molar fraction of D is 15/(15+58) = **20.5%** 1 mark

M(P1) = 15.03+58x44.05+72.06+15x104.15+35.45 = **4240** 2 marks

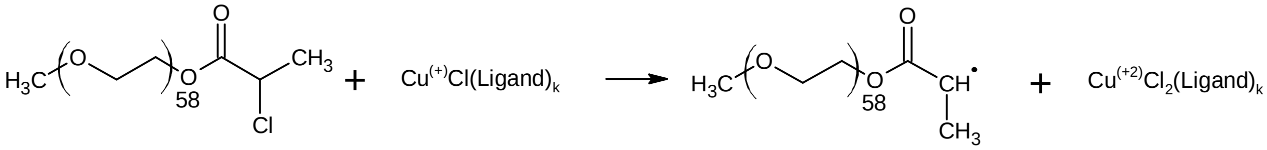
M(P2) = 15.03+58 x44.05+72.06+15x152.62+35.45 = **4967** 2 marks

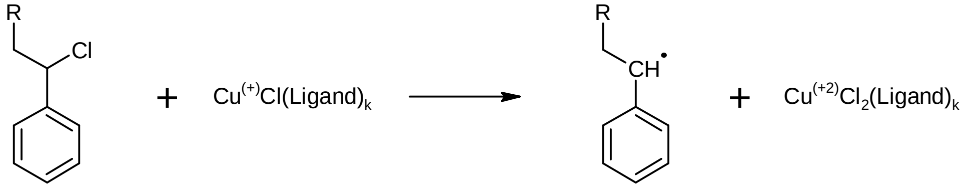
M(P1) = 4240	M(P2) = 4967
n(C) = 20.5%	n(D) = 20.5%
12 marks maximum	

8.3.3 *All possible reactions of activation occurring during the synthesis of P1 and P2.*

10 marks maximum

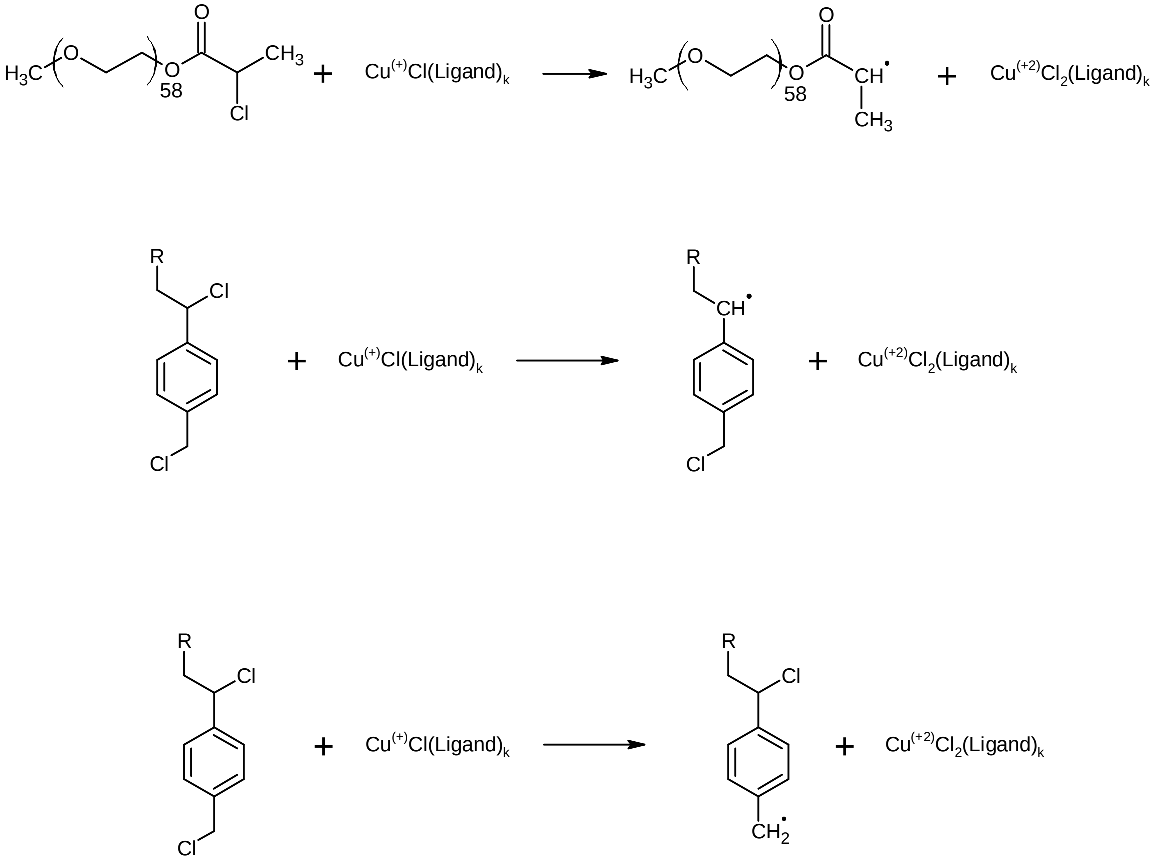
P1: (1.5+2) marks





Here R is used for the macroinitiator fragment with one or several styrene units attached.

P2: (1.5+2+3) marks



Here R is used for the macroinitiator fragment with one or several p-chloromethylstyrene units attached.

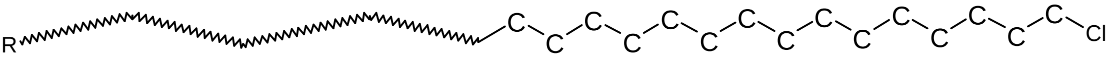
8.3.4 *The structure of P1 and one of possible structures of P2*

P1 is a block copolymer of PEO and PS. The PS block contains 15 units.

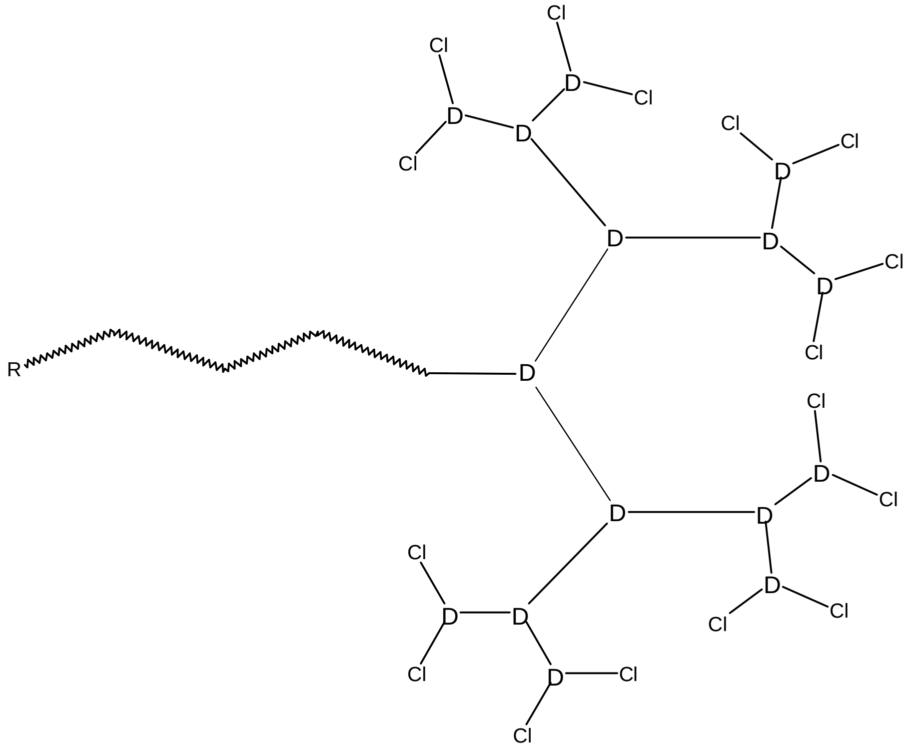
P2 is a block copolymer composed of PEO block and branched styrene block.

The integral intensity of multiplet f is 2.75, so 2.75/0.173=15.9, that is about 16 protons or 8 chloromethyl groups.

d) If there is no branching in molecule P2, it would contain 15 choromethyl groups. Each branching reduces the number of such groups by 1. Thus P2 has 15-8 = 7 branchings. Every structure with 7 branchings is correct if each monomer unit is linked with not more than 3 other monomer units

P1 

P2



13.5 marks maximum
2 marks for P1
7.5 marks for completely correct structure of P2
4 marks for structure of P2 with nonzero but incorrect number of branchings

4 marks penalty if there is a unit linked with more than 3 other monomer units