55TH INTERNATIONAL
CHEMISTRY OLYMPIAD
SWITZERLAND 2023

Solutions Preparatory Problems

Finding Solutions

2023-06-02, Version 3

Solution: The Sun-to-Fuel Project

1.1.

$M_{CeO_2} = 172.12\ g/mol$

Thus:

$O_2\ release = 0.0117\ mol\ mol_{CeO_2}^{-1}$

$H_2\ production = 0.0158\ mol\ mol_{CeO_2}^{-1}$

$CO\ production = 0.0067\ mol\ mol_{CeO_2}^{-1}$

The amount of syngas produced equals the amount of “O” released within the margin of error and δ is calculated to be:

$\delta = 2 * (O_2\ release) = 0.0234$

1.2.

Based on the oxygen balance, α can be determined:

$$2 - \delta_{ox} = 2 - \delta_{red} + 2 * \alpha$$

$$\alpha = \frac{\delta_{red} - \delta_{ox}}{2}$$

Thus:

i) $\frac{2}{\delta_{red}-\delta_{ox}}\ \mathrm{CeO}_{2-\delta_{ox}} \rightarrow \frac{2}{\delta_{red}-\delta_{ox}}\ \mathrm{CeO}_{2-\delta_{red}} + \mathrm{O}_2$

ii) $\frac{1}{\delta_{red}-\delta_{ox}}\ \mathrm{CeO}_{2-\delta_{red}} + \mathrm{CO}_2 \rightarrow \frac{1}{\delta_{red}-\delta_{ox}}\ \mathrm{CeO}_{2-\delta_{ox}} + \mathrm{CO}$

iii) $\frac{1}{\delta_{red}-\delta_{ox}}\ \mathrm{CeO}_{2-\delta_{red}} + H_2\mathrm{O} \rightarrow \frac{1}{\delta_{red}-\delta_{ox}}\ \mathrm{CeO}_{2-\delta_{ox}} + H_2$

To help understand this equation, assume $\delta_{ox} = 0.05$ and $\delta_{red} = 0.10$. Then:

Reduction: $40\ \mathrm{CeO}_{1.95} \rightarrow 40\ \mathrm{CeO}_{1.90} + \mathrm{O}_2$

Oxidation: $20\ \mathrm{CeO}_{1.90} + \mathrm{CO}_2 \rightarrow 20\ \mathrm{CeO}_{1.95} + \mathrm{CO}$

1.3.

α increases with increasing temperature and with decreasing O_2 partial pressure during the reduction process. High temperature and low O_2 partial pressure are the most suitable conditions.

1.4.

$$2\ \alpha_{1773} = exp\left(-0.2231\ log\ \left(\frac{0.1*10^{-3}\ bar}{1\ bar}\right) - 2.3040\right) = 0.0388$$

$$\alpha_{1773\ K} = \frac{\delta_{red} - \delta_{ox}}{2} \cong \frac{\delta_{red,1773\ K}}{2} = 0.0194$$

For the system in question 1, $\alpha = \frac{\delta}{2} = 0.0117 < \alpha_{1773\ K}$. This means that for the release of one O-atom, the system in question 1 requires $\frac{1}{0.0117} = 42.7$ CeO_2 units while the system here requires $\frac{1}{0.0388} = 25.8$ CeO_2 units only.

5.

$$2\,\alpha_{1673} = exp\left(-0.2105\,log\left(\frac{0.1*10^{-3}\,bar}{1\,bar}\right) - 2.613\right) = 0.0169$$

$$\alpha_{1673\,K} = \frac{\delta_{red} - \delta_{ox}}{2} \cong \frac{\delta_{red,1773\,K}}{2} = 0.0085$$

$$\frac{\alpha_{1673\,K} - \alpha_{1773\,K}}{\alpha_{1773\,K}} = \frac{0.0085 - 0.0194}{0.0194} = -0.562$$

The oxygen exchange capacity drops by 56.2%.

6.

$$\frac{n_{H_2}}{n_{CO_x}} = \frac{n_{H_2}}{n_{CO} + n_{CO_2}} = \frac{40.7}{4.3 + 22.4} = 1.52$$

7.

$$conv = \frac{n_{CO}}{n_{CO} + n_{CO_2}} = \frac{4.3}{4.3 + 22.4} = 0.16$$

8.

$$\frac{n_{H_2}}{n_{CO_x}} = \frac{n_{H_2}}{n_{CO} + n_{CO_2}} = \frac{59.9}{6.0 + 17.2} = 2.58$$

$$conv = \frac{n_{CO}}{n_{CO} + n_{CO_2}} = \frac{6.0}{6.0 + 17.2} = 0.26$$

9.

Alkanes: $n\,CO + (2n + 1)\,H_2 \rightarrow C_nH_{2n+2} + n\,H_2O$
Alkenes: $n\,CO + 2n\,H_2 \rightarrow C_nH_{2n} + n\,H_2O$

10.

H_2 + CO: $CO + 2\,H_2 \rightarrow CH_4O$
H_2 + CO_2: $CO_2 + 3\,H_2 \rightarrow CH_4O + H_2O$

11.

Liquid alkane/alkene production requires a H_2 to CO ratio of about 2, whereas the methanol production requires a H_2 to CO_x ratio of 2.5 – 2.8. Thus the 20 minute run is not ideal for either process, the short run is well suitable for the production of methanol.

12.

$$n_{H_2} = 59.5\% * \frac{96.2\,L}{22.4\,L} = 2.55\,mol$$

$$n_{CO} = 4.6\% * \frac{96.2\,L}{22.4\,L} = 0.20\,mol$$

$$n_{CO_2} = \frac{n_{H_2} - 2.69 * n_{CO}}{2.69} = 0.75\,mol$$

Judging from the stoichiometries in **10**, full conversion requires $2 * 0.20\,mol + 3 * 0.75\,mol = 2.65\,mol$ H_2. As such H_2 is the limiting component and the theoretical maximum amount of methanol produced is:

$$\frac{2.55\, mol}{2.65\, mol} * (0.20\, mol + 0.75\, mol) = 0.91\, mol$$

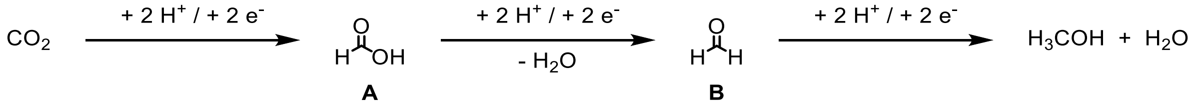
The mass of produced MeOH is then:

$$m_{MeOH} = 0.85 * 0.91\, mol * 32.04 \frac{g}{mol} = 24.8\, g$$

Solution: Many-faceted Oxides of Carbon

2.1.

a)



2.2. O activators: $X^{\delta+}$, $Z^{\delta+}$; C activators: $Y^{\delta-}$ or X = Lewis acid and Y = Lewis base

2.3.

$CaCO_3 \rightarrow CaO + CO_2$

$CaO + 3C \rightarrow CaC_2 + CO$

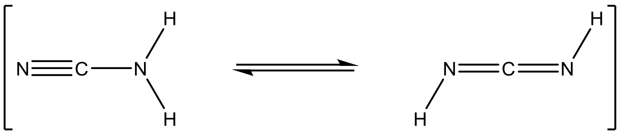
$CaC_2 + N_2 \rightarrow CaCN_2 + C$

$2\ CaCN_2 + 2\ H_2O \rightarrow Ca(OH)_2 + Ca(HCN_2)_2$

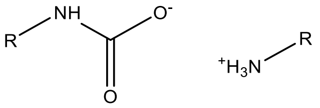
$Ca(HCN_2)_2 + H_2CO_3 \rightarrow CaCO_3 + 2\ H_2CN_2$

$H_2CN_2 + H_2O \rightarrow CO(NH_2)_2$

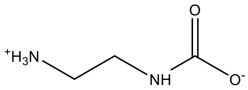
2.4. H_2CN_2 :

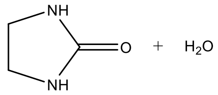


2.5. i) - Ammonium Carbamate:

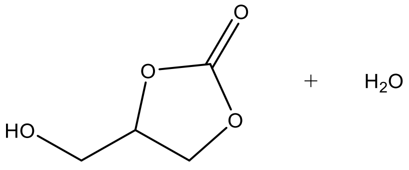


ii- Carbamate or dicarbamate:

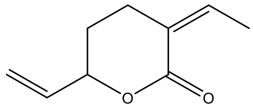


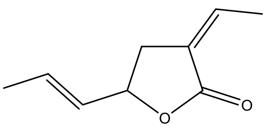


iii- cyclic ester:

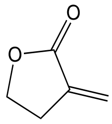


iv- Lactone from 2 butadien + CO_2 or 1 Butadien + CO_2:

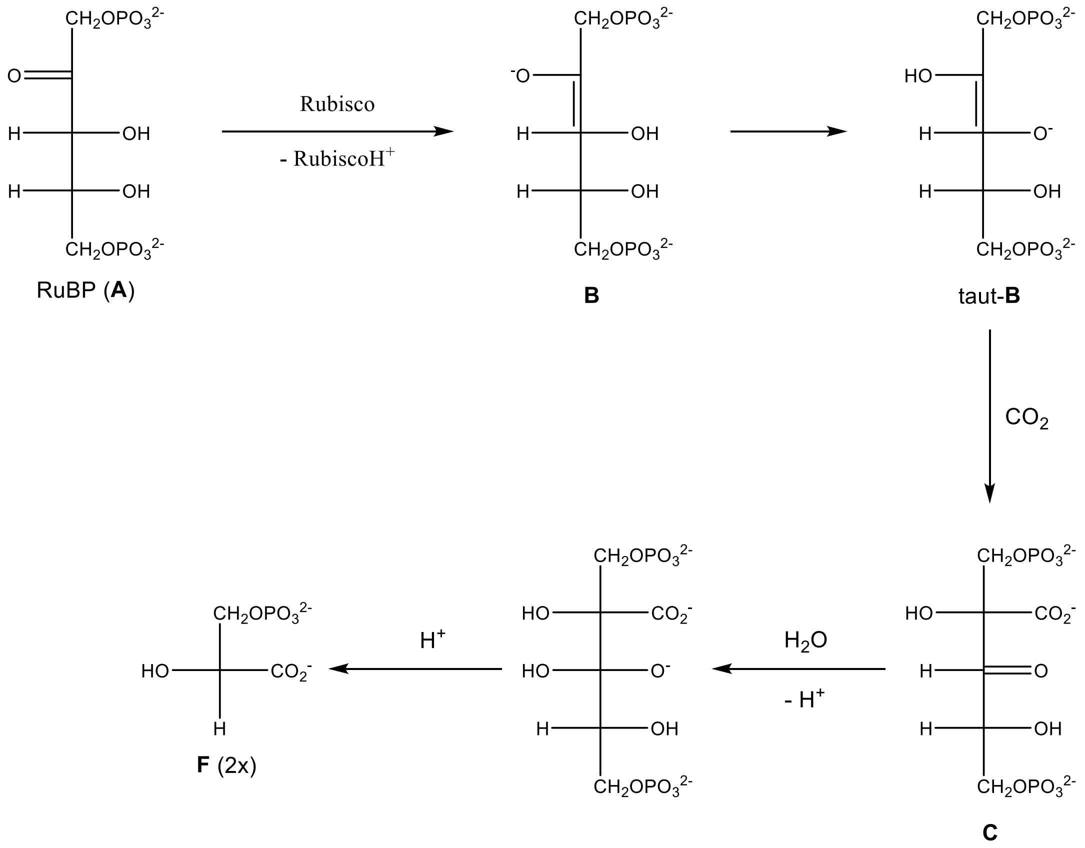




or

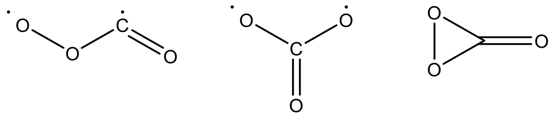


2.6.



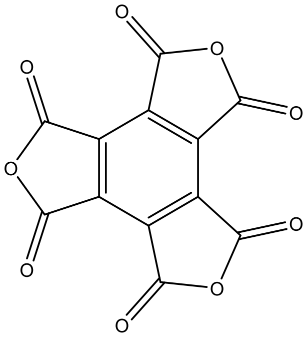
2.7.

1. CO_3, carbontrioxide



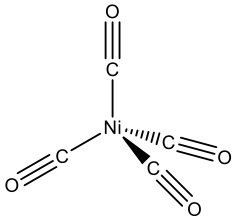
2. C_3O_2, carbonsuboxide $O{=}C{=}C{=}C{=}O$

3.



$C_{12}O_9$, mellitic anhydride

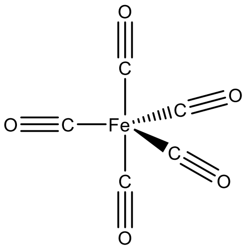
2.8.



tetrahedral

$Ni(CO)_4$

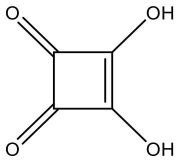
2.9.



$Fe(CO)_5$

trigonal bipyramidal

2.10.

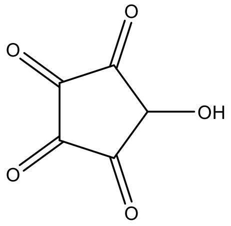


squaric acid

2.11

The dianion is resonance stabilized and the mono anion is stabilized by intramolecular hydrogen bonding.

2.12.

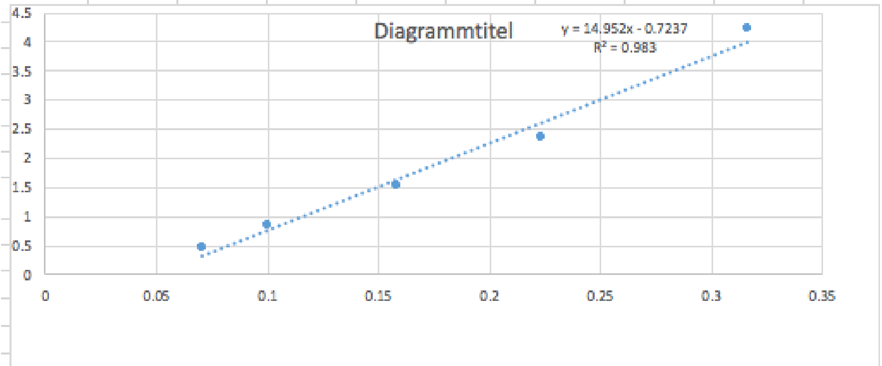


Croconic acid

Solutions - What to do with CO_2

3.1 The constant value k adds up to $2.69 \cdot 10^5 \cdot 1 \cdot 5 \cdot 10^{-6} \cdot 2.35 \cdot 10^{-3} = 3.15 \cdot 10^{-3}$ unit of k is C ($V^{-1/2}$ cm^{-2} $s^{-1/2}$)

3.2



y-axis: peak current in mA

x-axis: potential sweep rate in (V/s)$^{1/2}$

The plotted graph shows a slope of $14.94 \pm 0.5\ \mathrm{mA/(V/s)}^{1/2} = 14.94 \cdot 10^{-3}\ \mathrm{A/(V/s)}^{1/2}$. Since $k \cdot A = \mathrm{slope}$ we have $A = \mathrm{slope}/k$ and thus $A = 14.94/3.15 = 4.74 \pm 0.2\ \mathrm{cm}^2$.

3.3 $\mathrm{CO_2 + H_2O + 2e^- \rightarrow CO + 2OH^-}$
$\mathrm{2H_2O + 2e^- \rightarrow H_2 + 2OH^-}$

3.4 $n = \frac{Q}{z} \cdot F = I\frac{t}{z}F \implies I = nz\frac{F}{t} \implies I_{CO} = -(0.005\mathrm{mol} \cdot 2 \cdot 96485\mathrm{A\ s}\ /\ (36000\ \mathrm{s}) = -0.0268\mathrm{A} \implies I_{tot} = -0.0268\mathrm{A}/0.76 = -0.0352\mathrm{A} \implies j_{tot} = -0.0352\frac{\mathrm{A}}{10\ \mathrm{cm}^2} = -0.00352\mathrm{A\ cm}^{-2}$

$n = \frac{Q}{z} \cdot F = I\frac{t}{z}F \implies I = nz\frac{F}{t} \implies I_{CO} = -(0.005\mathrm{mol} \cdot 2 \cdot 96485\mathrm{A\ s}\ /\ (36000\ \mathrm{s}) = -0.0268\mathrm{A} \implies I_{tot} = -0.0268\mathrm{A}/0.76 = -0.0352\mathrm{A} \implies j_{tot} = -0.0352\frac{\mathrm{A}}{10\ \mathrm{cm}^2} = -0.00352\mathrm{A\ cm}^{-2}$

3.5 $j_{H_2} = j_{tot} \cdot FE_{H_2} = -0.00352\mathrm{A\ cm}^{-2} \cdot 0.24 = -0.00084\mathrm{A\ cm}^{-2}$ (of note, by convention cathodic currents have a negative sign.

3.6

$j_{tot} = -33.9 \text{ mA cm}^{-2}$

$FE_{product} = j_{product}/j_{tot} \rightarrow FE_{CO} = 14.1\%$

$FE_{H_2} = 25.1\%$

$FE_{CH_4} = 55.5\%$

$FE_{C_2H_6} = 5.3\%$

Solution - Pathways to H_2 and catalysts

Hydrides

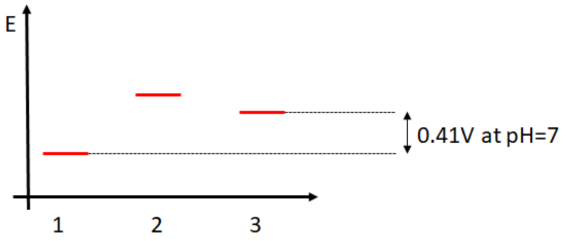
4.1. It is both, an acid base reaction, a proton is transferred from water to the hydride ion, and a redox reaction since it is a comproportionation: –I + +I → 0

4.2. The overall ΔG° of this reaction is -432+360=-72kJ/mol. Thus, the disproportionation may not be higher than +72kJ/mol. According to $\Delta G° = -n \cdot F \cdot \Delta E°$, this corresponds to a disproportionation potential of -0.75V.

4.3. The most common oxidation states of Co are +I (d^8), +II (d^7) and +III (d^6). Thus, Co-H is in the oxidation state +I as a hydride and +III as an acid. Formal comproportionation to +II.

4.4. If pK_{a1} goes up, pK_{a2} goes up: The ligand donates electrons to the metal center, making it electron rich. The more electron density is localized on the metal center, the more the pK_{a1} increases and the H becomes less acidic and more "hydridic".

4.5.



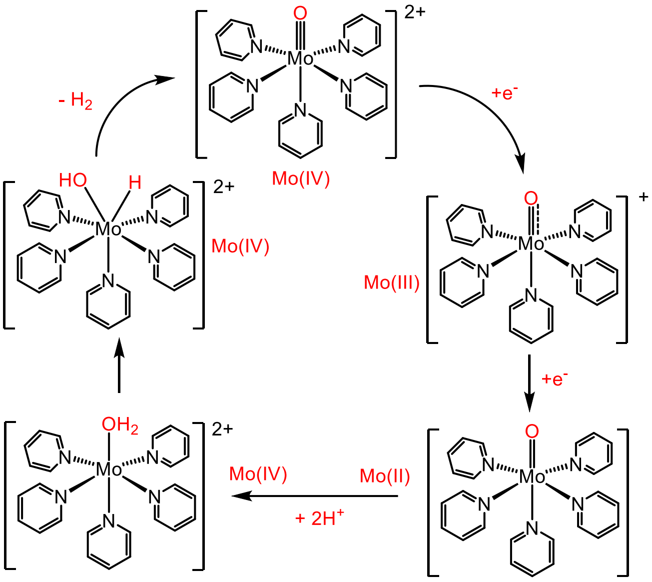
Since 2 disproportionates, its level must be above the line between 1 and 3. If the standard potential is about 0V, the potential at pH=7 is about -0.41V.

4.6. With the given data, the $T\Delta S°_r$ can be calculated: $T\Delta S°_r = 298*(205+2\cdot 41.6 - 2\cdot 43.6)/2 = 29.9$kJ/mol. With the Gibbs formula, $\Delta G°_r$ is thus -318kJ/mol.

For K=1, $\Delta G°_r$ is 0 or $\Delta H°_r = T\Delta S°_r$. or $348 = T\cdot 29.9$ and T=3462K assuming that $\Delta H°_r$ is temperature independent.

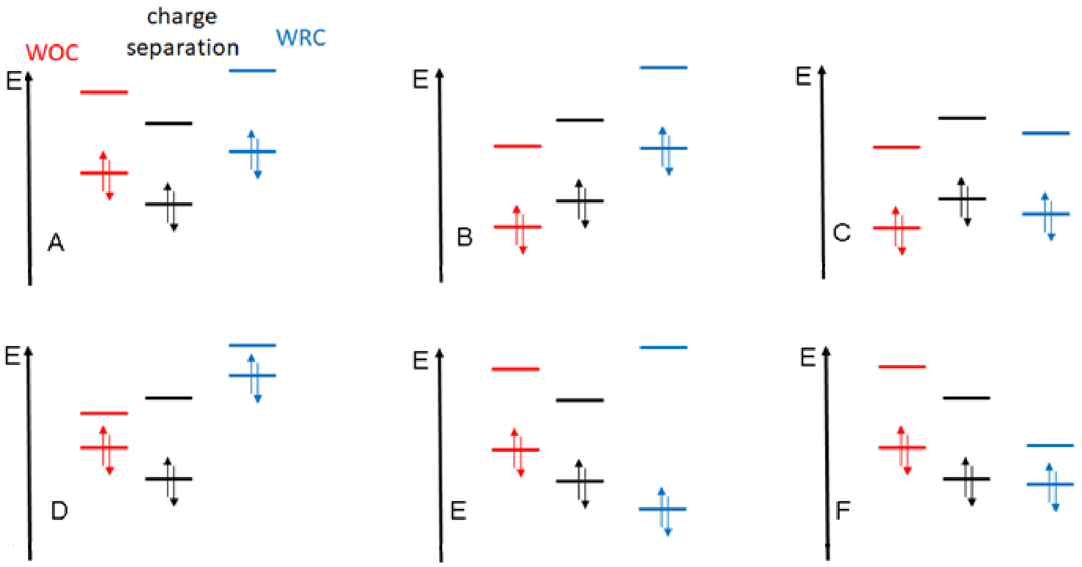
Catalysts

4.7.



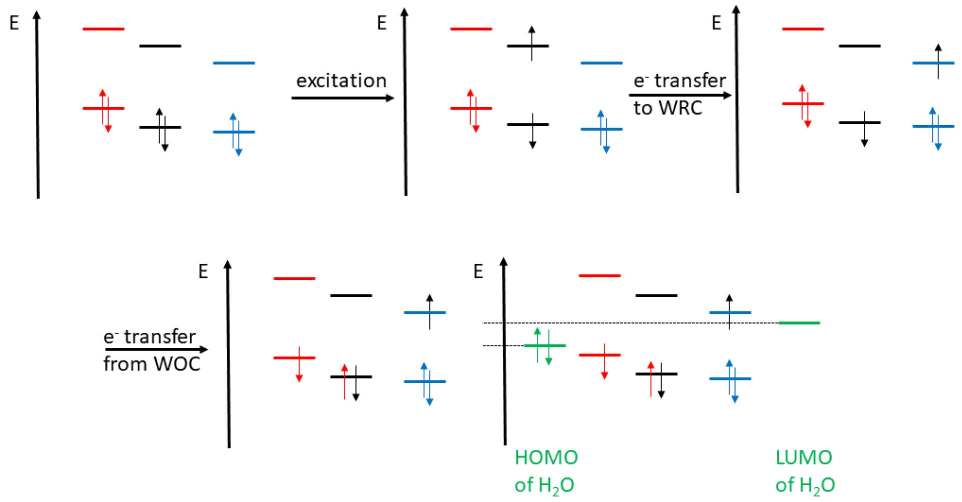
4.8. The $\Delta E^\circ_{1/2}$ for the reaction $[CuL_2]^{2+} + 1e^- \rightarrow [CuL_2]^+$ becomes more positive the bulkier the red groups are.

4.9.



F is the only possibility. After excitation, the electron is in a higher level than the LUMO of the WRC and can be transferred. The "hole" of the sensitizer can be filled with an electron from the HOMO of the WOC. These three processes lead to charge separation.

4.10.



Water transfers an electron from its highest occupied energy level to WOC and is thereby oxidized and WRC gives an electron from its lowest unoccupied energy level into the lowest unoccupied energy level of water.

4.11. $\Delta E°$ corresponds to 1.23eV per electron and thus to $1.97\cdot10^{-19}$J. With $E=h\cdot\nu=h\cdot c/\lambda$, we get for λ= 1003.8nm

4.12. $E_{tot} = E_{ps} + E_{ex}$ thus $h\cdot c/\lambda_{inc} = h\cdot c/\lambda_{ex} + h\cdot c/(1003)$ or $\lambda_{ex}= (\lambda_{inc}\cdot\lambda_{ps})(\lambda_{ps}-\lambda_{inc})$

For the 500nm photon, the excess energy would thus correspond to a photon of 994nm

Solution – Two Transition Metals – Many Oxidation States

5.1.

a) 1.4 V b) 2.0 V

The following information about the different species is given:

Species	Oxidation State of Ru	Charge of complex	Molecular Mass (g/mol)
A	+VI	-2	540.69
B	+III	none	261.42
C	+III	-2	> 260
D	+IV	-2	
E	+III	-3	

5.2 A $Cs_2[RuO_2Cl_4]$; calculation example:

oxidation state and anion charge require 8 neg. charges; counterion can only be Cs

possible composition of the anion (without charges)

$RuCl_8$

$RuOCl_6$

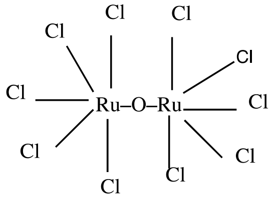
RuO_2Cl_4

$RuO_3Cl_2(H_2O)$

Only RuO_2Cl_4 is 6 coordinate and fits together with 2 Cs the MM of 540.69

B: $RuCl_3 * 3\ H_2O$ **C**: $[RuCl_5H_2O]^{2-}$ **D**: $[RuCl_6]^{2-}$ **E:** $[RuCl_6]^{3-}$

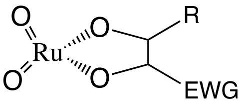
5.3 F contains a Ru-O-Ru unit:



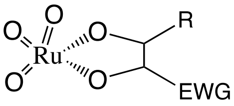
5.4 $RuO_4 + 2\ CsCl + 4\ HCl \rightarrow Cs_2[RuO_2Cl_4] + 2\ H_2O + Cl_2$

5.5 Draw the missing structures A, B, and C.

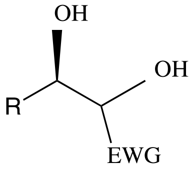
A Ester:



B oxidized ester



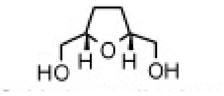
C dihydroxy compound



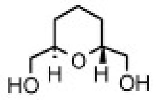
5.6. Ox states: RuO_4: VIII, A : +VI, B: +VIII,

5.7. tetrahydrofuran derivative

(a tetrahydropyran derivative is also possible)



5.8. tetrahydropyran derivative



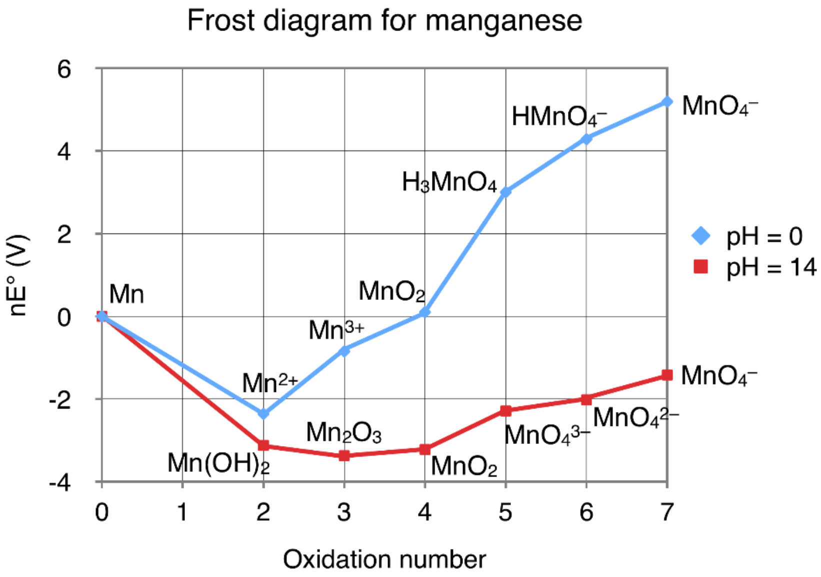
5.9.

Table 1

Redox reactions at pH 0	**E_0 / V**
$Mn^{2+} + 2e^- \rightarrow Mn$	-1.18
$Mn^{3+} + e^- \rightarrow Mn^{2+}$	1.51
$MnO_2 + 4H_3O^+ + e^- \rightarrow Mn^{3+} +. 6\ H_2O$	0.95
$H_3MnO_4 + H_3O^+ + e^- \rightarrow MnO_2 + 3\ H_2O$	2.90
$H_2MnO_4 + H_3O^+ + e^- \rightarrow H_3MnO_4. +. H_2O$	1.28
$MnO_4^- + 2H_3O^+ + e^- \rightarrow H_2MnO_4 +.3\ H_2O$	0.92

Table 2

Redox reactions at pH 14	**E_0 / V**
$Mn(OH)_2 + 2e^- \rightarrow Mn + 2\,OH^-$	-1.56
$Mn_2O_3 + 3H_2O + 2e^- \rightarrow 2Mn(OH)_2 + 2OH^-$	-0.25
$2MnO_2 + H_2O + 2e^- \rightarrow Mn_2O_3 + 2OH^-$	0.15
$MnO_4^{3-} + 2H_2O + e^- \rightarrow MnO_2 + 4OH^-$	0.97
$MnO_4^{2-} + e^- \rightarrow .\ MnO_4^{3-}$	0.27
$MnO_4^- + e^- \rightarrow MnO_4^{2-}$	0.56



5.10. pH 14

5.11.

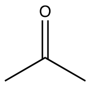
a) and b)

In both cases disproportionation ; they are above the line that connects their neighbours.

a) $2\,H_3MnO_4 \rightarrow MnO_2.\ +.\ H_2MnO_{4.} + 2\,H_2O$

b) $2\,Mn^{3+} + 2\,H_2O.\ \rightarrow.\ Mn^{2+}.\ +.\ MnO_2\ +.\ 4\,H^+$

5.12. 2 molecules of acetone.



5.13.

red.: $MnO_4^- + 3\ e^- + 4H^+ \rightarrow MnO_2 + 2\ H_2O$ (x 4)

ox.: $C_6H_{12} + 2\ H_2O \rightarrow 2\ (C_3H_6O) + 4\ e^- + 4\ H^+$ (x 3)

$\Rightarrow 4\ MnO_4^- + 4\ H^+ + 3\ (C_6H_{12}) \rightarrow 4\ MnO_2 + 2\ H_2O + 6\ (C_3H_6O)$

Solutions - Useful Radioactivity

6.1.

a) lnA – ln A_0 = –⍰⍰· t

A = 29 MBq

b)

1.02 MBq

c)

13:05:20

d)

$T_{1/2}$ = ln2/⍰ ⍰⍰ = 0.0001706 s^{-1}

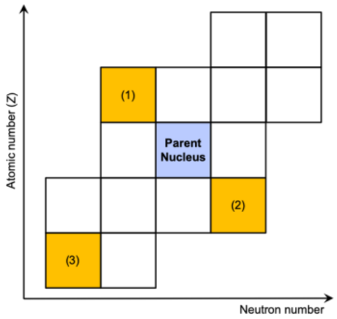
A = ⍰⍰⍰

1g = x N

1g ^{68}Ga = $8.855*10^{21}$ Teile

A= 0.0001706 s^{-1} x $8.855*10^{21}$ = $1.51*10^{18}$ Bq / gr = $1.51*10^{9}$ GBq / gr

6.2 (1) ⍰$^-$, (2) ⍰$^+$, (3) ⍰



6.3.

What are the isotopes **A** and **B**?

A = U-239 B = Np-239

6.4.

Th-232 (n) → Th-233 (⍰$^-$) → Pa-233 (⍰$^-$) → U-233

6.5.

$N = N_o\, e^{-⍰t}$ (1)

N_o can be replaced when the number of daughter nuclides (D) is taken into account:

$N_o = N + D$

Equation (1) can then be written as

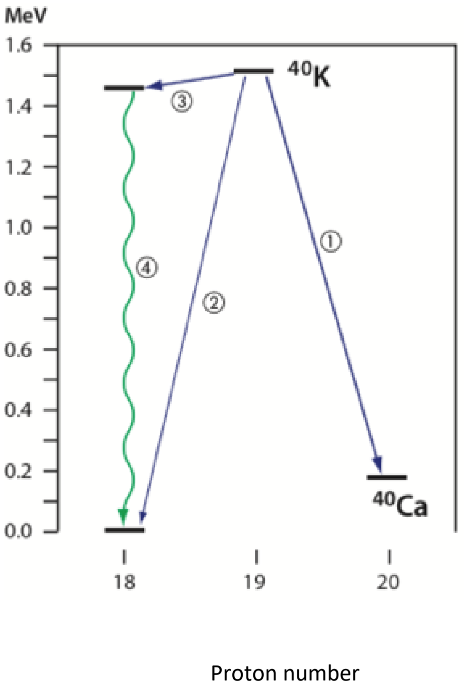
$N = (N + D) \cdot e^{-⍰t}$

$N \cdot e^{⍰t} = N + D$

$D = N \cdot (e^{⍰t} - 1)$ or, D being N_D and N = N_M, you get the above equation

$N_D = N_M\cdot(e^{\square t} - 1)$

6.6.



1) 89.14% undergo a β–decay to the ground state of ^{40}Ca.

2) 0.2% undergo an electron capture to the ground state of ^{40}Ar

1) 10.66% undergo an electron capture to the excited state of ^{40}Ar

□□□□□□Decay of the excited state of ^{40} Ar to the ground state under γ-*emission*

6.7.

$\lambda_{tot}=\lambda_\beta+\lambda_\varepsilon= 5.543\cdot10^{-10}\,\alpha^{-1}$ $N_{K\text{-}40} = 0.012\%$ of 0.14 kg * 40/39 = 0.0172 mg

$N_D = N_M\cdot(e^{\lambda t}-1)$

$N_{Ar\text{-}40} + N_{Ca\text{-}40} = N_{K\text{-}40}\cdot(e^{\lambda t}-1)$

$N_{Ar\text{-}40} + N_{Ca\text{-}40} = (\lambda_\beta + \lambda_\varepsilon)/\lambda_{tot}\cdot N_{K\text{-}40}\cdot(e^{\lambda t}-1)$

$N_{Ar\text{-}40} + N_{Ca\text{-}40} = \lambda_\varepsilon/\lambda_{tot}\cdot N_{K\text{-}40}\cdot(e^{\lambda t}-1) + \lambda_\beta/\lambda_{tot}\cdot N_{K\text{-}40}\cdot(e^{\lambda t}-1)$

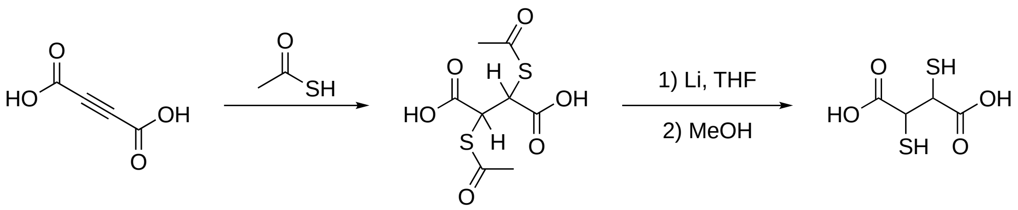
$\Rightarrow N_{Ar\text{-}40} = \lambda_\varepsilon/\lambda_{tot}\cdot N_{K\text{-}40}\cdot(e^{\lambda t}-1)$

$t = 1/\lambda_{tot}\cdot\ln(N_{Ar\text{-}40}/N_{K\text{-}40}\cdot\lambda_{tot}/\lambda_\varepsilon+1)$

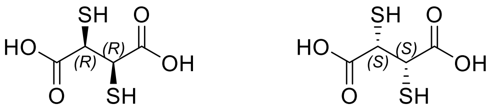
$t = 755\cdot10^3$ a

Solution – Heavy Metal Detoxification

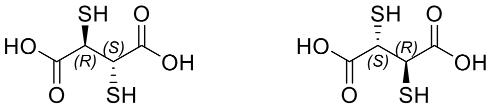
7.1.



7.2.



Enantiomers



meso

7.3. The meso form

7.4.

First Proton:

R-COOH → H^+ + R-COO–

0.1 – x x x

The resulting quadratic equation renders c(H^+) = c($RCOO^-$) = x = 0.013 mol/L.

pH = 1.886

Second proton

initial	R’-COOH	H^+ +	R’-COO^-
change	– y	+ y	+ y
equilibrium	0.013 – y	0.013 + y	y

The resulting quadratic equation renders y = 0.000262

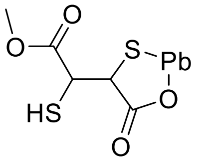
Thus c(H+) = 0.013 + y = 0.013 + 0.000262 = 0.01326

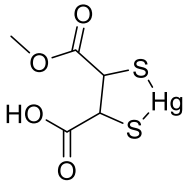
pH = 1.877

The S-H protons can be neglected. Also, the approximation of decoupling the two dissociation steps is justified, since the difference is small and otherwise the algebra would be much more complicated.

7.5.

Pb (and Cd): bonding through O and S; Hg bonding through the two S since the Hg IR spectrum shows no -COO^- band.





7.6. The Hg complex has two free carbonic acid group; when losing a proton the resulting carboxylate anion is stabilized by an additional hydrogen bond from the other carboxylic group. This reaction is similar to malonic acid.
The Pb complex has only one carboxylic group, the pka is in the range of acetic acid.

7.7.

	DMSA [mol/L]	Pb [mol/L]	Pb(DMSA)
Initial	4.12 E-4	4.12E-6	0
End	4.12E-4·0.995 = 4.0994 E-4	4.12E-6 – (4.12 E-4 · 0.005) = **2.06 E-6**	(4.12E-4 · 0.005) = 2.06 E-6

7.8.
We test for a first order reaction mechanism:

t in min	0	60	120	180	240	300	360
ln c (μmol/L)	0.722	0.507	0.293	0.074	-0.140	-0.356	-0.580

It gives a linear graph; thus:

a) $t_{1/2}$ = 192.5 min; k = – 0.0036 μmol $L^{-1}min^{-1}$

7.9. 90 μg/L = 0.494 μmol/l thus: 396.7 min

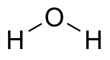
7.10. DMSA-Pb + Cd^{2+}(aq) → DMSA-Cd + Pb^{2+}(aq)
K = [DMSA-Cd] [Pb^{2+}(aq)]/ [DMSA-Pb] [Cd^{2+}(aq)]

7.11. K = K_{Cd} : K_{Pb} = $10^{16.5}$: $10^{17.6}$ = $\mathbf{10^{-1.1}}$

7.12. [Pb-DMSA]= 0.0847 mol/L; [Cd-DMSA] = 0.0153 mol/L
[Pb^{2+}]= 0.0153 mol/L; [Cd^{2+}] = 0.0347 mol/L

Vacuum-UV Modification of PDMS

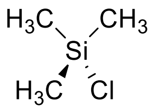
8.1



A

$H-Cl$

B



C

8.2

Process	Number
x-ray photon absorption	4
γ-photon absorption	5
IR-photon absorption	1
Electron transfer between molecules	2
Ionization of a molecule	3

8.3

$E_{photon} = h\,\nu = h\,c/\lambda = 6.6261\cdot10^{-34}$ J s $\cdot\ 3\cdot10^{8}$ m$\cdot$s^{-1} / 172 $\cdot\ 10^{-9}$ m = $1.155\cdot10^{-18}$ J

For 1 mol photons: $E_m = N_A \cdot E_{photon} = 6.0221\cdot10^{23}$ mol^{-1} = 695.4 kJ/mol. Hence, the absorption of one photon is sufficient to break the bond.

8.4

Lambert-Beer law: $A = \varepsilon\, l\, c$. We have 3.5 = 1 μm $\cdot\ \varepsilon\ c$, hence ε c = $3.5\cdot10^{6}$ m^{-1}. $A = \ln(I_0/I_S)$. If 99% of the light is absorbed, $A = \ln(1/0.01) = 4.605$. The material depth is $l = A/(\varepsilon\, c) = 4.605/3.5\cdot10^{6} = 1.32$ μm.

8.5

$\Delta G = G(\cdot\text{Si}\equiv) - G(\cdot\text{CH}_2\text{Si}\equiv) = -RT\ln K = -8.314$ J$\cdot$mol$^{-1}\cdot$K^{-1} $\cdot$ 298 K $\cdot$ ln(1/8) = 5.152 kJ/mol.

8.6

Since ^{13}C and ^{29}Si have low natural abundance, hyperfine splitting from only the protons with spin $I = ½$ is observed. Two protons lead to three lines.

8.7

☐ Oxidation reduces the molar extinction coefficient. Thus, more light penetrates into the sample in later pure nitrogen phases and more radicals are formed.

(this cannot be the case, as the light is completely absorbed in all cases, see task 1.4)

☐ During the whole experiment, radicals are formed with the same rate, but in the presence of oxygen their signal is invisible.

(this cannot be the case, since the signal is not immediately restored after switching back to nitrogen and since some signal is seen in the presence of oxygen).

☒ Oxidation creates sites in the modified polymer that are more susceptible to forming radicals.

(this is likely, since radicals are formed faster after the first oxidation period and more radicals are formed at this fast rate after additional oxidation periods)

☒ Some of the formed radical sites are stable in the presence of 2% oxygen.

(there is clearly a non-zero spin count during the oxidation periods)

8.8

The irradiated volume is $V = 0.26\cdot10^{-6}$ m · $1.5\cdot10^{-4}$ m^2 = $3.9\cdot10^{-11}$ m^3. The polymer mass is thus m = 950 kg · m^{-3} · $3.9\cdot10^{-11}$ m^3 = $3.705\cdot10^{-8}$ kg. The molar mass of the PDMS repeat unit is M = (28.09 g/mol + 16.00 g/mol + 2·12.01 g/mol + 6·1.0079 g/mol) = $74.16\cdot10^{-3}$ kg/mol. The number of irradiated repeat units is thus $N = \mathrm{N_A}\cdot 3.705\cdot10^{-8}$ kg / $74.16\cdot10^{-3}$ kg/mol = $6.0221\cdot10^{23}$ mol^{-1} · $5.00\cdot10^{-7}$ mol = $3.01\cdot10^{17}$. The number of $\cdot CH_2Si\equiv$ radicals is $2\cdot10^{15}\cdot(8/9) = 1.78\cdot10^{15}$. Hence, the percentage of PDMS repeat units that had been that had been transformed into $\cdot CH_2Si\equiv$ radicals is 100 % · $1.78\cdot10^{15}$ / $3.01\cdot10^{17}$ = 0.6 %.

8.9

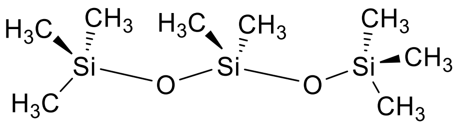
With $n(t) = n_\infty (1 - e^{-k\,t})$ we have $n_\infty = n(t)/(1 - e^{-k\,t})$. We insert $n(t) = 2\cdot10^{15}$ and $k\,t = 0.48$ and obtain $n_\infty = 5.25\cdot10^{15}$.

8.10

From $n_A(1\text{ h}) = n_{A,\infty}\,[1 - \exp(-48)] = n_B(1\text{ h}) = n_{B,\infty}\,[1 - \exp(-4)]$ we obtain $n_{B,\infty} = 1.019\cdot n_{A,\infty}$. After 15 min, we have $n_A(0.25\text{ h}) = n_{A,\infty}\,[1 - \exp(-12)] \approx n_{A,\infty}$ and $n_B(0.25\text{ h}) = 1.019\cdot n_{A,\infty}\,[1 - \exp(-1)] = 0.644\cdot n_{A,\infty}$. Hence, the ratio is $R_{AB} = 1/0.644 = 1.55$.

8.11

The ratio C:Si:H:O is 0.406/12.01:0.356/28.09:0.102/1.0079:0.136/16.00 = 3.98:1.49:11.9:1. We can thus expect an elemental formula $(C_8Si_3H_{24}O_2)_n$. All protons are aliphatic and, given the chemical shifts, probably methyl protons. The number of protons per heavy atoms excludes multiple bonds or a ring. We have $18n$ protons of one type and $6n$ protons of the other type. The $18n$ equivalent protons must be attached to carbon atoms ($6n$ equivalent methyl groups). With $n > 1$, it is impossible to realize that many equivalent methyl groups. Since there are no splittings in the ^{1}H NMR spectrum, the heavy atoms to which the hydrogen atoms are bound, must be separated by more than one bond. The 6 equivalent methyl groups can be bound only to two silicon atoms. The remaining 6 equivalent protons then must belong to two more methyl groups. Thus, only the following structure is consistent with the spectra and elemental composition:



8.12

☐ IR

☐ ^{1}H NMR

☐ ^{27}SI NMR

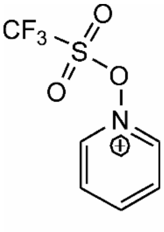
☒ Determination of molecular mass

☐ Elemental analysis

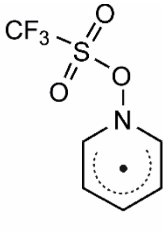
The two NMR methods will show only a single signal for any *n*. The IR spectra may differ in the fingerprint region. However, this region can be interpreted only if the spectra of individual members are already known. Elemental analysis gives the same result for all n. Only determination of molecular mass will distinguish the different oligomers.

Exciting Arenes

9.1

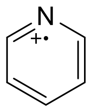


A

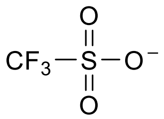


B

9.2

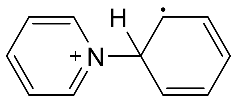


C



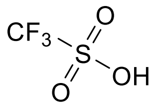
D

9.3

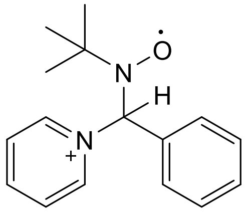


E

9.4



9.5



9.6

Isotope	Number of nuclei
^{1}H	1
^{14}N	2

One counts 18 = 2·3·3 lines. The number of lines is ⍰$_i$ $(2\ k_i\ I_i + 1)$, where index *I* runs over all groups of equivalent nuclei, k_i is the number of equivalent nuclei in a group, and I_i is the nuclear spin. The nuclear spins are I = ½ for ^{1}H and *I* = 1 for ^{14}N. The factor 2 can only arise from a single ^{1}H. Factors 3 can arise either from a single ^{14}N or from two equivalent ^{1}H. In the former case, the three lines have the same intensity, in the latter one, they have intensity ratio 1:2:1, which is not observed. Factors 6 or 9 from several equivalent ^{1}H or ^{14}N are also excluded by the intensity ratios.

9.7

☐ The photon energy alone is sufficient for cleaving the C-H bond.

☐ The energy for breaking the C-H bond is supplied by the catalyst.

☒ The energy for breaking the C-H bond cannot be discussed separately from bond formation in the same reaction step.

☐ The energy for breaking the C-H bond must be supplied by heating the solvent.

E_{photon} = h ⍰ = h c/⍰ = $6.6261 \cdot 10^{-34}$ J s · $3 \cdot 10^{8}$ m·s^{-1} / 439 · 10^{-9} m = $4.53 \cdot 10^{-19}$ J

For 1 mol photons: $E_{\mathrm{m}} = N_A \cdot E_{\mathrm{photon}}$ = $6.0221 \cdot 10^{23}$ mol^{-1} = 273 kJ/mol. Hence, the absorption of one photon is not sufficient to break the bond. The catalyst cannot supply the energy, because it is reformed in the catalytic cycle. Indeed, total energy of bond breaking and formation must be considered, which means that we cannot conclude without further information whether the step is endothermic.

9.8

⍰(UV) < ⍰(green light) < ⍰(red light) < ⍰(IR) < ⍰(microwave)

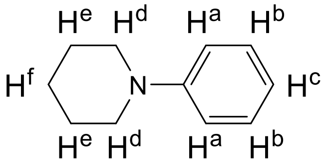
9.9

⍰$_R G^\circ = -zFU^\circ = -RT \ln K \Rightarrow K = \exp[(zFU^\circ/(RT)] = \exp[96485\ C \cdot mol^{-1} \cdot (-0.3 + 1.2)\ V/(298\ K \cdot 8.314\ J \cdot mol^{-1} \cdot K)]$ = $1.666 \cdot 10^{15}$.

9.10

If phosphorescence is half as large und quenching conditions, quenching has the same rate as emission. Thus, we have $v = k\,[R] = 1/(8.55 \cdot 10^{-7}\ s)$ with $[R] = 5 \cdot 10^{-3}$ M. We find $k = 2.34 \cdot 10^{8}\ s^{-1} \cdot M^{-1}$.

9.11



9.12

The elemental analysis is normalized to the element with lowest content: N

element	*Mol. mass*	*EA*	*M EA_N /M_N EA*
C	*12.000*	*53.18%*	*16*
H	*1.008*	*5.02%*	*18*
F	*18.998*	*15.77%*	*3*
N	*14.007*	*3.88%*	*1*
O	*15.999*		
S	*32.06*		

Mono isotopic mass of the compound is 212.1434. It only contains C,H and N. OR structure in 2.11 solved. The only suitable molecular formula is $C_{15}H_{18}N$. That leaves $C_1F_3O_eS_f$ for the counter ion.

(O+S)=100%-53.18%-5.02%-15.77%-3.88%=22.15%

f=	*expected % in EA*	*result*
1	*8.88*	*possible*
2	*17.76*	*possible*
3	*26.64*	*impossible*

f<3

e=		
1	*4.43*	*possible*
2	*8.86*	*possible*
3	*13.30*	*possible*
4	*17.73*	*possible*
5	*21.16*	*possible*

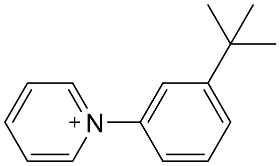
e<6

The sum of both elements must be 21.15%. This is true for

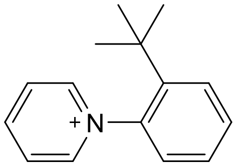
$CF_3OS_2^-$, $CF_3O_3S^-$ and $CF_3O_5^-$

$CF_3O_3S^-$ is known as triflate, $CF_3O_5^-$ has no possible structure and $CF_3OS_2^-$ is not a common organic counter ion

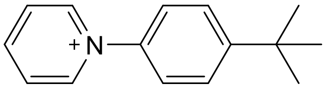
9.13



I



J



K

9.14

3

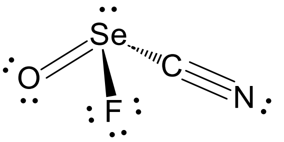
9.15

^{1}H NMR: 7: CH3 s; piperidine ring: CH2 multi, CH2 multi; phenyl ring: CH d, CH dd, CH d

^{13}C NMR: 12

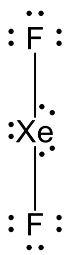
Unusual Fluorine Compounds

10.1.

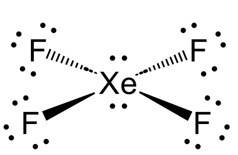


10.2. The angle C-Se-F is smallest due to the strong repulsion by the Se=O electron-pairs domain (calculated angles: C-Se-F = 90.6°; O-Se-F = 106.3°; C-Se-O = 103.9°)

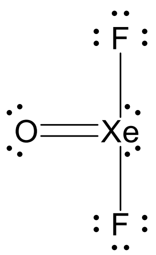
10.3. The geometry is given with respect to the arrangement of atoms. The geometry with respect to electron-pair domains is given in parentheses.



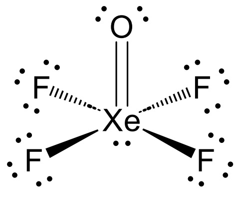
linear
(trigonal bipyramidal)



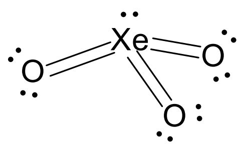
square planar
(octahedral)



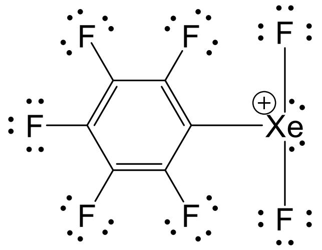
T-shaped
(trigonal bipyramidal)



square pyramidal
(octahedral)



trigonal pyramidal
(tetrahedral)



T-shaped
(trigonal bipyramidal)

10.4. For **B**, the smallest multiple of the molecular weight MW_n is computed as

$$MW_n = \frac{M(S)}{\omega(S)} = \frac{32.06\ \text{g mol}^{-1}}{0.4748} = 67.51\ \text{g mol}^{-1},$$

subtracting the molecular weight of the known element sulfur, we draw the conclusion that the remaining weight corresponds to one equivalent of chlorine:

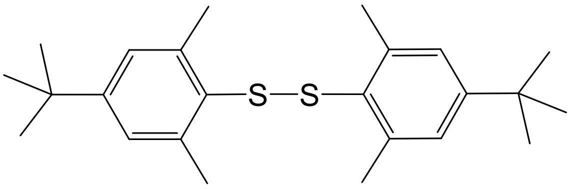
$$67.51\ \text{g mol}^{-1} - 32.06\ \text{g mol}^{-1} = 35.45\ \text{g mol}^{-1} \Rightarrow (\text{SCl})_n$$

Now, we can formulate formulae for each n until we find a chemically feasible structure (i.e. the Lewis structure can be drawn in a way to obtain a theoretically stable molecule):

n = 1: SCl not feasible

n = 2: S_2Cl_2 is a chemically feasible structure (see also 6.)

For **C**, the molecule must contain sulfur. With the given molecular weight small reasonable products can be excluded:



C (ArSSAr)

$\mathrm{SCl_2 + Cl_2 + 4\ KF \rightarrow SF_4 + 4\ KCl}$ (1)

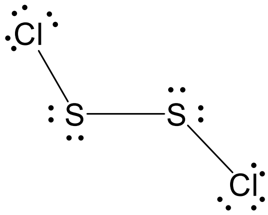
$\mathrm{3\ SCl_2 + 4\ KF \rightarrow SF_4 + S_2Cl_2 + 4\ KCl}$ (2)

$\mathrm{ArH + S_2Cl_2 \rightarrow ArSSAr + 2\ HCl}$ (3a)

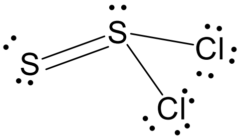
$\mathrm{ArSSAr + 3\ Cl_2 + 6\ KF \rightarrow ArSF_3 + 6\ KCl}$ (3b)

10.5. Disproportionation (sulfur is both oxidized, S(+II) to S(+IV), and reduced, S(+II) to S(+I))

10.6. Structure **B-b** is known only in the case of S_2F_2:

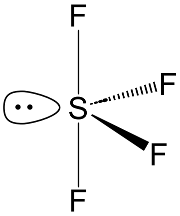


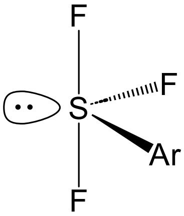
B-a



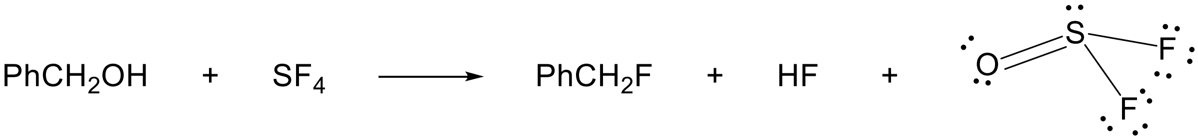
B-b

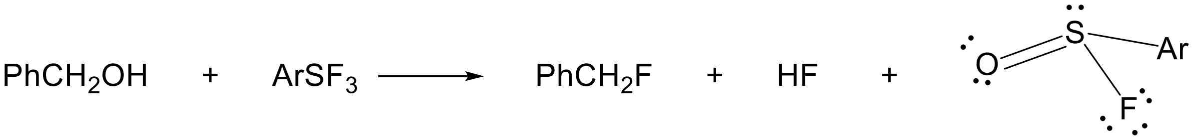
10.7. Both compounds have a trigonal bipyramidal geometry with respect to the valence-shell electron-pair domains. The non-bonding electron pair at the sulfur atom in both compounds as well as the Aryl substituent in Fluolead are in an equatorial position.


F
S
F
F
F


F
S
F
Ar
F

10.8.


PhCH2OH
+
SF4
PhCH2F
+
HF
+
O
S
F
F


PhCH2OH
+
ArSF3
PhCH2F
+
HF
+
O
S
Ar
F

Dynamic Phosphorus and Arsenic Compounds

11.1. *(S)*-**2**, *(R)-ent*-**2**

11.2. The Arrhenius equation is used to describe the dependence of the reaction rate constant as a function of temperature and the activation energy and is an empirical law. The Eyring equation is similar to that but uses a statistical mechanical treatment and transition-state model to find an expression for the temperature-dependence of a rate constant. In the exam, it will be clearly stated which treatment should be used (Eyring or Arrhenius):

$$\Delta G^{\ddagger}_{en} = RTln\left(\frac{k_BT}{k_{en}h}\right) \Leftrightarrow \frac{k_BT}{k_{en}h} = e^{\frac{\Delta G^{\ddagger}_{en}}{RT}} \Leftrightarrow k_{en} = \frac{k_BT}{h\, e^{\frac{\Delta G^{\ddagger}_{en}}{RT}}}$$

with $T = 100 + 273.15 \; = \; 373.15 \text{ K}$ and $\Delta G^{\ddagger}_{en} = 37.3 \text{ kcal mol}^{-1} \cdot 4.184 \text{ kJ kcal}^{-1} \cdot \; 1000 \text{ J kJ}^{-1} = 156000 \text{ J mol}^{-1}$:

$$k_{en} = \frac{k_BT}{h\, e^{\frac{\Delta G^{\ddagger}_{en}}{RT}}} = k_{en} = \frac{1.38 \cdot 10^{-23} \text{ J K}^{-1} \; 373.15 \text{ K}}{6.63 \cdot 10^{-34} \text{ J s}^{-1} \; \mathrm{e}^{\frac{156000 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1}\text{K}^{-1} \cdot 373.15 \text{ K}}}} = 1.13 \cdot 10^{-9} \text{ s}^{-1}$$

k_{en} is thus equal to $1.13 \cdot 10^{-9} \; s^{-1}$.

11.3. For first order kinetics, the rate law is described as:

$$v_{rac} = -k_{rac} \cdot [2] \cdot t \; = \; \frac{d[2]}{dt} \Leftrightarrow \ln\big([2](t)\big) = \ln([2]_0) - k_{rac} \cdot t$$

for the half-life, $ln([2](t_{1/2})) = ln\left(\frac{[2]_0}{2}\right)$ and thus

$$ln\left(\frac{[2]_0}{2}\right) \; = \; ln([2]_0) \; - k_{rac} \cdot t_{1/2} \;\; \Leftrightarrow \;\; t_{1/2} \; = \; \frac{ln(2)}{k_{rac}} = \frac{ln(2)}{2 \; k_{en}}$$

with this, the half-life is computed from the rate constant calculated in II. (the temperature stays the same) as

$$t_{1/2} = \frac{ln(2)}{2 \cdot 1.13 \cdot 10^{-9} \text{s}^{-1}} = 3.07 \cdot 10^{8} \text{s} \; = \; 3560 \text{ d} \; = \; 9.74 \text{ a}$$

The half-life for the racemization process is thus equal to 9.74 years.

11.4. The enantiomeric excess is described as $ee(\%) = \frac{|[S]-[R]|}{[S]+[R]} \cdot 100\%$, where $[S]$ and $[R]$ stands for the concentration of the enantiomers. In equilibrium, i.e. when $t \rightarrow \infty$, we obtain a racemic mixture of 50% $[S]$ and 50% (ee = 0). In other words, when the concentration of the enantiomerically pure $[S]$ sample was $[A]_0$, in equilibrium, $[A]_\infty = \frac{1}{2}[A]_0$.

To determine $[A]_t$, we express $[S]$ as $[A]_t$ and $[R]$ as $[A]_0 - [A]_t$, so that

$$ee = \frac{|[S]-[R]|}{[S]+[R]} = \frac{|[A]_t - ([A]_0 - [A]_t)|}{[A]_0 - [A]_t + [A]_t} = \frac{|2[A]_t - [A]_0|}{[A]_0}$$

$$\Leftrightarrow [A]_t = \frac{[A]_0}{2}(1+ee)$$

Inserting this into the original expression for the integrated rate law yields

$$ln\left(\frac{[A]_t - [A]_\infty}{[A]_0 - [A]_\infty}\right) = ln\left(\frac{\frac{[A]_0}{2}(1+ee) - \frac{1}{2}[A]_0}{[A]_0 - \frac{1}{2}[A]_0}\right) = ln\left(\frac{\frac{1}{2}[A]_0(1+ee-1)}{\frac{1}{2}[A]_0}\right)$$
$$= ln(ee) = -2 \cdot k_{en} \cdot t_{ee}$$

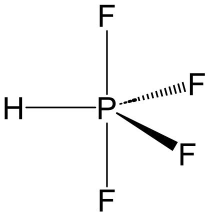
The rate constant is the same as derived in 2., as the temperature remains constant.

With that, we obtain

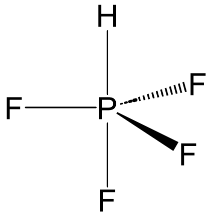
$$t_{ee(\%)} = \frac{ln(ee)}{-2 \cdot k_{en}} \Rightarrow t_{90} = \frac{ln(0.9)}{-2 \cdot 1.13 \cdot 10^{-9}\ \mathrm{s}^{-1}} = 4.66 \cdot 10^{7}\ \mathrm{s} = 539\ \mathrm{d} = 1.48\ \mathrm{a}$$

The time required to get to an ee of 90%, therefore, is equal to 539 days. This is in accordance with our previous result in V., as $t_{90} < t_{1/2}$.

11.5.



major



minor

11.6. Two signals for both isomers. However, the relative intensities and multiplicities (if recorded without decoupling) differ.

11.7. $\Delta G^0 = -R \cdot T \cdot \ln(K) \Leftrightarrow K = e^{-\frac{\Delta G^0}{R \cdot T}}$

with $T = 298.15\ K$ (standard conditions), $R = 8.314\ \mathrm{J\ mol^{-1}K^{-1}}$ and$\Delta \mathrm{G}^0 = 4.24\ \mathrm{kcal\ mol^{-1}} \cdot 4.184\ \mathrm{kJ\ kcal^{-1}} \cdot\ 1000\ \mathrm{J\ kJ^{-1}} =\ 17740\ \mathrm{J\ mol^{-1}}$:

$$K = e^{-\frac{\Delta G^0}{R \cdot T}} = e^{-\frac{17740\ \mathrm{J\ mol^{-1}}}{8.314\ \mathrm{J\ mol^{-1}K^{-1}} \cdot 298.15\ \mathrm{K}}} = 7.80 \cdot 10^{-4}$$

The equilibrium constant of such an isomerization process is thus equal to $7.80 \cdot 10^{-4}$.

The equilibrium composition could be calculated starting from only the preferred isomer:

Isomer	Major	Minor
Initial	1	0
Final	1-x	x

With the definition $K = [\text{minor}]/[\text{major}]$, it follows that:

$K = \frac{x}{1-x} \rightarrow x = \frac{K}{1+K} \cong K = 7.80 \cdot 10^{-4}$. Given the small K, the minor isomer makes up for only 0.08 mol% in equilibrium under standard conditions.

11.8. For the Arrhenius treatment, we use the relation $ln(k) = ln(A) - \frac{E_a}{RT}$, where $E_a = \Delta G^{\ddagger}$.

With two data points accessible, we can describe the difference as

$$ln(k_1) - ln(k_2) = ln\left(\frac{k_1}{k_2}\right) = -\frac{\Delta G^{\ddagger}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

and thus

$$\begin{aligned}\Delta G^{\ddagger} &= -R \cdot ln\left(\frac{k_1}{k_2}\right)\left(\frac{1}{T_1} - \frac{1}{T_2}\right)^{-1} \\ &= -8.314\ \mathrm{J\ mol^{-1}K^{-1}} \cdot ln\left(\frac{1.78}{5.47} \cdot \frac{10^{-5}\mathrm{s}^{-1}}{10^{-5}\mathrm{s}^{-1}}\right)\left(\frac{1}{333\ \mathrm{K}} - \frac{1}{363\ \mathrm{K}}\right)^{-1} \\ &= 37.6\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

As the rate constant is expressed in units of s^{-1}, the reaction follows a first-order rate law.

11.9. Diastereoisomers

Solution – From Curves to Straight Lines

A. Ideal gas law

12.1

Ideal gas law: $PV = nRT$. Thus, the linear graph would be $P = nRT \cdot \frac{1}{V}$ with coordinates *P* vs. $\frac{1}{V}$. As the other solution, the logarithmic form is also a linear function: $\ln P = \ln(nRT) - \ln V$ with the coordinates $\ln P$ vs. $\ln V$.

12.2

For the linear equation, $P = nRT \cdot \frac{1}{V}$ the slope is $tg\alpha = nRT$. For abscissa and ordinate, we have the interception at (0;0). If *T* rises, *tgα* also increases, so the graph keeps the same interception at (0;0) while rotating counterclockwise.

For the logarithmic function, $\ln P = \ln(nRT) - \ln V$ the slope is $tg\alpha = -1$. The *x*- and *y*-intercepts are both $\ln(nRT)$. At higher temperatures, the slope remains unchanged, while the graph lifts up due to higher values of intercepts.

12.3

At high pressure, the molecules are close enough to each other, thus, a model of an ideal gas (i.e., non-interacting molecules) is not applicable. And real gas equation cannot be linearized.

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT$$

B. Equilibrium constant

12.4

The Van't Hoff equation: $\ln K = -\frac{\Delta H^o}{R} \cdot \left(\frac{1}{T}\right) + \frac{\Delta S^o}{R}$. In short temperature ranges, when enthalpy and entropy changes are practically independent of temperature, the linear form is $\ln K = f\left(\frac{1}{T}\right)$.

12.5

The correct answers are:

c) Clausius–Clapeyron equation for phase equilibrium (liquid–gas):

$$\ln P = -\frac{\Delta H^o_{vap}}{R} \cdot \left(\frac{1}{T}\right) + C,\ tg\alpha = -\frac{\Delta H^o_{vap}}{R}$$

f) Arrhenius equation:

$$\ln k = \ln A - \frac{E_a}{R} \cdot \left(\frac{1}{T}\right),\ tg\alpha = -\frac{E_a}{R}$$

12.6

Indeed, as *K* depends directly on ΔG^o which is defined at constant pressure, $\frac{dK}{dP} = 0$, thus $K = f(P)$ is itself a linear function with the slope $tg\alpha = 0$. In fact, any other set of axes, where *y*-axis is a function of *K* and *x*-axis is the function of *P,* can be chosen in this case to represent a linear graph with the slope 0 as well.

C. Example mathematical function

12.7

The completed table:

No.	Linearized equation	Slope	Horizontal intercept	Vertical intercept
1	$\frac{x}{y} = \frac{1}{a} \cdot x + \frac{b}{a}$	$1/a$	$-b$	b/a
2	$\frac{1}{y} = \frac{b}{a} \cdot \frac{1}{x} + \frac{1}{a}$	b/a	$-1/b$	$1/a$
3	$y = -b \cdot \frac{y}{x} + a$	$-b$	a/b	a

D. Helix function

12.8

The helix height is the *z* value as the initial point of the function has $z = 0$. When the helix completes one turn the length projection on the horizontal *XY*-plane is a complete circle with the radius *r* and, thus, circumference $2\pi r$. Having the helix angle α as a parameter, we could find the height of one turn (known as pitch): $p = 2\pi r \cdot \mathrm{tg}\alpha$. If the helix has *N* turns ($N = \beta/2\pi$), the total height is $z = N \cdot p = \beta \cdot r \cdot \mathrm{tg}\alpha$.

12.9

As $\mathrm{tg}\alpha \approx \alpha$ for very small values of α, the height *z* will be a linear function of $\alpha \cdot \beta$ at any β values and very small values of α.

12.10

The linearization of *z* as a function of *x* or *y* is not possible: *z* depends linearly on β, while $x = r \cdot \sin\beta$ represents a periodic function (similarly for *y*). We can write that $\beta = \arcsin(x/r)$ and $z = \arcsin(x/r) \cdot r \cdot \mathrm{tg}\alpha$, but we will obtain multiple possible values of *z* for any given value of $x \le r$ (or $y \le r$), which can also be seen directly from the figure. Therefore, we can’t perform this linearization as for any linear function, only one value corresponds to one argument (and *vice versa*).

12.11

The height of the DNA molecule is $z = N \cdot p = N \cdot 2\pi \cdot r \cdot \mathrm{tg}\alpha$. The length L of one DNA chain is $L = z/\sin\alpha = N \cdot 2\pi \cdot r/\cos\alpha = 2023 \cdot 2\pi \cdot 20/\cos(20°) = 270533$ (Å). Having two helixes in the DNA molecule, the total length is $2L = 541066$ Å, i.e., ca. 0.054 mm.

Solution – Sweet Michaelis-Menten Kinetics

13.1

Let us write down the concentrations of the intermediates and reaction rate constants as follows:

$$[B]=\frac{k_1}{k_{-1}}[A];\quad [C]=\frac{k_2}{k_{-2}}[B];\quad [D]=\frac{k_3}{k_{-3}}[C];\quad [A]=\frac{k_4}{k_{-4}}[D]$$

Deriving $[A]$, we obtain:

$$[A]=\frac{k_4}{k_{-4}}[D]=\frac{k_4}{k_{-4}}\frac{k_3}{k_{-3}}[C]=\frac{k_4}{k_{-4}}\frac{k_3}{k_{-3}}\frac{k_2}{k_{-2}}[B]=\frac{k_4}{k_{-4}}\frac{k_3}{k_{-3}}\frac{k_2}{k_{-2}}\frac{k_1}{k_{-1}}[A]$$

From this, it follows that the product of the rate constants clockwise is equal to the product of the rate constants anti-clockwise:

$$k_1k_2k_3k_4=k_{-1}k_{-2}k_{-3}k_{-4}$$

13.2

From the detailed balance property, it follows that:

$$k_1\cdot 200\,\mathrm{M^{-1}s^{-1}}\cdot 40\,\mathrm{s^{-1}}\cdot 100\,\mathrm{s^{-1}}=k_{-1}\cdot 40\,\mathrm{M^{-1}s^{-1}}\cdot 100\,\mathrm{s^{-1}}\cdot 100\,\mathrm{s^{-1}}$$
$$k_1\cdot 800\,000\,\mathrm{M^{-1}s^{-3}}=k_{-1}\cdot 400\,000\,\mathrm{M^{-1}s^{-3}}$$
$$\frac{k_1}{k_{-1}}=\frac{400\,000\,\mathrm{M^{-1}s^{-3}}}{800\,000\,\mathrm{M^{-1}s^{-3}}}=\frac{1}{2}$$

To calculate the equilibrium constant from the detailed balance, we have the following:

$$K_{eq}=\frac{[P]_{eq}}{[S]_{eq}}=\frac{k_1}{k_{-1}}=\frac{1}{2}$$

As $K_{eq}<1$, the reverse rate constant is higher than the forward: $k_{-1}>k_1$. Thus, the equilibrium lies towards the formation of the substrate, i.e., the backward reaction.

The given ratio $\frac{[P]_{free}}{[S]_{free}}=10$ with respect to *K*$_{eq}$ indicates only that according to Le Chatelier's principle, in order to keep $K_{eq}=0.5$, the same will decrease, i.e., the net flow will be $\mathbf{P}\rightarrow\mathbf{S}$.

13.3

Using steady-state approximation, we can write the following expressions for the absolute flows at each step:

$$J_0=k_a[E][S]-k_d[ES_1]$$
$$J_1=k_1[ES_1]$$

$$J_2 = k_2[ES_2]$$
$$J_3 = k_3[ES_3]$$

At steady state, individual absolute flows J_i are equal to the general absolute flow J: $J_0 = J_1 = J_2 = J_3 = J$. Each intermediate can be expressed as $[ES_i] = \frac{J}{k_i}$ $(i = 1-3)$. For the considered reaction $\mathbf{S} \rightarrow \mathbf{P}$ under the given conditions, the general flow has the same value as the reaction rate *v*, which is defined as the rate of formation of product **P**, thus, $j = \frac{v}{[E]_0} = \frac{J}{[E]_0} = k_{cat}\frac{[S]}{K_M + [S]}$.

The concentration of an enzyme can be expressed as follows:

$$J = J_0 = k_a[E][S] - k_d[ES_1] = k_a[E][S] - k_d\frac{J}{k_1}$$

$$[E] = \frac{J + k_d\frac{J}{k_1}}{k_a[S]} = \frac{J}{k_a[S]}\left(\frac{k_1 + k_d}{k_1}\right)$$

From mass balance, it follows that:

$$[E]_0 = [E] + [ES_1] + [ES_2] + [ES_3]$$

$$[E]_0 = \frac{J}{k_a[S]}\left(\frac{k_1 + k_d}{k_1}\right) + \frac{J}{k_1} + \frac{J}{k_2} + \frac{J}{k_3} = J\left(\frac{1}{k_a[S]}\left(\frac{k_1 + k_d}{k_1}\right) + \frac{1}{k_1} + \frac{1}{k_2} + \frac{1}{k_3}\right)$$

$$j = \frac{J}{[E]_0} = \frac{1}{\frac{1}{k_a[S]}\left(\frac{k_1 + k_d}{k_1}\right) + \frac{1}{k_1} + \frac{1}{k_2} + \frac{1}{k_3}} = \frac{\frac{1}{\frac{1}{k_1} + \frac{1}{k_2} + \frac{1}{k_3}}[S]}{\frac{k_1 + k_d}{k_a k_1\left(\frac{1}{k_1} + \frac{1}{k_2} + \frac{1}{k_3}\right)} + [S]}$$

Considering the general form of the MM rate equation as:

$$j = \frac{J}{[E]_0} = k_{cat}\frac{[S]}{K_M + [S]}$$

It follows that:

$$k_{cat} = \frac{1}{\frac{1}{k_1} + \frac{1}{k_2} + \frac{1}{k_3}}$$

13.4

In case $K_M \gg [chocolate]$, the relative flow is the product of substrate concentration and catalytic efficiency ε:

$$j = k_{cat}\frac{[S]}{K_M + [S]} \approx k_{cat}\frac{[S]}{K_M} = \varepsilon[S]$$

In case $K_M \ll [chocolate]$, e.g., when Michi as the enzyme is completely “saturated” with chocolates as substrates, the relative flow becomes equal to the k_{cat}, i.e., turnover number (*TON*):

$$j = k_{cat}\frac{[S]}{K_M + [S]} \approx k_{cat}\frac{[S]}{[S]} = k_{cat} = TON$$

13.5

As there was a relatively big number of chocolates in the Magic Box, Michi can be treated as completely “saturated” with chocolates. Thus, the ratio of relative flows is equal to the ratio of $k_{cat,i}$. The fact that Michi produced *n* times more *X* chocolate papers than *Y* in one year implies that the ratio of flows is *n* as well:

$$\frac{j_X}{j_Y} = \frac{k_{cat,X}}{k_{cat,Y}} = n$$

The sum of Michi’s k_{cat} for *X* and *Y* is 2 week^{-1}, or 2·52.5 = 105 year^{-1}, which means that he ate 105 chocolates in total in one year: $k_{cat,X} + k_{cat,Y} = 105\ \text{year}^{-1}$. Knowing that *n* is an integer two-digit number, there are only 3 valid options: a) *n* = 102/3 = 34; b) *n* = 100/5 = 20; c) *n* = 98/7 = 14.

Let’s consider that initially, there were 2*m* chocolates in the Magic Box, i.e., *m* chocolates of each brand. Considering the first option, the ratio between chocolates left in the Magic Box after one year:

$$\frac{N_Y}{N_X} = \frac{m-3}{m-102} = 1.150$$

From this equation, we obtain *m* = 762. Thus, the total initial number of chocolates in the Magic Box was 2*m* = 1524. Other options don’t give integer values of *m*. That means that the ratio of chocolate papers and, therefore, flows is *n* = 34.

Solution - Enzymes that have Everything "in Order"

14.1

a) Rapid equilibrium for the formation of **EA**: $K_1 = \dfrac{[E][A]}{[EA]} \Rightarrow [E] = \dfrac{K_1}{[A]}[EA]$

Steady state for complex **EAB**:

$$\frac{d[EAB]}{dt} = 0 = k_2[EA][B] - (k_{-2} + k_3)[EAB]$$

$$[EAB] = \frac{k_2[EA][B]}{k_{-2} + k_3} \Rightarrow [EA] = \frac{k_{-2} + k_3}{k_2[B]}[EAB] \Rightarrow [E] = \frac{K_1(k_{-2} + k_3)}{k_2[A][B]}[EAB]$$

b) Using mass balance for enzyme:

$$[E]_0 = [E] + [EA] + [EAB] = \left(\frac{K_1(k_{-2} + k_3)}{k_2[A][B]} + \frac{k_{-2} + k_3}{k_2[B]} + 1\right)[EAB]$$

$$\alpha_{EAB} = \frac{[EAB]}{[E]_0} = \frac{1}{\dfrac{K_1(k_{-2} + k_3)}{k_2[A][B]} + \dfrac{k_{-2} + k_3}{k_2[B]} + 1}$$

c) Initial rate of products formation:

$$v = k_3[EAB] = k_3\alpha_{EAB}[E]_0 = \frac{k_3[E]_0}{\dfrac{K_1(k_{-2} + k_3)}{k_2[A][B]} + \dfrac{k_{-2} + k_3}{k_2[B]} + 1}$$

14.2

The statements:

a) If the concentration of **A** is kept constant (c_0), the initial rate *increases* with increasing [*B*] and has a minimum value $v_{\min}$ = 0 M·s^{-1} and a maximum value ($v_{\max}$), which *doesn't depend* on c_0.

b) If the concentration of **B** is kept constant (c_0), the initial rate *increases* with increasing [*A*] and has a minimum value $v_{\min}$ = 0 M·s^{-1} and a maximum value ($v_{\max}$), which *depends* on c_0.

14.3

Deriving the expressions for v_{max}:

a) If $[A]$ is kept constant ($c_{A,0}$):

$$v = \frac{k_3[E]_0}{\dfrac{K_1(k_{-2}+k_3)}{k_2 c_{A,0}[B]} + \dfrac{k_{-2}+k_3}{k_2[B]} + 1} = \frac{k_3[E]_0}{\dfrac{k_{-2}+k_3}{k_2[B]}\left(\dfrac{K_1}{c_{A,0}}+1\right)+1}$$

$$v_{\max} = v([B]\to\infty) = k_3[E]_0$$

b) If $[B]$ is kept constant ($c_{B,0}$):

$$v = \frac{k_3[E]_0}{\dfrac{K_1(k_{-2}+k_3)}{k_2[A]c_{B,0}} + \dfrac{k_{-2}+k_3}{k_2 c_{B,0}} + 1}$$

$$v_{\max} = v([A]\to\infty) = \frac{k_3[E]_0}{\dfrac{k_{-2}+k_3}{k_2 c_{B,0}}+1}$$

14.4

Classical Michaelis–Menten equation for a substrate **S**:

$$v = \frac{v_{\max}[S]}{K_M + [S]} = \frac{v_{\max}}{\dfrac{K_M}{[S]}+1}$$

a) Michaelis constant K_M if $[A]$ is kept constant (c_0):

$$v = \frac{k_3[E]_0}{\dfrac{k_{-2}+k_3}{k_2[B]}\left(\dfrac{K_1}{c_{A,0}}+1\right)+1} = \frac{v_{\max}}{\dfrac{k_{-2}+k_3}{k_2[B]}\left(\dfrac{K_1}{c_{A,0}}+1\right)+1} = \frac{v_{\max}}{\dfrac{K_M}{[B]}+1}$$

$$K_M = \frac{k_{-2}+k_3}{k_2}\left(\frac{K_1}{c_{A,0}}+1\right)$$

b) From 3b follows: $k_3[E]_0 = v_{\max}\left(\dfrac{k_{-2}+k_3}{k_2 c_{B,0}}+1\right)$

Michaelis constant K_M if $[B]$ is kept constant (c_0):

$$v=\frac{k_3[E]_0}{\frac{K_1(k_{-2}+k_3)}{k_2[A]c_{B,0}}+\left(\frac{k_{-2}+k_3}{k_2c_{B,0}}+1\right)}=\frac{v_{\max}\left(\frac{k_{-2}+k_3}{k_2c_{B,0}}+1\right)}{\frac{K_1(k_{-2}+k_3)}{k_2[A]c_{B,0}}+\left(\frac{k_{-2}+k_3}{k_2c_{B,0}}+1\right)}=\frac{v_{\max}}{\frac{K_1(k_{-2}+k_3)}{k_2[A]c_{B,0}}\Big/\left(\frac{k_{-2}+k_3}{k_2c_{B,0}}+1\right)+1}=$$

$$\frac{v_{\max}}{\frac{K_1(k_{-2}+k_3)}{k_2[A]c_{B,0}}\Big/\frac{k_{-2}+k_3+k_2c_{B,0}}{k_2c_{B,0}}+1}=\frac{v_{\max}}{\frac{K_1(k_{-2}+k_3)}{k_2[A]c_{B,0}}\cdot\frac{k_2c_{B,0}}{k_{-2}+k_3+k_2c_{B,0}}+1}=\frac{v_{\max}}{\frac{K_1(k_{-2}+k_3)}{(k_{-2}+k_3+k_2c_{B,0})[A]}+1}=\frac{v_{\max}}{\frac{K_M}{[A]}+1}$$

$$K_M=\frac{K_1(k_{-2}+k_3)}{k_{-2}+k_3+k_2c_{B,0}}$$

14.5

Substrate inhibition of **EA** with another molecule of **A** takes place (equilibrium is also assumed) – one additional step:

$$\mathbf{EA}+\mathbf{A}\underset{k_{-i}}{\overset{k_i}{\rightleftarrows}}\mathbf{EA_2}$$

$$K_I=\frac{k_{-i}}{k_i}=\frac{[EA][A]}{[EA_2]}$$

14.6

Derivation of initial rate in case of substrate inhibition:

$$[E]=\frac{K_1(k_{-2}+k_3)}{k_2[A][B]}[EAB];\quad [EA]=\frac{k_{-2}+k_3}{k_2[B]}[EAB];\quad [EA_2]=\frac{[EA][A]}{K_I}$$

$$[E]_0=[E]+[EA]+[EA_2]+[EAB]=[EAB]\left(\frac{K_1(k_{-2}+k_3)}{k_2[A][B]}+\frac{k_{-2}+k_3}{k_2[B]}\left(1+\frac{[A]}{K_I}\right)+1\right)$$

$$\alpha_{EAB}=\frac{[EAB]}{[E]_0}=\frac{1}{\frac{K_1(k_{-2}+k_3)}{k_2[A][B]}+\frac{k_{-2}+k_3}{k_2[B]}\left(1+\frac{[A]}{K_I}\right)+1}$$

$$v=k_3[EAB]=k_3\alpha_{EAB}[E]_0=\frac{k_3[E]_0}{\frac{K_1(k_{-2}+k_3)}{k_2[A][B]}+\frac{k_{-2}+k_3}{k_2[B]}\left(1+\frac{[A]}{K_I}\right)+1}=\frac{k_3[E]_0}{\frac{k_{-2}+k_3}{k_2[B]}\left(\frac{K_1}{[A]}+1+\frac{[A]}{K_I}\right)+1}$$

In the case of a constant concentration of **B** ($[B]_0$), the expression for v has a maximum when the denominator and, hence, $\frac{K_1}{[A]}+\frac{[A]}{K_I}$ is at a minimum. With a given hint, this happens when:

$$\frac{K_1}{[A]_{\max}} = \frac{[A]_{\max}}{K_I} \Rightarrow [A]_{\max} = \sqrt{K_1 K_I}$$

Thus, the maximum rate is:

$$v_{\max} = \frac{k_3[E]_0}{\frac{k_{-2}+k_3}{k_2[B]_0}\left(1+2\sqrt{\frac{K_1}{K_I}}\right)+1}$$

And the constants:

$$v_{\max} = \frac{k_3[E]_0}{\frac{k_{-2}+k_3}{k_2[B]_0}\left(1+2\sqrt{\frac{K_1}{K_I}}\right)+1} = \frac{k_3[E]_0}{\frac{\alpha}{[B]_0}(1+2\beta)+1}$$

$$\alpha = \frac{k_{-2}+k_3}{k_2}, \quad \beta = \sqrt{\frac{K_1}{K_I}}$$

$^{16}O/^{18}O$ Isotope Exchange

15.1.

α is number of ^{18}O atoms divided by total number of all oxygen atoms

$$\alpha = \frac{f_{36} + \frac{1}{2} f_{34}}{f_{36} + f_{34} + f_{32}} = f_{36} + \frac{1}{2} f_{34}$$

15.2.

From $\alpha = f_{36} + \frac{1}{2} f_{34}$ can get $f_{36} = \alpha - \frac{1}{2} f_{34}$. Since $f_{36} + f_{34} + f_{32} = 1$, $f_{32} = 1 - f_{36} - f_{34} = 1 - \left(\alpha - \frac{1}{2} f_{34}\right) - f_{34} = 1 - \alpha - \frac{1}{2} f_{34}$

15.3.

$$\Delta_r G^0_{298} = \Delta H^0_{298} - 298 * \Delta S^0_{298} = -298\, K \cdot 11.3\, J \cdot mol^{-1} \cdot K^{-1} = -3.43\, kJ \cdot mol^{-1}$$

$$K = e^{\frac{-\Delta_r G^0_{298}}{RT}} = e^{\frac{-\Delta_r H^0_{298}}{RT}} \cdot e^{\frac{\Delta_r S^0_{298}}{R}} = e^0 \cdot e^{2ln2} = 4$$

The change in enthalpy is equal to zero. Therefore, at any temperature $K = e^{\frac{\Delta_r S^0_{298}}{R}} = 4$. Same conclusion origins from Chatelier's principle.

- ☐ The constant increases with increase in temperature.
- ☐ The constant decreases with increase in temperature.
- ✓ Temperature has no effect on the constant.

15.4.

In the course of reaction x mole of both $^{16}O_2$ and $^{18}O_2$ are transformed into 2·x mole of $^{16}O^{18}O$.
The total amount of oxygen remains constant and equal to 1 mole, therefore at equilibrium fraction of $^{16}O_2$ and $^{18}O_2$ are equal to $0.5 - x$, fraction of $^{16}O^{18}O$ is equal to $2x$.

$$K = \frac{\left(f^{eq}_{34}\right)^2}{f^{eq}_{36} \cdot f^{eq}_{32}} = \frac{(2x)^2}{(0.5 - x) \cdot (0.5 - x)} = 4$$

Taking square roots from both sides

$$2 = \frac{2x}{0.5 - x};\ x = 0.25$$

$$f_{36} = f_{32} = 0.5 - 0.25 = 0.25; f_{34} = 0.25 * 2 = 0.5$$

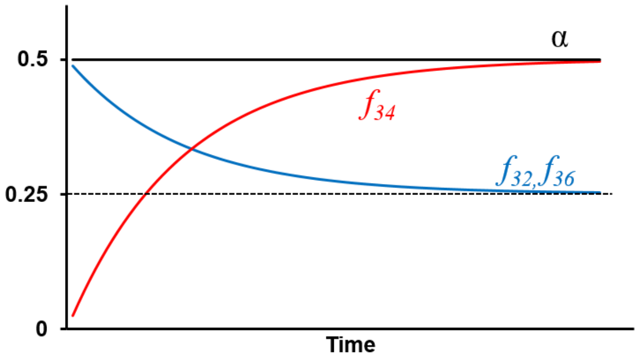
$$\alpha = \frac{N(^{18}O)}{N(^{18}O) + N(^{16}O)} = \frac{N(^{18}O)}{N(^{18}O) + N(^{16}O)} = \frac{0.25 \cdot 2 + 0.5 \cdot 1}{(0.25 \cdot 2 + 0.5 \cdot 1) + (0.5 * 1 + 0.25 \cdot 2)} = 0.5$$

System at equilibrium contains 50% of $^{16}O^{18}O$, 25% of $^{16}O_2$ and 25% of $^{18}O_2$, $\alpha = 0.5$.

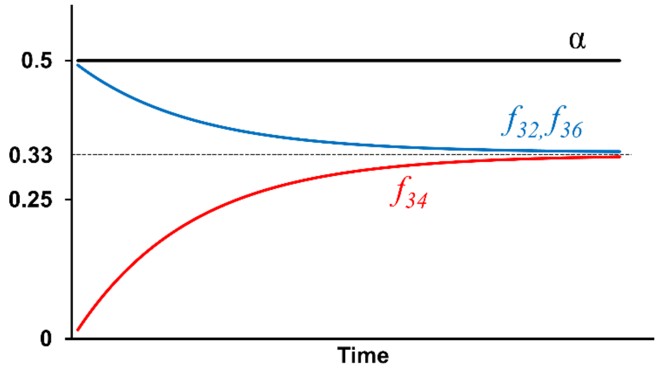
15.5.

α is constant during the experiment, while the second is differential equation for the first-order reaction and indicates that parameter f_{34} tends to f^{eq}_{34} exponentially. Simultaneously, f_{32} and f_{36} are exponentially decreasing to f^{eq}_{32} and f^{eq}_{36}.

For $f_{36} = f_{32} = 0.25;\ f_{34} = 0.5$ graph is the following:



For $f_{36}^{eq} = f_{34}^{eq} = f_{32}^{eq} = \frac{1}{3}$ the schematic graph will be the following:



15.6.

For the isotopologues containing exclusively one type of isotope in composition ($^{16}O_3$ and $^{18}O_3$) the only distribution of atoms in the structure exists, therefore the number of isotopomers is equal to one. For the isotopologues containing two isotopes of one sort and one isotope of another sort ($^{18}O^{16}O_2$ and $^{16}O^{18}O_2$) the "lonely" isotope can occupy position either in the center or on the edge. Therefore, for such isotopologues the number of possible isotopomers is equal to two.

$^{16}O_3$ -1, $^{18}O^{16}O_2$-2, $^{16}O^{18}O_2$-2, $^{18}O_3$-1

isotopologue	number of isotopomers		
	1	2	3
$^{16}O_3$	x		
$^{18}O^{16}O_2$		x	
$^{16}O^{18}O_2$		x	
$^{18}O_3$	x		

15.7.

for $^{16}O_3$ $n = 3; m = 0;\ W(^{16}O_3) = C_0^3 = \frac{3!}{0!(3-0)!} = 1$

for $^{18}O^{16}O_2$ $n = 3; m = 1;\ W(^{18}O^{16}O_2) = C_1^3 = \frac{3!}{1!(3-1)!} = 3$

for $^{16}O^{18}O_2$ $n = 3; m = 2;\ W(^{16}O^{18}O_2) = C_2^3 = \frac{3!}{2!(3-2)!} = 3$

for $^{18}O_3$ $n = 3; m = 3;\ W(^{18}O_3) = C_3^3 = \frac{3!}{3!(3-3)!} = 1$

15.8.

$$\Delta_r S^0 = k_b \cdot ln3 + k_b \cdot ln3 - k_b \cdot ln1 - k_b \cdot ln1 = 2.97 \cdot 10^{-23}\, J \cdot K^{-1}\ (17.9\, J \cdot mol^{-1} \cdot K^{-1})$$
$$\Delta_r G_{298}^0 = \Delta_r H_{298}^0 - 298 * \Delta_r S_{298}^0 = -298\, K \cdot 17.9\, J \cdot mol^{-1} \cdot K^{-1} = -5.33\, kJ \cdot mol^{-1}$$
$$K = e^{\frac{-\Delta_r G_{298}^0}{RT}} = e^{\frac{-\Delta_r H_{298}^0}{RT}} \cdot e^{\frac{\Delta_r S_{298}^0}{R}} = e^0 \cdot e^{2ln3} = 9$$

For calculation where W=1 for $^{16}O_3$ and $^{18}O_3$ and W=4 for other isotopologues

$$\Delta_r S^0 = k_b \cdot ln4 + k_b \cdot ln4 - k_b \cdot ln1 - k_b \cdot ln1 = 3.74 \cdot 10^{-23}\, J \cdot K^{-1}\ (22.6\, J \cdot mol^{-1} \cdot K^{-1})$$
$$\Delta_r G_{298}^0 = \Delta_r H_{298}^0 - 298 * \Delta_r S_{298}^0 = -298\, K \cdot 17.9\, J \cdot mol^{-1} \cdot K^{-1} = -6.86\, kJ \cdot mol^{-1}$$
$$K = e^{\frac{-\Delta_r G_{298}^0}{RT}} = e^{\frac{-\Delta_r H_{298}^0}{RT}} \cdot e^{\frac{\Delta_r S_{298}^0}{R}} = e^0 \cdot e^{2ln4} = 16$$

Diffusion of Oxygen Isotopes

16.1.

Before reaction: $n_{18O2}= \frac{p\,V}{R\,T} = \frac{0.52856 * 10^5\ Pa * 0.00150\ m^3}{8.3146 \frac{J}{mol\,K} * 298.0\ K} = 0.03200\ mol$; → 0.06400 mol ^{18}O present

n_{SmCoO3} = m / M = 0.4860 g / 257.29 g/mol = 0.001889 mol -> 0.005667 mol Oxygen atoms present

After reaction: $n_{18O2}= \frac{p\,V}{R\,T} = \frac{0.5127 * 10^5\ Pa * 0.00150\ m^3}{8.3146 \frac{J}{mol\,K} * 298.0\ K} = 0.03104\ mol$;

$n_{16O2}= \frac{p\,V}{R\,T} = \frac{0.002640 * 10^5\ Pa * 0.00150\ m^3}{8.3146 \frac{J}{mol\,K} * 298.0\ K} = 0.0001598\ mol$; $n_{18O16O}= \frac{m}{M} = \frac{0.02721\ g}{34 \frac{g}{mol}} = 0.0008003\ mol$;

Number of exchanged oxygen atoms = 0.06400 – 2 * 0.03104 – 0.00080 = 0.00112 mol

Stoichiometric formula: 0.00112 mol / 0.001889 mol = 0.593 → $SmCo^{16}O_{2.407}{}^{18}O_{0.593}$

x = 2.407, y = 0.593

16.2.

Diffusion coefficient is proportional to $\frac{1}{\sqrt{M}}$, therefore heavier isotopologues have lower diffusion coefficients.

- ✓ $D(^{16}O_2) > D(^{16}O^{18}O) > D(^{18}O_2)$.
- ☐ $D(^{18}O_2) > D(^{16}O^{18}O) > D(^{16}O_2)$.
- ☐ $D(^{16}O_2) = D(^{16}O^{18}O) = D(^{18}O_2)$.

16.3.

$$t = \frac{L^2}{D} = \frac{(\sqrt[3]{\frac{3V}{4\pi}})^2}{A \cdot \frac{1}{\sqrt{M}} \cdot \frac{T^{\frac{3}{2}}}{p}} = \frac{(\sqrt[3]{\frac{3 \cdot 1.5 \cdot 10^{-3}}{4\pi}})^2\ m^2}{2.23 \cdot 10^{-3} \frac{1}{\sqrt{36}} \cdot \frac{298^{\frac{3}{2}}}{52856}\ m^2 \cdot s^{-1}} = 1.96 \cdot 10^3\ s$$

16.4.

Wavenumber $\tilde{\nu} = \frac{\nu}{c} = \frac{\omega}{2\,\pi\,c}$, where c is the speed of light and ν the vibrational frequency in Hz

$\tilde{\nu} = \frac{1}{2\,\pi\,c}\sqrt{\frac{k}{\mu}}$ → with k being equal for vibrations of both $^{16}O_2$ and $^{18}O_2$ and π and c being constants, one obtains:

$\tilde{\nu}_{18O2} = \tilde{\nu}_{16O2} * \sqrt{\frac{\mu_{16O2}}{\mu_{18O2}}} = \tilde{\nu}_{16O2} * 0.9428$

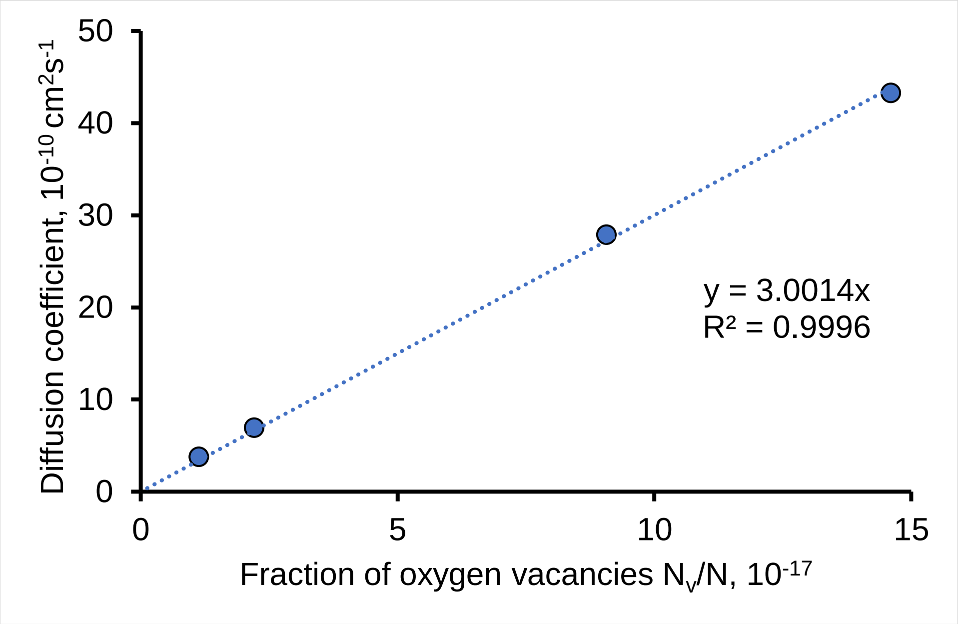
2237 cm^{-1} -> 2109 cm^{-1}

16.5.

0.005667 mol O atoms = N (see exercise a). N_V = N * $\exp\left(-\frac{Q_V}{R\,T}\right) = 3.308 * 10^4\ vacancies$

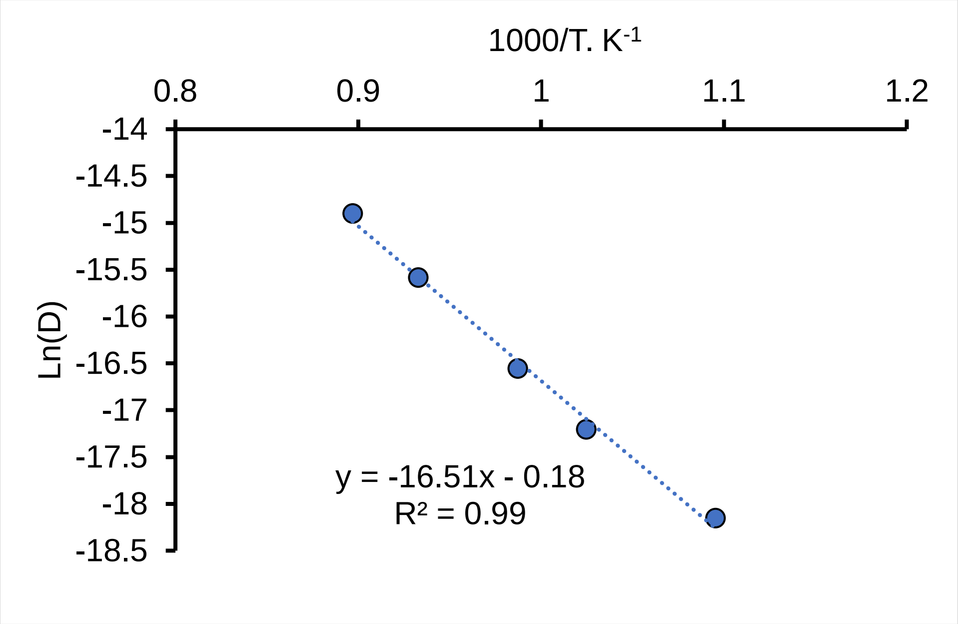
16.6.

First row to second, N_v / N increases by a factor of 1.799 and D by 1.83; first row to third – N_V / N increases by factor 7.398, D by 7.34; first row to fourth - N_V / N increases by factor 11.92, D by 11.4 → linear increase



Diffusion coefficient: $D = 3 \cdot 10^7 * \left(\frac{N_V}{N}\right)^1$

16.7.



A linear regression of ln(D) with 1 / T (in Kelvin) gave -16510.7 as a slope. E_A = - slope * R = 137 kJ / mol.

Solution – A Cheaper Storage Battery

17.1

Total reaction equation:

$2Mg + Mo_6S_8 \leftrightarrow Mg_2Mo_6S_8$

The standard electromotive force (voltage) of the battery:

$E^0_{cell} = E^0_{cathode}\text{-}E^0_{anode} = -1.3\ V - (-2.4\ V) = 1.1\ V$

The standard Gibbs energy of the reaction:

$\Delta G^0 = -nFE^0_{cell} = -4 \times 96485\ C\ mol^{-1} \times 1.1\ V = -\ 424\ kJ\ mol^{-1}$

17.2

To answer the second part of the question, one should calculate the specific energy density of the described Mg-ion battery (in Wh kg^{-1}).

Let's assume that the battery is composed of 1 mol of Mo_6S_8 and 2 mol of Mg, which can deliver 4 mol of electrons (4 mol of electrons moves from Magnesium anode to Mo_6S_8 cathode). Therefore, the charge (in Ah), which can be delivered by this battery can be calculated as follows (considering that $1\ Ah = 3600\ C$):

$\frac{96485\ C\ mol^{-1}\ \times 4\ mol \times 1\ Ah}{3600\ C} = 107.2$ Ah

Taking into account that the sum of masses of the Mg foil and Mo_6S_8 takes 50% of the total mass of the battery, one can calculate the mass of this battery:

$\frac{M(Mg) g\ mol^{-1}\ \times 2\ mol + M(Mo_6S_8)\ g\ mol^{-1} \times 1\ mol}{0.5} = \frac{24.3\ g\ mol^{-1}\ \times 2\ mol + 832.1\ g\ mol^{-1} \times 1\ mol}{0.5} = 1761.44$ g = 1.76144 kg

Thus, the specific capacity of the discussed Mg-ion battery is $\frac{107.2\ Ah\ \times 1\ kg}{1.76144\ kg}$=60.86 Ah kg^{-1} and its specific energy density is 60.86 Ah kg^{-1} × 1.1 V = 66.95 Wh kg^{-1}

Considering that energy density of Tesla powerwall Li-ion battery is 200 Wh kg^{-1}, the Mg-ion battery (which can store the same amount of energy) will be $\frac{200\ Wh\ kg^{-1}}{60.86\ Wh\ kg^{-1}} =$

3 times heavier.

17.3

$$\begin{aligned} &m(Mg\ foil\ \ used\ during\ discharge) \\ &= \frac{m(Mo_6S_8)\ g}{M(Mo_6S_8)\ g\ mol^{-1}} \times M(Mg) g\ mol^{-1} \\ &\times n\ mol (moles\ of\ Mg\ per\ 1 mol\ of\ Mo_6S_8) \\ &= \frac{2.5\ g}{832.12\ g\ mol^{-1}} \times 24.3\ g\ mol^{-1} \times 2 = 0.146\ g \end{aligned}$$

$$V(Mg\ foil\ \ used\ during\ discharge) = \frac{0.146\ g}{1.738\ g\ cm^{-3}} = 0.084\ cm^3$$

$$Thickness\ (Mg\ foil\ \ used\ during\ discharge\ assuming\ that\ surface\ area\ of\ foil\ is\ 100\ cm^2) = \frac{0.084\ \ cm^3}{100\ cm^2} = 0.00084\ cm =\ 8.4\ \mu m$$

Therefore, the thickness of the Mg foil, left after complete discharge of Mg-ion battery is 10 µm – 8.4 µm = 1.6 µm

17.4

Gravimetric specific capacity (in mAh g^{-1}) of Mo_6S_8

Considering that 1 mol of Mo_6S_8 can accept 4 mol of electrons, the electric charge, which can be accepted by 1 mol of Mo_6S_8 equals $4 \times F = 4\,mol \times 96485\ C\ mol^{-1} = 385940\ C$

$1\ Ah = 3600\ C$, thus the electric charge in Ah equals $\frac{1\ Ah \times 385940\ C}{3600\ C} = 107.2\ Ah$

Since M(Mo_6S_8) = 832.12 $g\ mol^{-1}$, gravimetric specific capacity (in mAh g^{-1}) of Mo_6S_8 can be calculated as follows: $\frac{107.2\ Ah\ mol^{-1}}{832.12\ \ g\ mol^{-1}} = 0.129\ \ Ah\ g^{-1} = 129\ \ mAh\ g^{-1}$

Gravimetric specific capacity (in mAh g^{-1}) of Mg

Considering that 1 mol of Mg can release 2 mol of electrons, the electric charge, which can be released by 1 mol of Mg equals $2 \times F = 2\,mol \times 96485\ C\ mol^{-1} = 192970\ C$

$1\ Ah = 3600\ C$, thus, the electric charge in Ah equals $\frac{1\ Ah \times 385940\ C}{3600\ C} = 53.6\ Ah$

Since M(Mg) = 24.3 $g\ mol^{-1}$, gravimetric specific capacity (in mAh g^{-1}) of Mg can be calculated as follows: $\frac{53.6\ Ah\ mol^{-1}}{24.3\ \ g\ mol^{-1}} = 2.206\ \ Ah\ g^{-1} = 2206\ \ mAh\ g^{-1}$

17.5

Solution 1:

Mg-ion battery has a total capacity of 500 mAh. This means that during discharge of this battery, 500 mAh of charge of electrons moves from Magnesium anode to Mo_6S_8 cathode. Considering that $1\ Ah = 3600\ C$, one can calculate moles of electrons, which moves from anode to cathode:

$$\frac{3600\ C \times 0.5\ Ah}{1\ Ah \times F} = \frac{3600\ C \times 0.5\ Ah}{1\ Ah \times 96485\ C\ mol^{-1}} = 0.0187\ mol$$

Taking into account that 1 mol of Mg releases 2 moles of electrons and 1 mol of Mo_6S_8 accepts 4 moles of electrons, masses of Mg and Mo_6S_8 can be calculated as follows:

m(Mg) = $\frac{0.0187\ mol}{2} \times \mathrm{M(Mg)}\ g\ mol^{-1} = \frac{0.0187\ mol}{2} \times 24.3\ \ g\ mol^{-1} = 0.227\ g$

m(Mo_6S_8) = $\frac{0.0187\ mol}{4} \times \mathrm{M(Mo6S8)}\ g\ mol^{-1} = \frac{0.0187\ mol}{4} \times 832.12\ \ g\ mol^{-1} = 3.9\ g$

Since the battery was assembled with 10 wt% of excess of Mg, thus, the mass of Mg used in the battery is 0.227+0.227*0.1=0.25 g

Total mass of the Mo_6S_8 and Mg is 3.9 g + 0.25 g = 4.15 g

Total mass of the battery = 4.15/0.5 = 8.3 g

Solution 2 (using previously calculated specific capacities of Mg and Mo6S8):

m(Mo_6S_8) = $\frac{Capacity\ of\ battery\ mAh}{specific\ capacity\ of\ Mo6S8\ mAh\ g^{-1}} = \frac{500\ mAh}{129\ mAh\ g^{-1}} = 3.9\ g$

To charge-balance the cathode half-reaction, one should take m(Mg) = $\frac{Capacity\ of\ battery\ mAh}{specific\ capacity\ of\ Mg} = \frac{500\ mAh}{2206\ mAh\ g^{-1}} = 0.227\ g$

Since the battery was assembled with 10 wt% of excess of Mg, thus, the mass of Mg used in the battery is 0.227+0.227*0.1=0.25 g

Total mass of the Mo_6S_8 and Mg is 3.9 g + 0.25 g = 4.15 g

Total mass of the battery = 4.15/0.5 = 8.3 g

17.6

The analyzed Mg-ion battery has a total capacity of 500 mAh. This means that during discharge of this battery, 500 mAh of charge of electrons moves from Mg_3Bi_2 anode to Mo_6S_8 cathode.

Considering that $1\ Ah = 3600\ C$, one can calculate moles of electrons, which moves from anode to cathode:

$$\frac{3600\ C \times 0.5\ Ah}{1\ Ah \times F} = \frac{3600\ C \times 0.5\ Ah}{1\ Ah \times 96485\ C\ mol^{-1}} = 0.0187\ mol$$

Taking into account that 1 mol of Mg_3Bi_2 releases 6 moles of electrons and 1 mol of Mo_6S_8 accepts 4 moles of electrons, masses of Mg_3Bi_2 and Mo_6S_8 can be calculated as follows:

m(Mg) = $\frac{0.0187\ mol}{6} \times \mathrm{M(Mg3Bi2)}\ g\ mol^{-1} = \frac{0.0187\ mol}{2} \times 490.88\ \ g\ mol^{-1} = 1.53\ g$

m(Mo_6S_8) = $\frac{0.0187\ mol}{4} \times \mathrm{M(Mo6S8)}\ g\ mol^{-1} = \frac{0.0187\ mol}{4} \times 832.12\ \ g\ mol^{-1} = 3.9\ g$

Total mass of the Mo_6S_8 and Mg_3Bi_2 is 3.9 g + 1.53 g = 5.43 g

Total mass of the battery = 5.43 /0.5 = 10.9 g

<u>Mass increase = 10.9 g - 8.3 g = 2.6 g</u>

Magnets Going Nano

18.1.

$$2\ \mathrm{C_{24}H_{45}FeO_6} + 64.5\ \mathrm{O_2} \rightarrow 48\ \mathrm{CO_2} + 45\ \mathrm{H_2O} + 2\ \mathrm{Fe} \quad (1)$$

$$\mathrm{C_4H_8O} + 5.5\ \mathrm{O_2} \rightarrow 4\ \mathrm{CO_2} + 4\ \mathrm{H_2O} \quad (2)$$

18.2. We first calculate the molecular weights and the amounts of both compounds fed into the flame:

$$\begin{aligned} M_{\mathrm{Fe(2-EHA)_3}} &= 24 * M_{\mathrm{C}} + 45 * M_{\mathrm{H}} + M_{\mathrm{Fe}} + 6 * M_{\mathrm{O}} \\ &= 24 * 12.01\frac{\mathrm{g}}{\mathrm{mol}} + 45 * 1.008\frac{\mathrm{g}}{\mathrm{mol}} + 55.85\frac{\mathrm{g}}{\mathrm{mol}} + 6 * 16.00\frac{\mathrm{g}}{\mathrm{mol}} \\ &= 485.45\frac{\mathrm{g}}{\mathrm{mol}} \end{aligned}$$

$$M_{\mathrm{THF}} = 4 * M_{\mathrm{C}} + 8 * M_{\mathrm{H}} + M_{\mathrm{O}} = 4 * 12.01\frac{\mathrm{g}}{\mathrm{mol}} + 8 * 1.008\frac{\mathrm{g}}{\mathrm{mol}} + 16.00\frac{\mathrm{g}}{\mathrm{mol}} = 72.10\frac{\mathrm{g}}{\mathrm{mol}}$$

$$\dot{n}_{\mathrm{Fe(2-EHA)_3}} = \frac{\dot{m}_{\mathrm{Fe(2-EHA)_3}}}{M_{\mathrm{Fe(2-EHA)_3}}} = \frac{2.7\ \mathrm{g/min}}{485.45\ \mathrm{g/mol}} = 5.56 * 10^{-3}\ \mathrm{mol/min}$$

$$\dot{n}_{\mathrm{THF}} = \frac{\dot{m}_{\mathrm{THF}}}{M_{\mathrm{THF}}} = \frac{1.8\ \mathrm{g/min}}{72.10\ \mathrm{g/mol}} = 25.0 * 10^{-3}\ \mathrm{mol/min}$$

The stoichiometric amount of O_2 based on feeds and reaction equations in task 1 are:

$$\dot{n}_{\mathrm{O_2,(1)}} = \frac{\nu_{\mathrm{O_2,(1)}}}{\nu_{\mathrm{Fe(2-EHA)_3,(1)}}} * \dot{n}_{\mathrm{Fe(2-EHA)_3}} = \frac{64.5}{2} * 5.56 * 10^{-3}\ \mathrm{mol/min} = 0.179\ \mathrm{mol/min}$$

$$\dot{n}_{\mathrm{O_2,(2)}} = \frac{\nu_{\mathrm{O_2,(2)}}}{\nu_{\mathrm{THF,(2)}}} * \dot{n}_{THF} = \frac{5.5}{1} * 25.0 * 10^{-3}\ \mathrm{mol/min} = 0.138\ \mathrm{mol/min}$$

$$\dot{n}_{\mathrm{O_2}} = \dot{n}_{\mathrm{O_2,(1)}} + \dot{n}_{\mathrm{O_2,(2)}} = 0.317\ \mathrm{mol/min}$$

Using the hint, the same total is found:

$$\dot{n}_{\mathrm{O_2,(1)}} = \frac{\nu_{\mathrm{O_2,(1)}}}{\nu_{\mathrm{Fe(2-EHA)_3,(1)}}} * \dot{n}_{\mathrm{Fe(2-EHA)_3}} = 30 * 5.56 * 10^{-3}\ \mathrm{mol/min} = 0.167\ \mathrm{mol/min}$$

$$\dot{n}_{\mathrm{O_2,(2)}} = \frac{\nu_{\mathrm{O_2,(2)}}}{\nu_{\mathrm{THF,(2)}}} * \dot{n}_{\mathrm{THF}} = 6 * 25.0 * 10^{-3}\ \mathrm{mol/min} = 0.150\ \mathrm{mol/min}$$

$$\dot{n}_{\mathrm{O_2}} = \dot{n}_{\mathrm{O_2,(1)}} + \dot{n}_{\mathrm{O_2,(2)}} = 0.317\ \mathrm{mol/min}$$

The required volume feed of oxygen can then be calculated from the ideal gas law:

$$\dot{V}_{\mathrm{O_2}} = \frac{\dot{n}_{\mathrm{O_2}} * R * T}{p} = \frac{0.317\ \mathrm{mol/min} * 8.3145\ \mathrm{J/mol/K} * 298\ \mathrm{K}}{10^5\ \mathrm{Pa}} = 7.85 * 10^{-3}\frac{\mathrm{m^3}}{\mathrm{min}} = 7.85\frac{\mathrm{L}}{\mathrm{min}}$$

The same result can be obtained by performing the calculation for a fixed time interval, e.g. 1 min.

18.3. To formulate the solution, four variables $\alpha = 1, \beta = 0.07, \gamma = 3.87$, and $\delta = 0.24$ are introduced:

$$\alpha\ \mathrm{C_4H_8OFe_\beta} + \gamma\ \mathrm{O_2} \rightarrow a\ \mathrm{CO_2} + b\ \mathrm{CO} + c\ \mathrm{H_2O} + d\ \mathrm{FeC_\delta}$$

This defines the following systems of equations based on the atom balance and the hint:

$4 * \alpha = a + b + d * \delta$ C balance

$8 * \alpha = 2 * c$ H balance

$\alpha + 2 * \gamma = 2 * a + b + c$ O balance

$\alpha * \beta = d$ Fe balance

The system of equations can unambiguously be solved:

$c = \frac{8}{2} * \alpha = \frac{8}{2} * 1 = 4$ By H balance

$d = \alpha * \beta = 1 * 0.07 = 0.07$ By Fe balance

$a = -3 * \alpha + 2 * \gamma - c + d * \delta$

$= -3 * 1 + 2 * 3.87 - 4 + 0.07 * 0.24 = 0.757$ By subtracting C balance from O balance

$b = 4 * \alpha - a - d * \delta = 4 * 1 - 0.757 - 0.07 * 0.24 = 3.23$ By C balance

The $\mathrm{CO_2}$ to CO ratio is then calculated as:

$a/b = 0.757/3.23 = 0.234$

which corresponds to $\mathrm{CO_2} : \mathrm{CO} = 19 : 81$.

The same result may be obtained by omitting the particles since their contribution to the C balance $(0.07 * 0.24 = 0.02)$ is negligible.

18.4. The stoichiometric of the particles produced in task 3 is $\mathrm{FeC_{0.24}}$. Its carbon mass fraction is calculated as:

$$wt\%_{\mathrm{C}} = \frac{0.24 * MW_{\mathrm{C}}}{MW_{\mathrm{Fe}} + 0.24 * MW_{\mathrm{C}}} = \frac{0.24 * 12.01 \frac{\mathrm{g}}{\mathrm{mol}}}{55.85 \frac{\mathrm{g}}{\mathrm{mol}} + 0.24 * 12.01 \frac{\mathrm{g}}{\mathrm{mol}}} = 4.90\%$$

Therefore, the correct answer is: “The particles are comprised of γ-iron and iron carbide.”

18.5. Based on the information provided for task 4, $wt\%_{C,avg} = 9.4\ \%$ corresponds to carbon-coated iron carbide particles. The core volume is calculated as:

$$V_{core} = \frac{4}{3} \cdot \pi \cdot r_{core}^3 = \frac{4}{3} \cdot \pi \cdot (30.0\ \text{nm})^3 = 113100\ \text{nm}^3$$

The average carbon mass fraction of the whole particles can be expressed as:

$$wt\%_{C,avg} = \frac{wt\%_{C,core} \cdot \rho_{core} \cdot V_{core} + wt\%_{C,shell} \cdot \rho_{shell} \cdot V_{shell}}{\rho_{core} \cdot V_{core} + \rho_{shell} \cdot V_{shell}}$$

Solving for V_{shell} gives:

$$V_{shell} = \frac{\rho_{core}}{\rho_{shell}} \cdot \frac{wt\%_{C,avg} - wt\%_{C,core}}{wt\%_{C,shell} - wt\%_{C,avg}} \cdot V_{core} = \frac{7.69 \frac{g}{cm^3}}{2.26 \frac{g}{cm^3}} \cdot \frac{0.094 - 0.067}{1.000 - 0.094} \cdot 113100\ \text{nm}^3 = 11500\ \text{nm}^3$$

The total volume of a particle is then:

$$V_{particle} = V_{core} + V_{shell} = 113100\ \text{nm}^3 + 11500\ \text{nm}^3 = 124600\ \text{nm}^3$$

18.6. The carbon shell thickness can be obtained by subtracting the core radius from the radius of the total particle:

$$r_{total} = \sqrt[3]{\frac{V_{particle}}{\frac{4}{3} \cdot \pi}} = \sqrt[3]{\frac{124600\ \text{nm}^3}{\frac{4}{3} \cdot \pi}} = 31.0\ \text{nm}$$

$$d_{shell} = r_{total} - r_{core} = 31.0\ \text{nm} - 30.0\ \text{nm} = 1.0\ \text{nm}$$

Using the hint, $r_{total} = 32.0\ \text{nm}$ and $d_{shell} = 2.0\ \text{nm}$ is obtained.

18.7. The number of graphene layers is obtained as:

$$n_{layer} = \frac{d_{shell}}{d_{graphite}} = \frac{1.0\ \text{nm}}{0.335\ \text{nm}} = 3.0$$

Using the hint on either task 6 or 7, $n_{layer} = 6.0$ is obtained.

18.8. R

$-NH_2 + ClOC(CH_2)_{16}CH_3 \rightarrow R\text{-}NHOC(CH_2)_{16}CH_3 + HCl$

18.9. The loading of H and N before and after the reaction can be calculated as:

$$q_{NH_2,before} = \frac{wt\%_{N,before}}{MW_N} = \frac{1.6\,\frac{\mathrm{mg}}{\mathrm{g}}}{14.01\,\frac{\mathrm{g}}{\mathrm{mol}}} = 0.11\,\frac{\mathrm{mmol}}{\mathrm{g}}$$

$$q_{H,before} = \frac{wt\%_{H,before}}{MW_H} = \frac{0.2\,\frac{\mathrm{mg}}{\mathrm{g}}}{1.01\,\frac{\mathrm{g}}{\mathrm{mol}}} = 0.20\,\frac{\mathrm{mmol}}{\mathrm{g}}$$

$$q_{H,after} = \frac{wt\%_{H,before}}{MW_H} = \frac{3.1\,\frac{\mathrm{mg}}{\mathrm{g}}}{1.01\,\frac{\mathrm{g}}{\mathrm{mol}}} = 3.07\,\frac{\mathrm{mmol}}{\mathrm{g}}$$

Using the reaction equation found in task 8, the yield can be calculated based on the increase in the loading of H due to bound stearyl amide:

$$yield = \frac{q_{amide,after}}{q_{NH_2,before}} = \frac{\left(q_{H,after} - q_{H,before}\right)/34}{q_{NH_2,before}}$$
$$= \frac{\left(3.07\,\frac{\mathrm{mmol}}{\mathrm{g}} - 0.20\,\frac{\mathrm{mmol}}{\mathrm{g}}\right)/34}{0.11\,\frac{\mathrm{mmol}}{\mathrm{g}}} = 77\ \%$$

18.10. The specific surface area of the particles prior to functionalization is:

$$SSA = \frac{A_{particle}}{m_{particle}} = \frac{4 \cdot \pi \cdot r_{total}^2}{\rho_{core} \cdot V_{core} + \rho_{shell} \cdot V_{shell}}$$
$$= \frac{4 \cdot \pi \cdot (31.0\ \mathrm{nm})^2}{7.69\,\frac{\mathrm{g}}{\mathrm{cm}^3} \cdot \left(\frac{1\ \mathrm{cm}}{10^7\ \mathrm{nm}}\right)^3 \cdot 113100\ \mathrm{nm}^3 + 2.26\,\frac{\mathrm{g}}{\mathrm{cm}^3} \cdot \left(\frac{1\ \mathrm{cm}}{10^7\ \mathrm{nm}}\right)^3 \cdot 11500\ \mathrm{nm}^3}$$
$$= 1.35 \cdot 10^{19}\ \mathrm{nm}^2/\mathrm{g}$$

Accordingly, the amine loading can be expressed as a coverage instead:

$$\alpha_{NH_2} = \frac{q_{NH_2,before} \cdot N_A}{SSA} = \frac{0.11 \cdot 10^{-3}\,\frac{\mathrm{mol}}{\mathrm{g}} \cdot 6.022 \cdot 10^{23}\ \mathrm{mol}^{-1}}{1.35 \cdot 10^{19}\,\frac{\mathrm{nm}^2}{\mathrm{g}}} = 4.91\ \mathrm{nm}^{-2}$$

Predicting Indices

19.1. Starting from $t_6 = 100\ \text{s}$, all retention times can be calculated by iterative multiplication with factor $f = 1.6$:

$t_7 = 1.6 * t_6 = 1.6 * 100\ \text{s} = 160\ \text{s}$
$t_8 = 1.6 * t_7 = 1.6 * 160\ \text{s} = 256\ \text{s}$
$t_9 = 1.6 * t_8 = 1.6 * 256\ \text{s} = 410\ \text{s}$
$t_{10} = 1.6 * t_9 = 1.6 * 410\ \text{s} = 655\ \text{s}$

Given the multiplicative nature, the formula $\log(t_n) = a * n + b$ can be assumed. Using any two data points, the following relationship can be found:

$$\log(t_n) = 0.204 * n + 0.775$$

19.2. Subtracting two consecutive data points, the following formula can be found:

$$\log(t_{n+1}) = \log(t_n) + 0.204$$

19.3. Based on the retention time, the leading and trailing *n*-alkanes are C_7H_{16} and C_8H_{18}, respectively. Using the formula, the retention index can be calculated:

$$R_{\mathbf{X}} = 100 * n + \frac{\log\,(t_{\mathbf{X}}/t_7)}{\log\,(t_8/t_7)} = 100 * 7 + \frac{\log\,(200\ \text{s}/160\ \text{s})}{\log\,(256\ \text{s}/160\ \text{s})} = 747.5$$

19.4. Using the formula, the retention time can be calculated:

$$t'_{\mathbf{X}} = \frac{t'_8 - t'_7}{100} * (R'_{\mathbf{X}} - 100 * n) + t'_7 = \frac{200\ \text{s} - 180\ \text{s}}{100} * (747.5 - 100 * 7) + 180\ \text{s} = 189.5\ \text{s}$$

Using the hint, $t_{\mathbf{X}} = 184.0\ \text{s}$ is found instead.

19.5. $(C_{15}H_{31}CO_2)_3C_3H_5 + 3\ C_2H_5OH \rightarrow 3\ C_{15}H_{31}CO_2C_2H_5 + C_3H_8O_3$

19.6. The linear series is 16.43, 17.38, 18.33, 19.28, and 20.23 min where the retention times correspond to the formula: $t''_{n+1} = t''_n + 0.95$. They correspond to the *n*-alkanes with C_{18} to C_{22}.

Thus, the retention indices of the three other peaks are:

18.13 min: $R'' = 1900 + 100 * (18.13 - 17.33)/(18.33 - 17.38) = 1979$
19.75 min: $R'' = 2100 + 100 * (19.75 - 19.28)/(20.23 - 19.28) = 2149$
19.99 min: $R'' = 2100 + 100 * (19.99 - 19.28)/(20.23 - 19.28) = 2175$

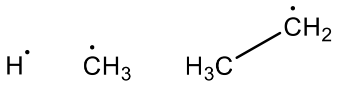
The peaks at 18.13 min and at 19.99 min have retention indexes 1979 and 2175, which are "exactly" 200 in difference: they belong to the same family of saturated ethyl *n*-carboxylates. Using rule 2), they are ethyl palmitate ($C_{15}H_{31}CO_2C_2H_5$) and ethyl stearate ($C_{17}H_{35}CO_2C_2H_5$).

Based on rules 1) and 2), the peak at 19.75 min is neither an *n*-alkane nor a saturated ethyl *n*-carboxylate. As its retention index is 29 less than ethyl stearate, it corresponds to ethyl oleate ($CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2C_2H_5$, exact location of double bond not important) based on rule 3).

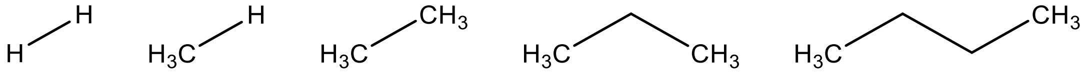
Breaking Alkanes Apart

20.1. As the three possible fragments are $H^\bullet$, $CH_3^\bullet$, and $C_2H_5^\bullet$, four new molecules can be produced by recombination in the ethane radiolysis. Ethane can also be reformed.

Fragments:



Products:



20.2. As ethane contains 6 C–H bonds and 1 C–C bond, the probability of forming $H^\bullet$ + $C_2H_5^\bullet$ is 6/7 and the probability of forming 2 $CH_3^\bullet$ is 1/7. For a large number n of molecules, the number of radicals and their probability can be calculated:

Species	Number	Probability
$H^\bullet$	$6n/7$	$(6n/7)/2n = 3/7$
$CH_3^\bullet$	$2n/7$	$(2n/7)/2n = 1/7$
$C_2H_5^\bullet$	$6n/7$	$(6n/7)/2n = 3/7$
Total	$14n/7 = 2n$	1

20.3. Using the provided formulae, the product distribution can be calculated by accounting for all recombination possibilities:

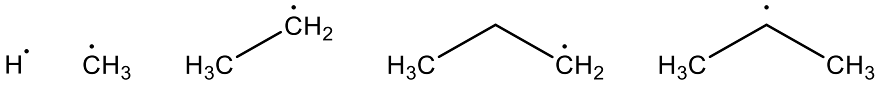
Product	Recombination of	Probability	Using hint
H_2	$H^\bullet$ + $H^\bullet$	$(3/7) * (3/7) = 9/49$	$(1/4) * (1/4) = 1/16$
CH_4	$H^\bullet$ + $CH_3^\bullet$	$2 * (3/7) * (1/7) = 6/49$	$2 * (1/4) * (2/4) = 4/16$
C_2H_6	$H^\bullet$ + $C_2H_5^\bullet$	$2 * (3/7) * (3/7) = 18/49$	$2 * (1/4) * (1/4) = 2/16$
C_2H_6	$CH_3^\bullet$ + $CH_3^\bullet$	$(1/7) * (1/7) = 1/49$	$(2/4) * (2/4) = 4/16$
C_3H_8	$CH_3^\bullet$ + $C_2H_5^\bullet$	$2 * (1/7) * (3/7) = 6/49$	$2 * (2/4) * (1/4) = 4/16$
C_4H_{10}	$C_2H_5^\bullet$ + $C_2H_5^\bullet$	$(3/7) * (3/7) = 9/49$	$(1/4) * (1/4) = 1/16$
Total		1	1

Thus, the ratio of all formed products is obtained by adding the recombination pathways for individual products and dividing by the lowest probability:

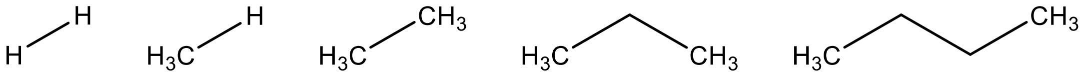
Product	Ratio	Using hint
H_2	9	1
CH_4	6	4
C_2H_6	19	6
C_3H_8	6	4
C_4H_{10}	9	1

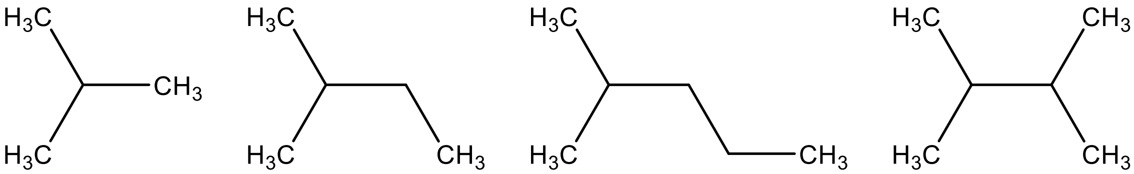
20.4. As the five possible fragments are $H^{\bullet}$, $CH_3^{\bullet}$, $C_2H_5^{\bullet}$, 1-$C_3H_7^{\bullet}$, and 2-$C_3H_7^{\bullet}$, 10 new molecules can be produced by recombination in the propane radiolysis. Propane can also be reformed.

Fragments:



Products:





20.5. It can be deduced that the least likely product must result from the symmetric combination of one of the least likely radicals. This leaves only C_2H_6, C_4H_{10}, and $(CH_3)_2CHCH(CH_3)_2$ as candidates. Since C_2H_6 and C_4H_{10} can also be obtained by other pathways, the most branched product $(CH_3)_2CHCH(CH_3)_2$ is the least likely product.

It can be concluded that the reformation of propane gives the most likely product. The same conclusions can be reached by explicit calculation (see below).

20.6. As propane contains 6 C_{prim}–H bonds, 2 C_{sec}–H bonds, and 2 C–C bonds, their ruptures produced 20 fragments (assuming equal probability):

Rupture	Number of … radicals formed				
	$H^{\bullet}$	$CH_3^{\bullet}$	$C_2H_5^{\bullet}$	1-$C_3H_7^{\bullet}$	2-$C_3H_7^{\bullet}$
6 C_{prim}–H	6	0	0	6	0
2 C_{sec}–H	2	0	0	0	2
2 C–C	0	2	2	0	0

For a large number n of molecules, the number of radicals and their probability can be calculated:

Species	Number	Probability
$H^{\bullet}$	$8n/10$	$(8n/10)/2n = 4/10$
$CH_3^{\bullet}$	$2n/10$	$(2n/10)/2n = 1/10$
$C_2H_5^{\bullet}$	$2n/10$	$(2n/10)/2n = 1/10$
1-$C_3H_7^{\bullet}$	$6n/10$	$(6n/10)/2n = 3/10$
2-$C_3H_7^{\bullet}$	$2n/10$	$(2n/10)/2n = 1/10$

Total	$20n/10 = 2n$	1

Similar to task 3, the product distribution can be calculated by accounting for all recombination possibilities:

Product	Recombination of	Probability
H_2	$H^\bullet$ + $H^\bullet$	$(4/10) \ast (4/10) = 16/100$
CH_4	$H^\bullet$ + $CH_3^\bullet$	$2 \ast (4/10) \ast (1/10) = 8/100$
C_2H_6	$H^\bullet$ + $C_2H_5^\bullet$	$2 \ast (4/10) \ast (1/10) = 8/100$
C_3H_8	$H^\bullet$ + 1-$C_3H_7^\bullet$	$2 \ast (4/10) \ast (3/10) = 24/100$
C_3H_8	$H^\bullet$ + 2-$C_3H_7^\bullet$	$2 \ast (4/10) \ast (1/10) = 8/100$
C_2H_6	$CH_3^\bullet$ + $CH_3^\bullet$	$(1/10) \ast (1/10) = 1/100$
C_3H_8	$CH_3^\bullet$ + $C_2H_5^\bullet$	$2 \ast (1/10) \ast (1/10) = 2/100$
C_4H_{10}	$CH_3^\bullet$ + 1-$C_3H_7^\bullet$	$2 \ast (1/10) \ast (3/10) = 6/100$
$(CH_3)_2CHCH_3$	$CH_3^\bullet$ + 2-$C_3H_7^\bullet$	$2 \ast (1/10) \ast (1/10) = 2/100$
C_4H_{10}	$C_2H_5^\bullet$ + $C_2H_5^\bullet$	$(1/10) \ast (1/10) = 1/100$
C_5H_{12}	$C_2H_5^\bullet$ + 1-$C_3H_7^\bullet$	$2 \ast (1/10) \ast (3/10) = 6/100$
$(CH_3)_2CHCH_2CH_3$	$C_2H_5^\bullet$ + 2-$C_3H_7^\bullet$	$2 \ast (1/10) \ast (1/10) = 2/100$
C_6H_{14}	1-$C_3H_7^\bullet$ + 1-$C_3H_7^\bullet$	$(3/10) \ast (3/10) = 9/100$
$(CH_3)_2CHCH_2CH_2CH_3$	1-$C_3H_7^\bullet$ + 2-$C_3H_7^\bullet$	$2 \ast (3/10) \ast (1/10) = 6/100$
$(CH_3)_2CHCH(CH_3)_2$	2-$C_3H_7^\bullet$ + 2-$C_3H_7^\bullet$	$(1/10) \ast (1/10) = 1/100$
Total		1

Product	Ratio
H_2	16
CH_4	8
C_2H_6	9
C_3H_8	34
C_4H_{10}	7
C_5H_{12}	6
C_6H_{14}	9
$(CH_3)_2CHCH_3$	2
$(CH_3)_2CHCH_2CH_3$	2
$(CH_3)_2CHCH_2CH_2CH_3$	6
$(CH_3)_2CHCH(CH_3)_2$	1

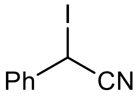
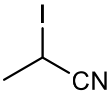
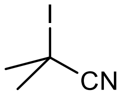
The formed *n*-alkanes are in the proportions:

CH_4 : C_2H_6 : C_3H_8 : C_4H_{10} : C_5H_{12} : C_6H_{14} = 8 : 9 : 34 : 7 : 6 : 9.

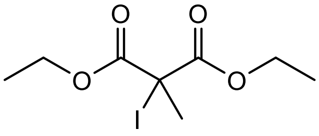
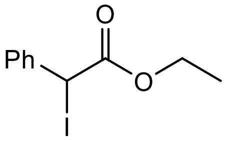
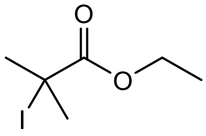
Solution: Quite Radical

21.1

a)

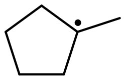
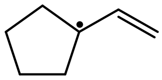
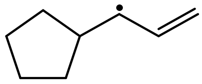
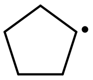
		
3	1	2

b)

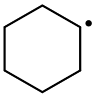
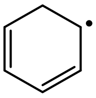
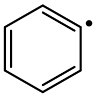
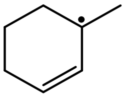
		
3	2	1

21.2

a)

			
2	4	3	1

b)

			
2	4	1	3

21.3

The reactivity of tert., sec. and prim. H-atoms decreases in the order tert > sec > prim with the ratio 5:4:1. Thus by multiplying the reactivity with the number of H atoms of the four different types you can calculate the product ratio. Thus: 1-chloro-2-methylbutane 27.3; 2-chloro-2-methylbutane 22.7 %; 2-chloro-3-methylbutane. 36.4%; and 1-chloro-3-methylbutane 13.6%.

21.4

1. step: radical forming

$(CH_3)_3CO\text{-}OC(CH_3)_3 \rightarrow 2\ (CH_3)_3CO\bullet$

2. step:

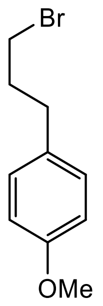
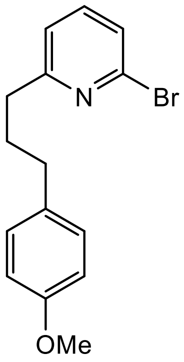
$(CH_3)_3CO\bullet + (CH_3)_3CH \rightarrow (CH_3)_3COH + (CH_3)_3C\bullet$

3. step: propagation

$(CH_3)_3C\bullet + CCl_4 \rightarrow (CH_3)_3CCl + CCl_3\bullet$

$CCl_3\bullet + (CH_3)_3CH \rightarrow (CH_3)_3C\bullet + Cl_3CH$

21.5

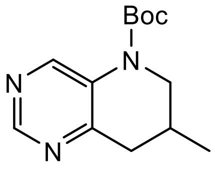
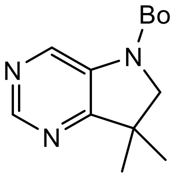
A	**B**
	

Starting molecule to **A**: radical hydrobromination

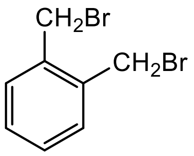
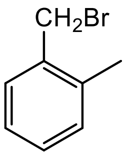
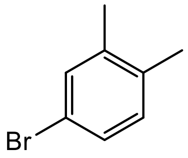
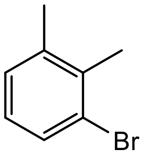
A to **B**: formation of alkyl zinc bromide (RZnBr), cross coupling (Negishi reaction)

B to final product: transition metal catalyzed C-O coupling (Ullmann type reaction), – HBr

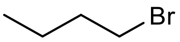
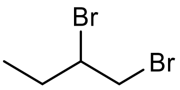
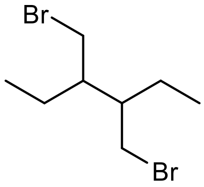
21.6

D	**E**
 Minor product	 Major product

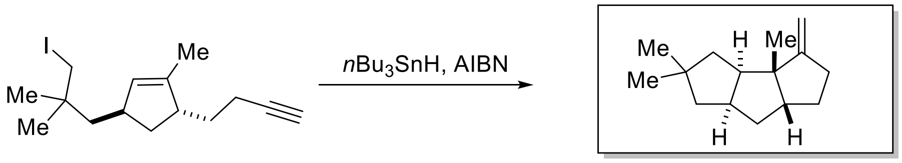
21.7

F 	**G** 
H 	**I** 

21.8

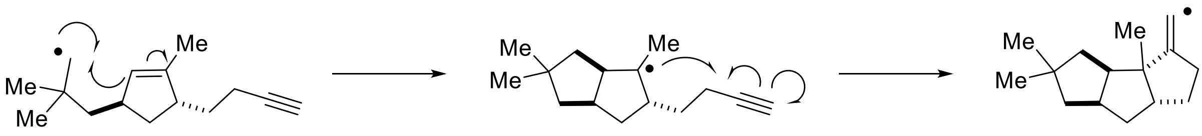
J 	**K** Br_2	**L** 
M 		

21.9



N

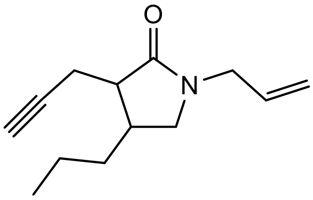
via



Solution - Enabling Electricity

22.1

A



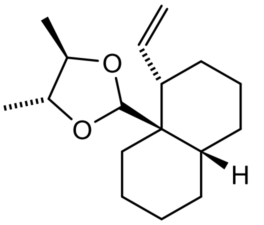
22.2

$$moles\ of\ e^{-} = x * 2 * \frac{100\%}{29\%} = 0.0028\,mol * 2 * \frac{100}{29} = 0.0193\,mol$$

$$Q = F * 0.00193\,mol = 96485.33\,\frac{C}{mol} * 0.00193\,mol = 1863.16\,C$$

22.3

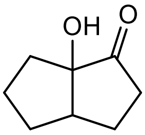
B



cyclisation by anodic oxidation

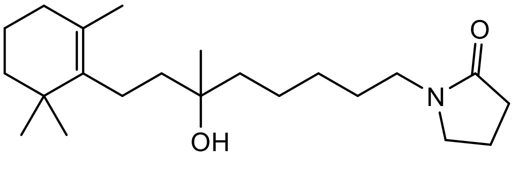
22.4

C

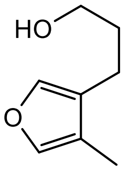
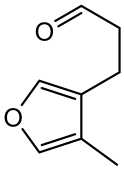
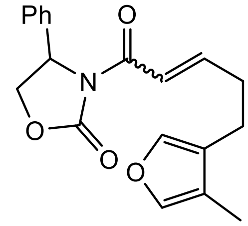
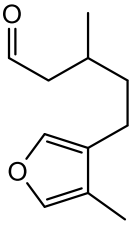
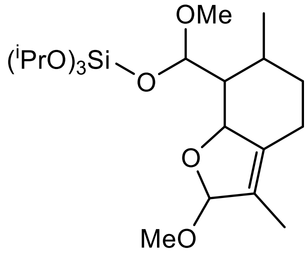


22.5

D



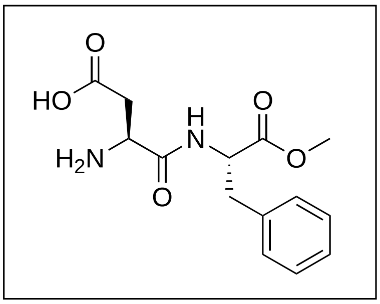
22.6

E 	**F** 	**G** 
H 	**I** 	

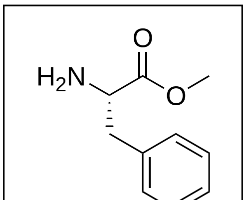
Reaction from **F** to **G** is a Wittig type reaction (HWE-reaction)
To **H**: splitting of the amide bond by DIBAL-H
H to the given formula is a protective silylation of the enol
Final step: oxidative ring closure and radical capture by methanol

Solution – A Sweet Introduction to Peptides

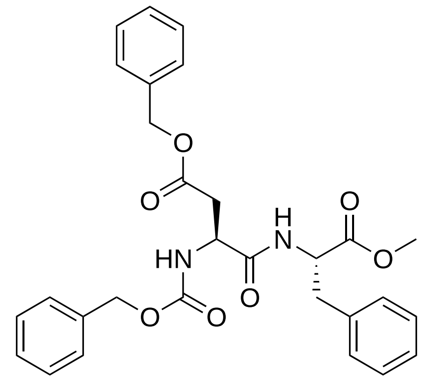
23.1



23.2



H-Phe-OCH$_3$



B

Code for compound **A** using the three-letter amino acid notation:

☐ Boc-Asp(^{t}Bu)-CO$_2$H

☐ Boc-Asp(^{t}Bu)-OH

☐ Boc-Asp(^{t}Bu)-H

☐ Cbz-Asp(Bn)-CO$_2$H

☒ **Cbz-Asp(Bn)-OH**

☐ Cbz-Asp(Bn)-H

Reagent **C**:

☐ 1% CF_3CO_2H in CH_2Cl_2

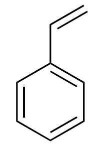
☒ **H_2 (g), Pd/C**

☐ 4M aqueous HCl

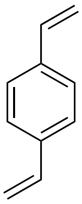
☐ LiOH in THF

☐ 20% piperidine in DMF

23.3



D (99%)



E (1%)

Initiator **F**:

☒ **azobis(isobutyronitrile) (AIBN)**

☒ **benzoyl peroxide $(BzO)_2$**

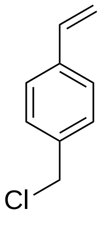
☐ *tert*-butyl peroxide $(^tBuO)_2$

☐ *N*,*N′*-dicyclohexylcarbodiimide (DCC)

☐ diisopropylethylamine (DIPEA)

Note: tert-butyl peroxide is not a suitable radical initiator for styrene polymerization as oxygen-centered radicals are not prone to radical addition but rather hydrogen abstraction.

23.4



G (*x*%)

Reagent **H**:

☒ **CH_3OCH_2Cl, H_2SO_4**

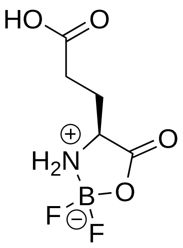
☐ CH_2Cl_2, KOH

☐ $CHCl_3$, $(^tBuO)_2$

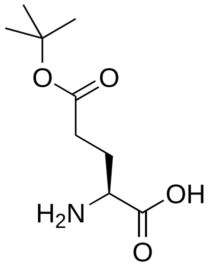
☐ Cl_2, *hv*

☒ **formaldehyde, HCl, $ZnCl_2$**

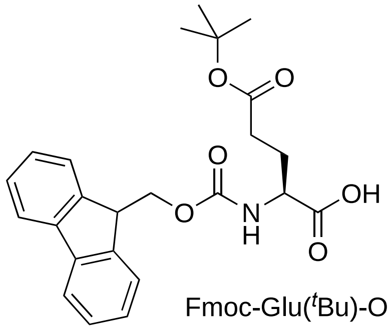
23.5



I

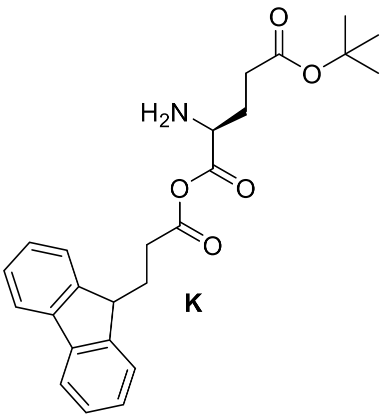


J

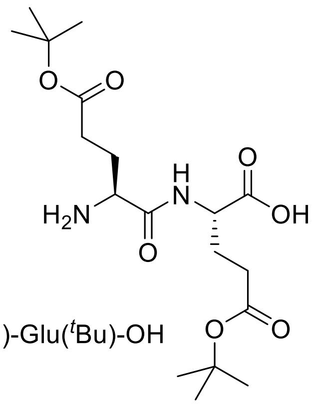


Fmoc-Glu(^{t}Bu)-OH

23.6

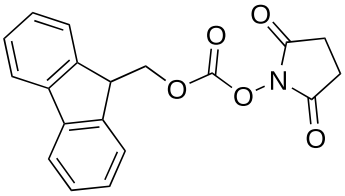


K



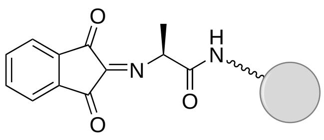
H-Glu(^{t}Bu)-Glu(^{t}Bu)-OH

Note: The intermediate **K** is a mixed anhydride, an activated derivative of the carboxylic acid which readily reacts with another molecule of **J**. To prevent the dimerization, Fmoc-OSu (NHS ester) is often preferred.

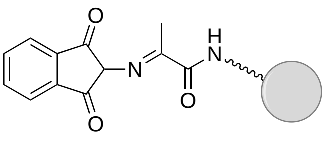


Fmoc-OSu

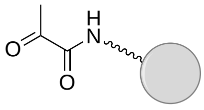
23.7



L



M



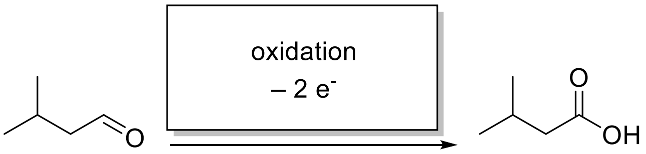
N

23.8

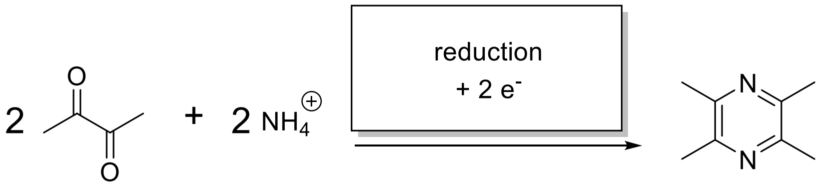
Proline

Solution - Switzerland – the country of cheese

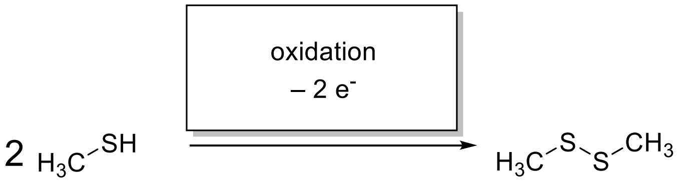
24.1



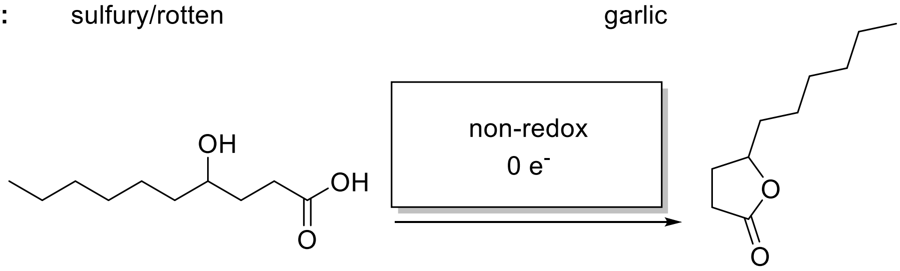
Name: isovaleraldehyde → isovaleric acid
Flavor: malty → cheesy



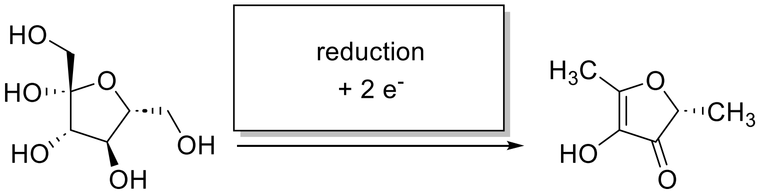
Name: diacetyl, ammonium → tetramethylpyrazine
Flavor: buttery, liquorice → musty/fermented



Name: methanethiol → dimethyl disulfide
Flavor: sulfury/rotten → garlic

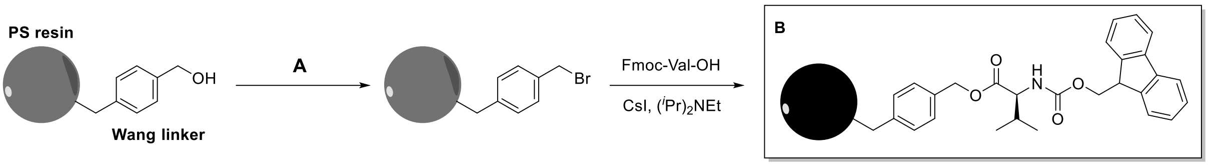


Name: 4-hydroxydecanoic acid → γ-decalactone
Flavor: soapy → peach



Name: fructose → furaneol
Flavor: sweet → strawberry

24.2



Reagent **A**:

☐ AgOH, Br_2

☐ Br_2, *hn*

☒ CBr_4, PPh_3

☐ KBr, acetone

☐ LiBr, H_3PO_2

24.3

☒ Catalyst – iodide is both a better nucleophile than the carboxylate and a better leaving group than the bromide.

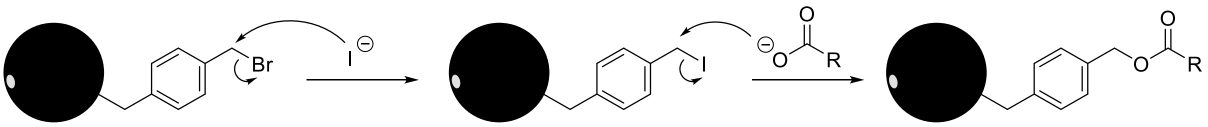
☐ Increasing ionic strength – the ionic species stabilize the charged intermediate formed during the reaction.

☐ Inhibitor of undesired side-reactions – the mildly acidic salt buffers the basicity of $({}^{i}Pr)_2NEt$ and prevents premature cleavage of the Fmoc protecting group.

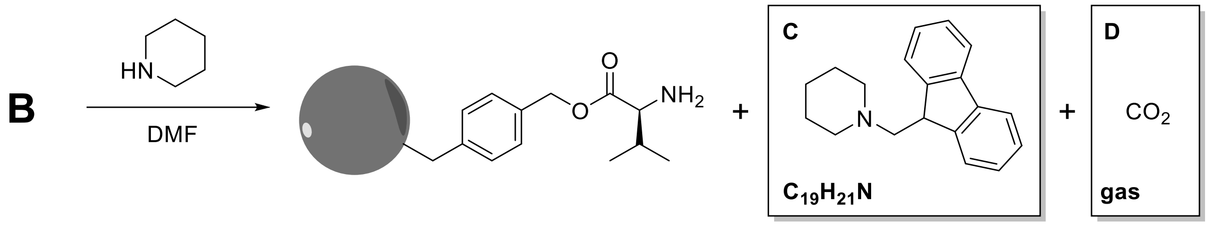
☐ Solubilizer – the cesium salt of Fmoc-Val-OH is highly soluble in most organic solvents.

☐ Swelling agent – the charged species compete with π-π interactions within the resin, improving the accessibility of all linker groups.

Mechanism of the catalyzed, two-step process:



24.4



24.5

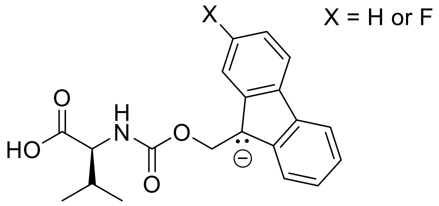
☐ Slower – a carbocation intermediate is formed during the reaction which is destabilized by the electronegative fluorine substituent.

☐ Slower – the sterically demanding fluorine substituent hinders the approach of the piperidine reagent.

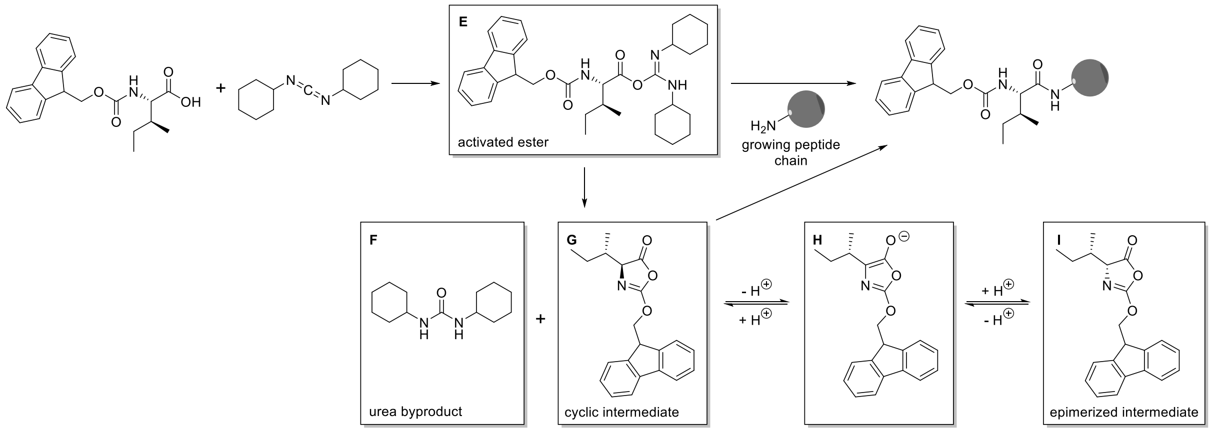
☒ Faster – a carbanion intermediate is formed during the reaction which is stabilized by the electronegative fluorine substituent.

☐ Faster – the fluorine substituent coordinates to the piperidine reagent, thus promoting its reaction with the adjacent fluorenylmethyl group.

The reaction runs via an E1cB mechanism. Structure of the intermediate:



24.6



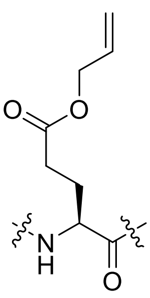
24.7

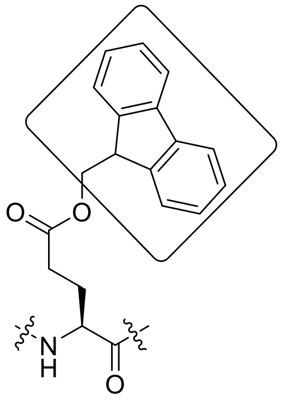
Tyr	**PG-6**
Gln	**PG-8** (no PG is also a valid answer here)
Glu	**PG-6**
Arg	**PG-3**

Note: **PG-8** (Xan) is not a common protecting group but the students should be able to deduce its lability and deprotection mechanism by associating it with the common *p*-methoxybenzyl (PMB) protecting group.

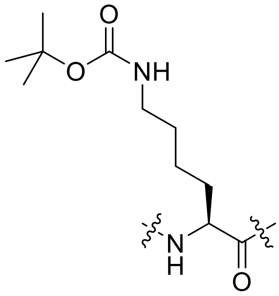
24.8

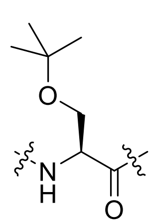
a. *cleavage condition:* 20% piperidine in DMF, 15 min YES


allyl ester

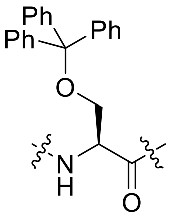

fluorenylmethyl ester

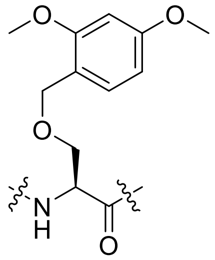
b. *cleavage condition:* 95% CF_3CO_2H, 60 min NO


Boc amine

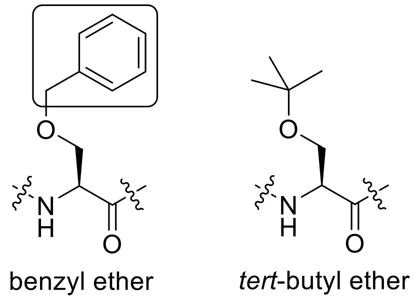

tert-butyl ether

c. *cleavage condition:* 1% CF_3CO_2H in CH_2Cl_2, 15 min NO

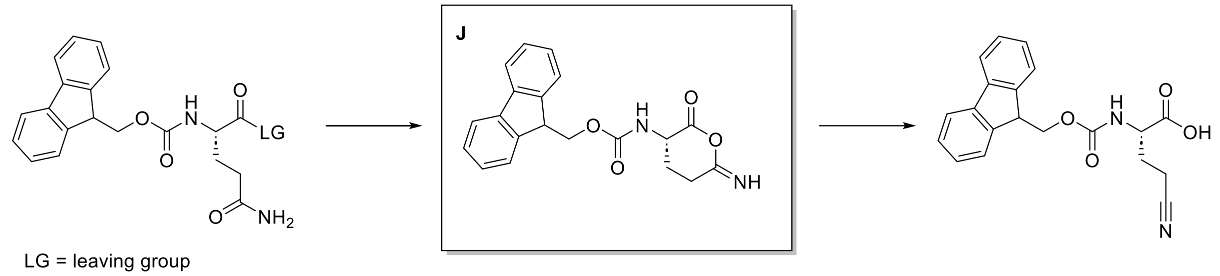

trityl ether


2,4-dimethoxybenzyl ether

d. *cleavage condition:* H_2 (g), Pd on charcoal, 60 min YES



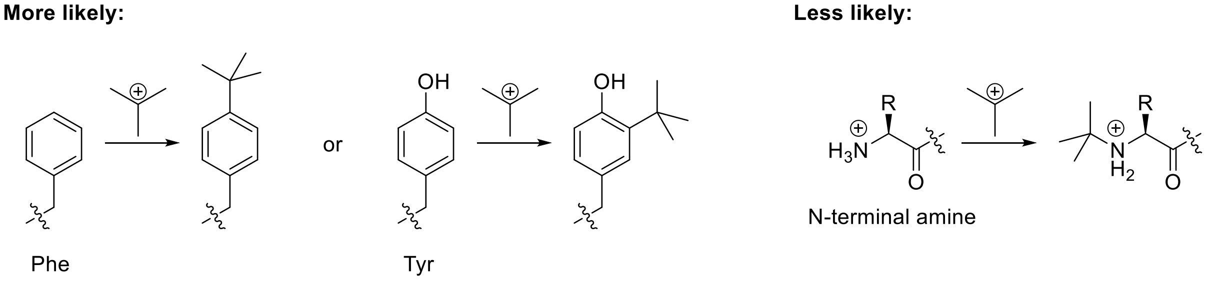
24.9



24.10

$\Delta m/z = 1937 - 1881 = 56$

The increase in mass by 56 amu corresponds to a *tert*-butyl group. The *tert*-butyl carbocation is formed as an intermediate during removal of Boc a ^{t}Bu protecting groups. In the absence of additives, the *tert*-butyl carbocation may react with nucleophilic groups present in the peptide. The most probable sites of attachment are aromatic sidechains of Phe and Tyr via electrophilic aromatic substitution. Attachment to the N-terminal amino group of the peptide is less likely as this functionality is fully protonated under the strongly acidic conditions.



24.11

General strategy: multiply yields for each step raised to the power corresponding to the number of repetitions of this step

$$Yield = loading \times deprotection^{17} \times coupling^{16} \times cleavage$$

a. $Yield = 0.9 \times 0.9^{17} \times 0.9^{16} \times 0.9 = 0.9^{35} = 0.025 \implies \mathbf{2.5\%}$

b. $Yield = 0.9 \times 0.99^{17} \times 0.97^{16} \times 0.9 = 0.42 \implies \mathbf{42}\%$

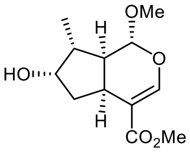
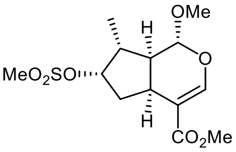
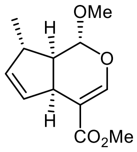
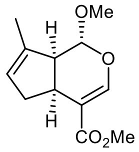
Solution: Gentian goes chemistry

25.1

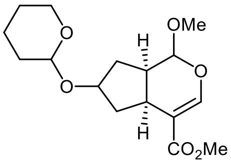
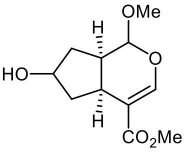
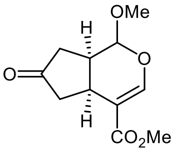
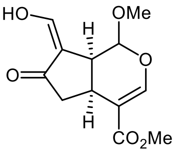
with sugar moiety: 10 stereocenters ---> $2^{10} = 1024$ possible stereoisomers

without sugar moiety: 5 stereocenters ---> $2^5 = 32$ possible stereoisomers

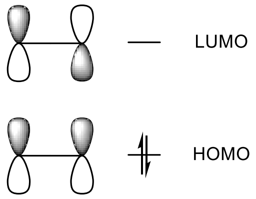
25.2

A 	**B** 	**C** 
D 		

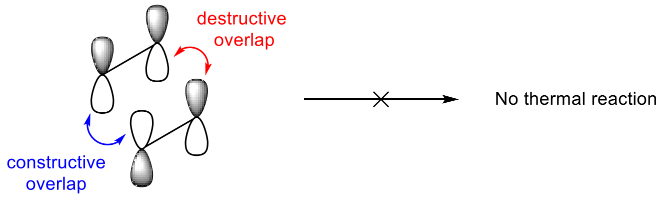
25.3

F 	**G** 	**H** 
I  or tautomers		

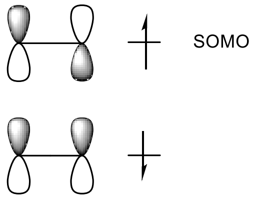
25.4



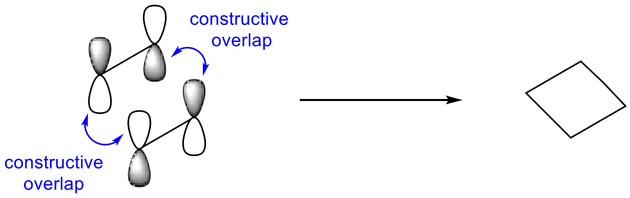
FMO of an alkene



Thereby the [2+2] cycloaddition is forbidden under thermal conditions.



FMO of photoexcited alkene

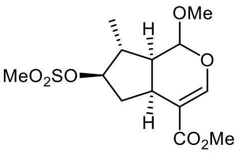
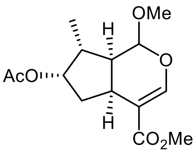
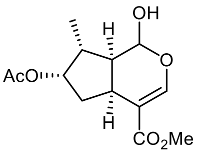


[2+2] Reaction allowed under photochemical conditions.

conditions **E**: Considering the FMO-interactions, the desired reaction must be conducted under photochemical conditions.

25.5

conditions **J**: NaBH$_4$ at 0 °C in MeOH

K	**L**	**M**
		

Solution - The Chemistry of Scent and Fragrance

26.1

The signs indicate in which direction the enantiomer rotates the plane of polarized light in a polarimetry experiment. By convention, the (+) sign is dextrorotatory (clockwise), the (–) sign is for compounds that have levorotatory (counter-clockwise) optical rotation.

26.2

(*R*)-carvone (–)-carvone

(*S*)-carvone (+)-carvone

26.3

a) (*R*)-isomer is always (–)
b) (*S*)-isomer is always (–)
c) (*R*)-isomer is always (+)
d) There is no relationship between the stereodescriptors.

The (*R*) and (*S*) designation describes the absolute configuration of a specific stereocenter in the molecule, whereas the (+) and (–) prefixes describe a property of the molecule as a whole. There is no relationship between the *R*/*S* designation and the sign of its specific rotation, (+) or (–). We have to experimentally measure the optical rotation by polarimetry.

26.4

The measured optical rotation is –23°, which means it is levorotary. The major enantiomer in the mixture therefore has to be the (–)-carvone (the *R*-enantiomer).

$$Rotation(mix) = [Fraction(S) \times Rotation(S)] + [Fraction(R) \times Rotation(R)]$$

If we set $Fraction(S) = x$, then $Fraction(R) = 1 - x$ and

$$Rotation(mix) = [x \times Rotation(S)] + [(1 - x) \times Rotation(R)]$$

We obtain:

$$-23 = [x \times (+61)] + [(1 - x) \times (-61)]$$

Solve for x:

$$x = 0.3114$$

$$(1-x) = 0.6885$$

The mixture consists of 69% of (*R*)-carvone and 31% of (*R*)-carvone.

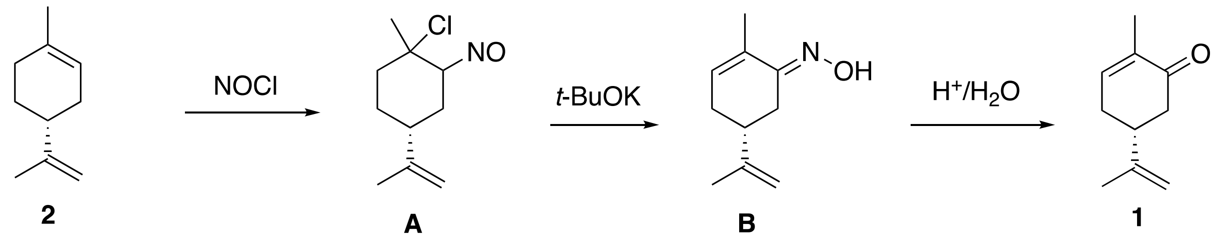
The enantiomeric excess is of the mixture is 37.8%:

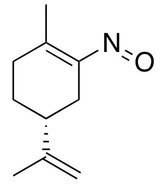
$$\% \, ee = \frac{(R-S)}{(R+S)} = \frac{(69-31)}{(100)} = 38\%$$

26.5

a) Distillation
b) Sublimation
c) Chiral column chromatography
d) Column chromatography on silica gel

26.6



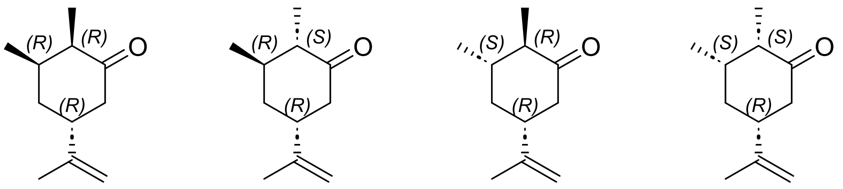


B’

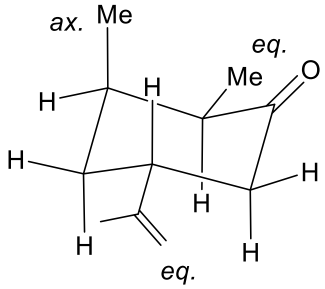
Compound A – (+)-limonene nitrosochloride
Compound B – (–)-carvone oxime (the tautomer B’ also correct)

26.7

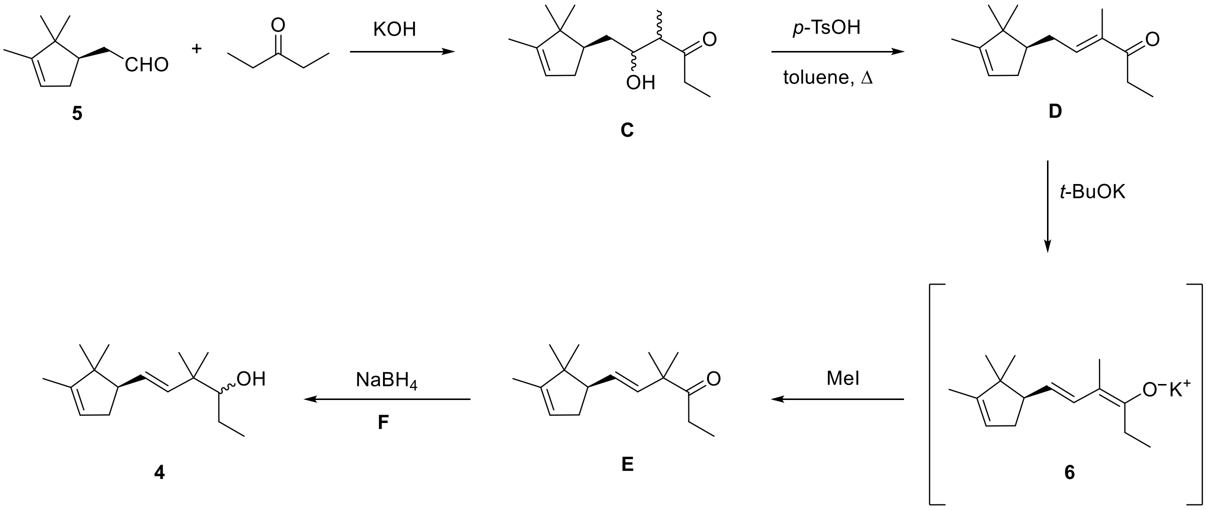
Since we start from an optically pure (–)-carvone, there are 4 possible stereoisomers that can form: (2*R*,3*R*,5*R*), (2S,3*R*,5*R*), (2*R*,3*S*,5*R*), (2*S*,3*S*,5*R*).

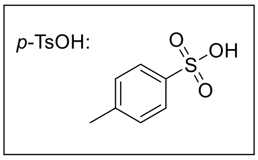


The lowest energy conformation of (2*R*,3*R*,5*R*) isomer is the chair conformation with two substituents in the equatorial position and one in the axial.



26.8





Note: Deprotonation of **D** to give **6** is performed under thermodynamic conditions, while alkylation of **6** with MeI under kinetic control.

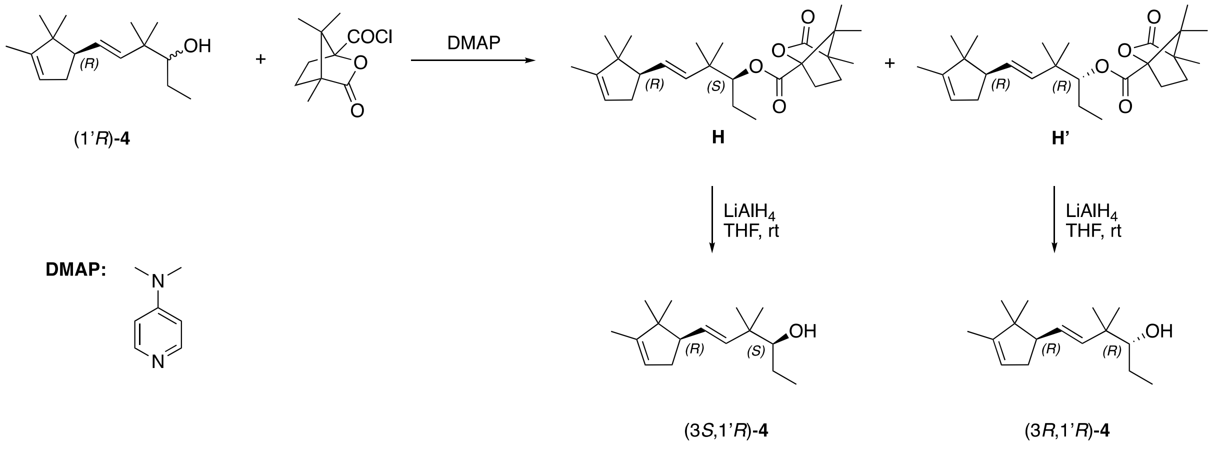
Conditions **F**:

- **a) $LiAlH_4$**
- b) NaOH
- **c) $NaBH_4$**
- d) H_2, Pd/C

26.9

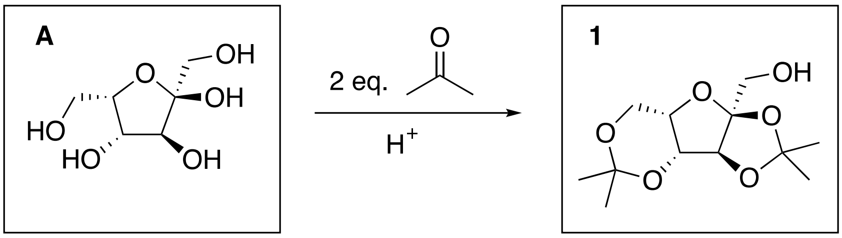
- **a) Addition of 3Å molecular sieves**
- b) Addition of zinc powder
- c) Using anhydrous toluene as solvent
- **d) Addition of anhydrous $MgSO_4$**

26.10

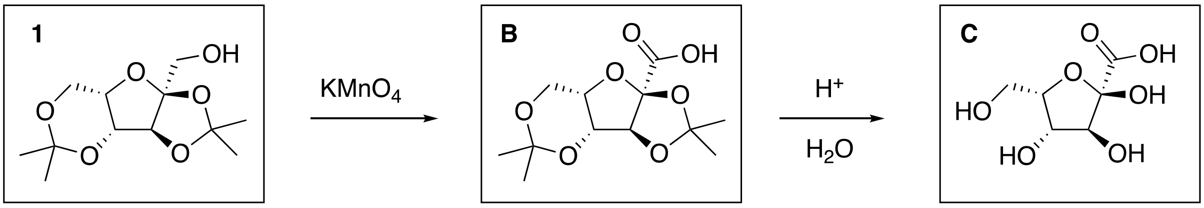

OH
(R)
(1'R)-4
+
COCl
O
O
DMAP
O
O
O
(R)
(S)
O
O
H
+
O
O
O
(R)
(R)
O
O
H'
LiAlH$_4$
THF, rt
LiAlH$_4$
THF, rt
DMAP:
N
N
(R)
(S)
OH
(3S,1'R)-4
(R)
(R)
OH
(3R,1'R)-4

Solution – Vitamin C

27.1



27.2



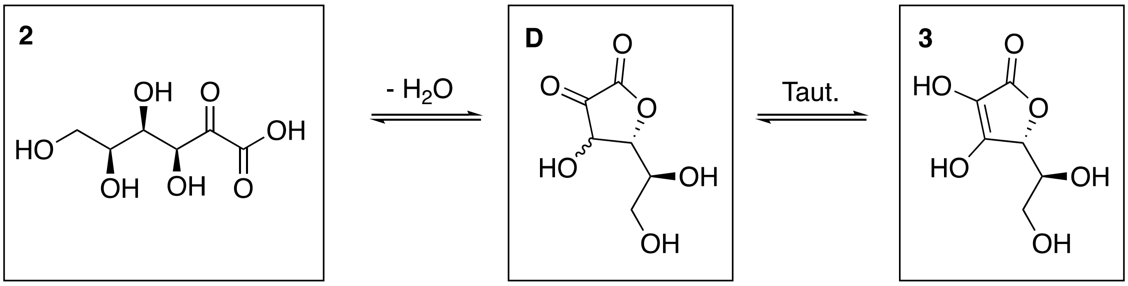
27.3

☒ Protecting group (**a**)

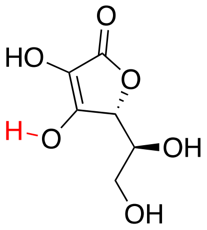
☐ Solubilizing group (**b**)

☐ Directing group (**c**)

27.4

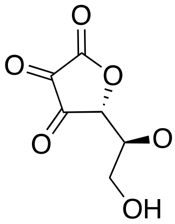


27.5

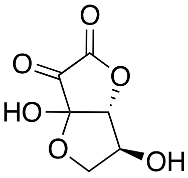


Similar to *e.g.* a carboxylic acid RCOOH

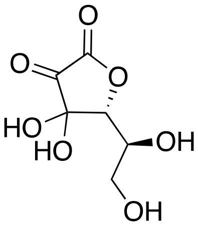
27.6



or

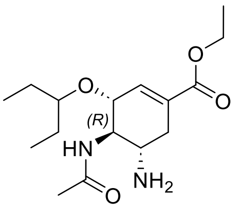


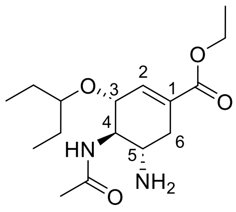
or



Solution: Antiviral Drug Tamiflu

28.1

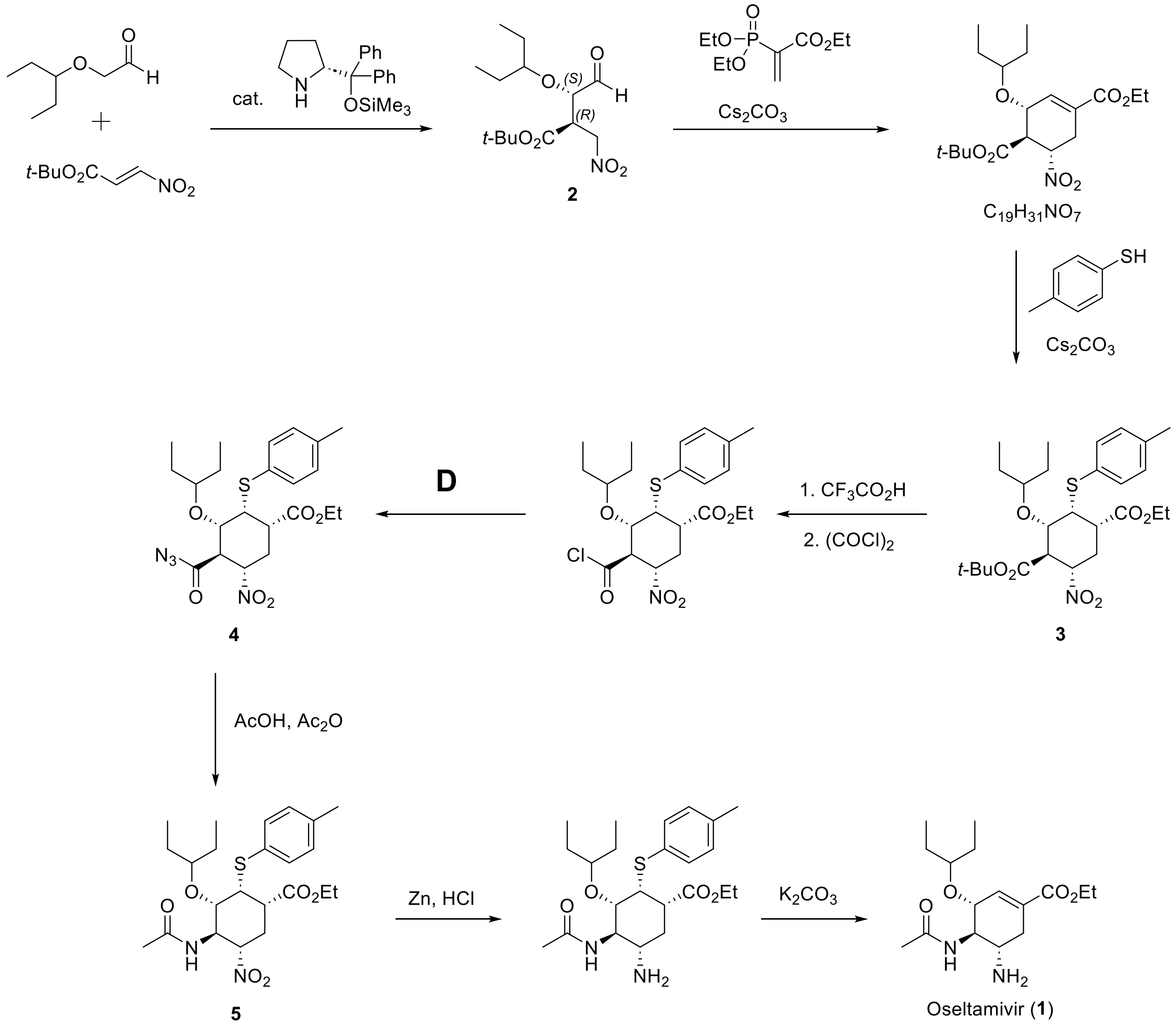




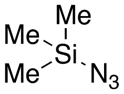
28.2

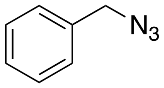
a. Cis
b. Trans
c. Syn
d. Anti

28.3



Reagent **D**:

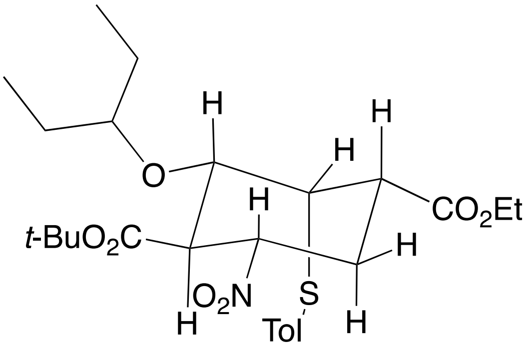




NaN_3 CH_2N_2 NH_3

S £ S £ £

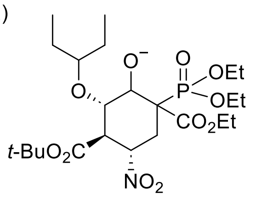
28.4



3

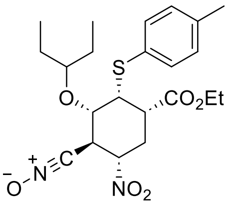
28.5

a)



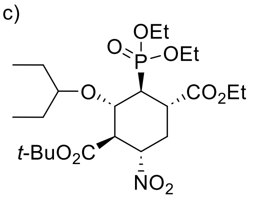
YES

b)



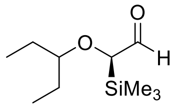
NO

c)



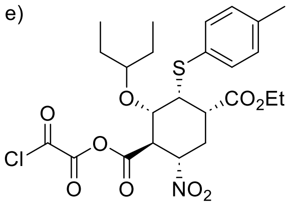
NO

d)



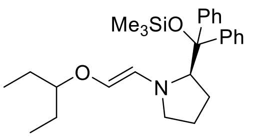
NO

e)



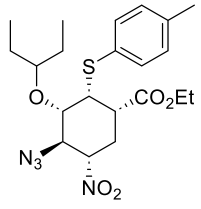
YES

f)



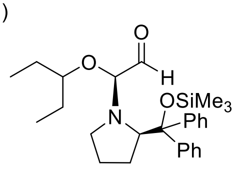
YES

g)



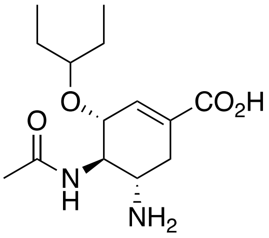
NO

h)



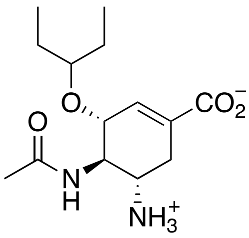
NO

28.6



F

or



F

Solution: Diarylethenes as Photoswitches

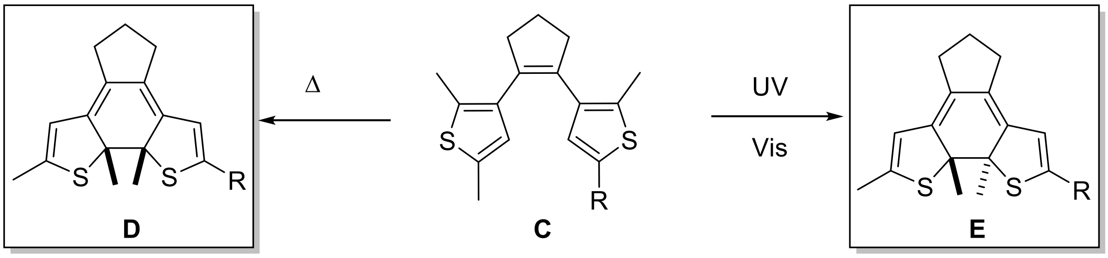
29.1

6 π-electrons

29.2

conrotatory

29.3



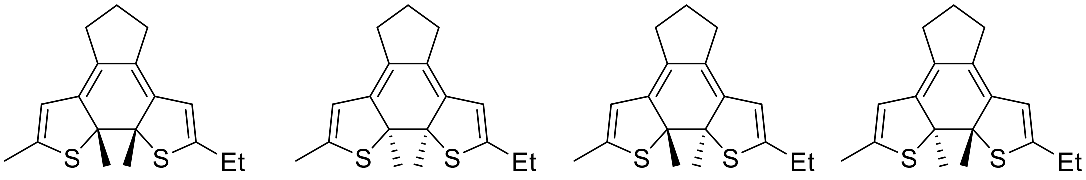
29.4

a) diastereomers

c) epimers

29.5

4 products

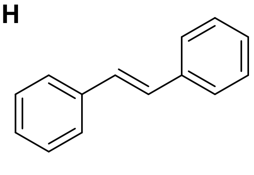


29.6

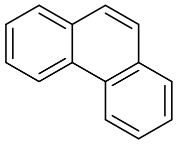
b) enantiomers

29.7

H



I



29.8

a) presence of methyl groups instead of H-atoms prevents irreversible oxidation to form a polycyclic aromatic system

c) the cyclopentene backbone prevents *Z* to *E* isomerization

29.9

b) the wavenumbers of the absorption maxima, relevant for photo switching between **A** and **B**, follow $\tilde{\upsilon}_{MAX,A} > \tilde{\upsilon}_{MAX,B}$

e) the absorption spectrum of **A** is represented by the straight line

f) the absorption spectrum of **B** is represented by the dashed lines

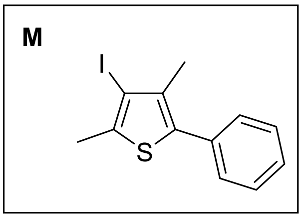
29.10

500 - 650 nm

29.11

Appropriate Pd^0 catalyst or precursor *e.g.* $[Pd(PPh_3)_4]$ and an aryl halide *e.g* PhI

29.12



29.13

a) deprotonation and transmetalation (**J to K**)

b) metal-catalysed cross coupling reaction (**K to L**)

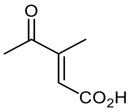
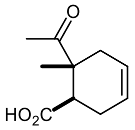
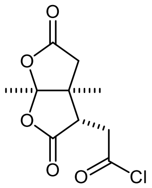
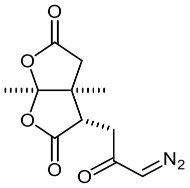
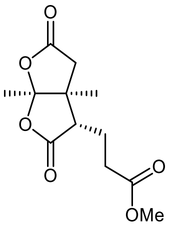
c) halogen-metal exchange (**M to N**)

d) oxidation by stoichiometric amounts of a transition metal

e) olefin cross-metathesis

Solution: Studies on Vitamin B_{12}

30.1

A	B	C
		
D	**E**	
		

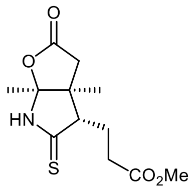
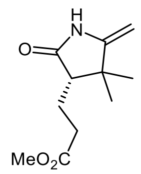
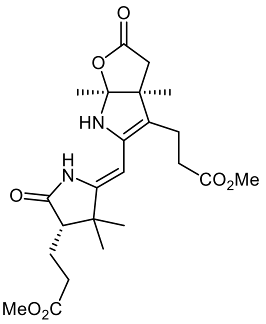
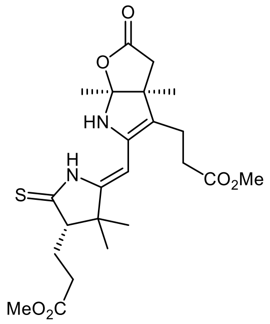
The sequence from the carboxylic acid intermediate to **E** is known as Arndt-Eistert homologation.

30.2

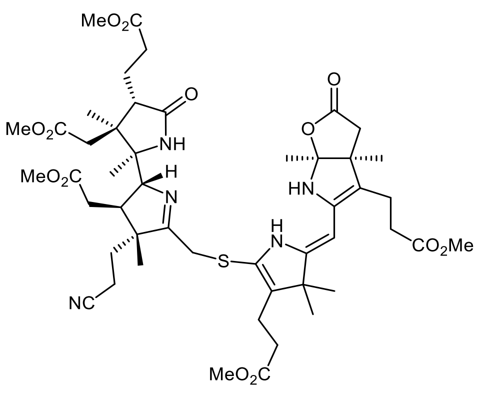
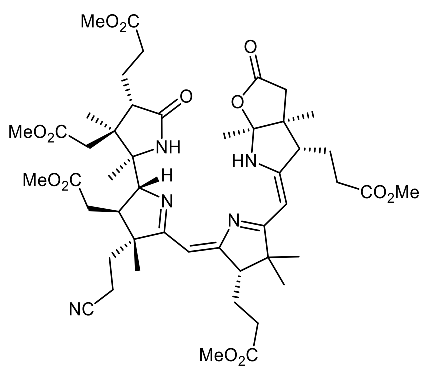
Intermediate **A** takes part in a Diels-Alder reaction. $SnCl_4$ acts as Lewis acid, lowering the energy of the LUMO orbital and facilitating reactivity. A more complete explanation can be given via FMOs.

30.3

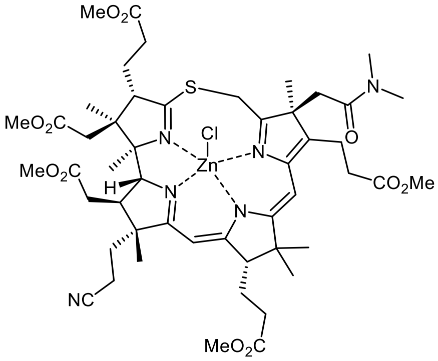
Note that in the following structures (especially **G**, **H**, **I**, **M** and **N**) various tautomers are in principle valid answers. The structures presented here are what was observed by the researchers, more broadly If there are no additional hints given (*i.e.* spectroscopic data) the students are not required to know whether a given structure (*i.e.* H) exists as the Imine, the enamine, or a mixture thereof.

F	**G**	**H**
		
I		
		

30.4

J	**K**
	

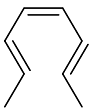
30.5

L	M	N
I_2		PR_3 (like *e.g.* $P(OEt)_3$ or $P(CH_2CH_2CN)_3$)

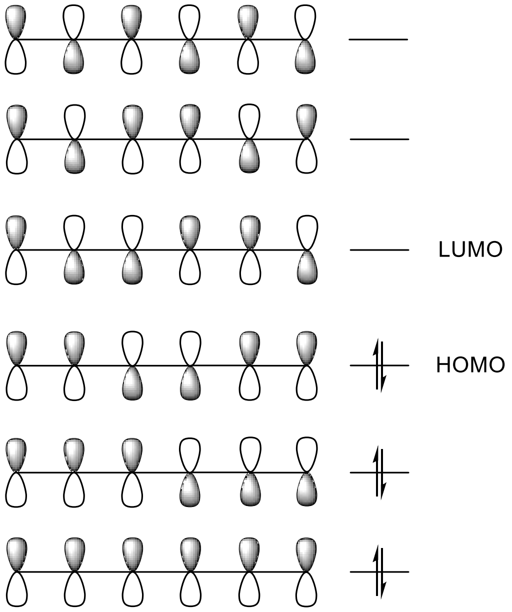
30.6

The coordination of the Zn(II) brings together the reacting termini – thereby accelerating the reaction (preorganization).

30.7

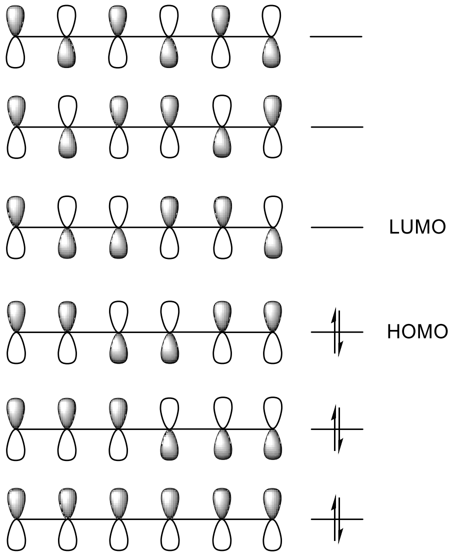


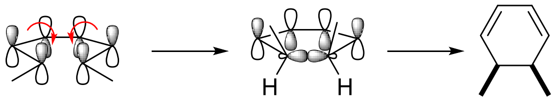
FMO's for the triene are given to the right - important are the orientation of the lobes of the HOMO and LUMO



30.8

Under thermal conditions, the reaction is disrotatory, with both residues (in the example from Vitamin B_{12} The H and methyl group) ending up syn with respect to each other.

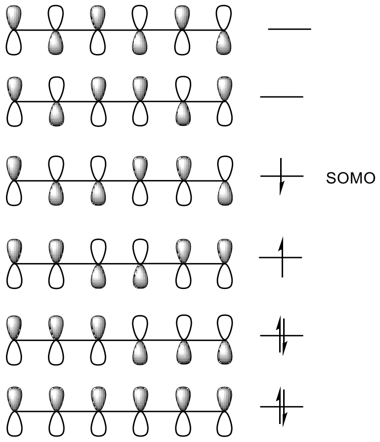


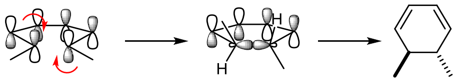


In order for constructive orbital overlap, the outmost P-orbitals have to rotate in opposite directions - disrotatory. This results in a new sigma bond, and the two residues (here methyl groups) both pointing in the same direction.

30.9

Under photochemical conditions, an electron is promoted into the SOMO, resulting in a conrotatory ring closure:





Upon photoexcitation, one electron of the HOMO is promoted into the LUMO. The reaction can now take place from this singly occupied molecular orbital (SOMO). Constructive overlap between the outmost p-orbitals only occurs, if they rotate in the same direction - conrotatory. This results in the same constitution as before, but with the two residues (here methyl groups) pointing in opposite directions.

Solution: Essential Medicines

Part A

1.1.

Formula	**Trade name (example)**	**Medical use**
C	*CharcoAid*	Poisonings (non-specific antidote)
$Fe_4[Fe(CN)_6]_3$	*Radiogardase*	Thallium and radioactive caesium poisonings
As_2O_3	*Trisenox*	Cancer
$FeSO_4 \cdot 7H_2O$	*Feosol*	Iron deficiency
$Na_2[Fe(CN)_5(NO)] \cdot 2H_2O$	*Nipride*	Hypertensive crisis (high blood pressure)
$KMnO_4$	*Permitabs*	Dermatological infections
$BaSO_4$	*Varibar*	X-ray imaging (radiocontrast agent)
I_2	*Iodosorb*	Iodine deficiency, antiseptic
$[Ag(NH_3)_2]F$	*Saforide*	Dental caries prevention, antimicrobial

1.2.

Vial	Compound	Reasoning
1	C	Black powder, insoluble in water and petroleum ether
2	$FeSO_4 \cdot 7H_2O$	Blue-green crystals, colourless to light-green solution in water depending on the concentration, insoluble in petroleum ether
3	$KMnO_4$	Purple-black crystals, purple solution in water, insoluble in petroleum ether
4	I_2	Grey solid, slightly and slowly dissolves in water to form a light-brown solution, purple solution in petroleum ether

1.3.

Conditions	Reaction equation with observations
without H_2SO_4	$3FeSO_4 + KMnO_4 + 2H_2O = 3Fe(OH)SO_4 + KOH + MnO_2\downarrow$ or $6FeSO_4 + 2KMnO_4 + 4H_2O = [Fe(OH)_2]_2SO_4 + 4Fe(OH)SO_4 + K_2SO_4 + 2MnO_2\downarrow$ (disappearance of purple colour, brown precipitate, colourles solution)
with H_2SO_4	$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O$ (disappearance of purple colour, colourless solution)

Part B

1.4.

Formula	Letter	Medical use
$NaNO_2$	C	Cyanide poisoning
$NaHCO_3$	A	Severe metabolic acidosis
$Na_2S_2O_3$	D	Cyanide poisoning and fungal skin infections
NaF	B	Dental caries prevention
NaClO	E	Disinfectant

1.5.

Compound	Formula	Reaction(s) equation(s) with observations
I	NaClO	$4NaClO + 2H_2SO_4 = 2Na_2SO_4 + Cl_2\uparrow + O_2\uparrow + 2H_2O$ (green solution, gas) $NaClO + 2FeSO_4 + H_2O = NaCl + 2Fe(OH)SO_4\downarrow$ (brown precipitate) $5NaClO + I_{2\,(org)} + H_2O = 5NaCl + 2HIO_3$ (disappearance of the purple colour of the organic phase)

II	$NaHCO_3$	$2NaHCO_3 + H_2SO_4 = Na_2SO_4 + 2H_2O + 2CO_2\uparrow$ (odourless colourless gas) $2NaHCO_3 + FeSO_4 = FeCO_3\downarrow + Na_2SO_4 + H_2O + CO_2\uparrow$ (green precipitate which turns brown with time due to oxidation on air, the formation of gas is hardly visible)
III	NaF	$2NaF + FeSO_4 = FeF_2\downarrow + Na_2SO_4$ (pale yellow opaque solution, slow formation of precipitate)
IV	$NaNO_2$	$2NaNO_2 + 4FeSO_4 + 2H_2SO_4 + 8H_2O = 2[Fe(NO)(H_2O)_5]SO_4 + Fe_2(SO_4)_3 + Na_2SO_4$ (brown solution due to formation of nitrosyl complex) $5NaNO_2 + 2KMnO_4 + 3H_2SO_4 = 5NaNO_3 + 2MnSO_4 + K_2SO_4 + 3H_2O$ (purple colour disappearance, colourless solution)
V	$Na_2S_2O_3$	$Na_2S_2O_3 + H_2SO_4 = Na_2SO_4 + SO_2\uparrow + S\downarrow + H_2O$ (colloidal precipitate, odorous gas) $3Na_2S_2O_3 + 8KMnO_4 + H_2O = 3K_2SO_4 + 8MnO_2\downarrow + 3Na_2SO_4 + 2KOH$ (purple colour disappearance, dark-brown precipitate) $5Na_2S_2O_3 + 8KMnO_4 + 7H_2SO_4 = 4K_2SO_4 + 8MnSO_4 + 5Na_2SO_4 + 7H_2O$ (purple colour disappearance, colourless solution) $2Na_2S_2O_3 + I_{2\,(org)} = Na_2S_4O_6 + 2NaI$ (disappearance of the purple colour of the organic phase)

Part C

1.6.

Mixture	**Compound**	**Medical use**
1	Li_2CO_3	Bipolar disorders
	KI	Hyperthyroidism, radiation accidents, fungal infections
2	$MgSO_4$	Anticonvulsant
	$ZnSO_4$	Diarrhoea
3	$CaCl_2$	Corresponding metal supplement
	CH_3COOH	Infections of the ear canal

1.7.

Mixtures	**A**	**B**	**C**
+A	▨	white ↓	–
+B	white ↓	▨	colourless ↑, then white ↓ (excess of **B**)
+C	–	colourless ↑	▨

1.8.

A	
$MgSO_4$	$ZnSO_4$

B	
Li_2CO_3	KI

C	
$CaCl_2$	CH_3COOH

Combination	**Ionic equation(s)**
A+B	$2Mg^{2+} + 3CO_3^{2-} + 2H_2O = (MgOH)_2CO_3\downarrow + 2HCO_3^-$ $2Zn^{2+} + 3CO_3^{2-} + 2H_2O = (ZnOH)_2CO_3\downarrow + 2HCO_3^-$
A+C	If recommended concentrations are used, there are no visible observations. However, if calcium salt is prepared with a higher concentration, then the white precipitate can be observed upon mixing with sulfates: $Ca^{2+} + SO_4^{2-} = CaSO_4\downarrow$
B+C	When **C** is added to **B** dropwise: $CO_3^{2-} + 2CH_3COOH = CO_2\uparrow + 2CH_3COO^- + H_2O$ When **B** is added to **C** dropwise: $2CH_3COOH + CO_3^{2-} = CO_2\uparrow + 2CH_3COO^- + H_2O$, then: $Ca^{2+} + CO_3^{2-} = CaCO_3\downarrow$ (when the excess of **B** is used)

Solution: Cantons of Switzerland

Chemicals

Chemical	Hazards	GHS Hazard Statements
Zinc formate, $Zn(HCOO)_2$ (557-41-5)	Harmful Environmental hazard	H302, H319, H410 P264, P280, P301+P330+P331, P312, P337+P313
Sodium tungstate dihydrate, $Na_2WO_4{\cdot}2H_2O$ (10213-10-2)	Harmful	H302 P280, P301+P312, P303+P361+P353, P305+P351+P338
Strontium hydroxide octahydrate, $Sr(OH)_2{\cdot}8H_2O$ (1311-10-0)	Corrosive	H314 P280, P301+P330+P331, P303+P361+P353, P305+P351+P338, P310
Barium sulfide, BaS (21109-95-5)	Toxic Corrosive Environmental hazard	H290, H301, H314, H332, H400 P260, P273, P280, P303+P361+P353, P304+P340+P310, P305+P351+P338
Aluminium iodide, AlI_3 (7784-23-8)	Corrosive	H314 P260, P280, P301+P330+P331, P303+P361+P353, P304+P340+P310, P305+P351+P338
Ammonia solution, NH_3, 1 M (1336-21-6)	Corrosive Environmental hazard	H315, H318, H410 P264, P273, P280, P302+P352, P305+P351+P338, P332+P313
Sulfuric acid, H_2SO_4, 1 M (7664-93-9)	Corrosive	H290, H315, H319 P234, P264, P280, P302+P352, P305+P351+P338, P332+P313
Cesium formate, CsHCOO (3495-36-1)	Harmful Health hazard	H302, H319, H371, H373 P301+P312+P330, P305+P351+P338, P308+P311
Cadmium formate, $Cd(HCOO)_2$ (4464-23-7)	Toxic Health hazard Environmental hazard	H301+H331, H351, H373, H410 P202, P260, P264, P273, P301+P310, P304+P340+P311
Calcium formate, $Ca(HCOO)_2$ (544-17-2)	Corrosive	H318 P280, P305+P351+P338+P310
Zinc dust, Zn (7440-66-6)	Environmental hazard	H410 P273, P391, P501
Copper(II) formate tetrahydrate, $Cu(HCOO)_2{\cdot}4H_2O$, (5893-61-8)	Harmful Corrosive Environmental hazard	H302, H315, H318, H335, H410 P280, P301+P330+P331, P302+P352, P304+P340, P305+P351+P338, P310, P332+P313
Vanadyl sulfate hydrate, $VOSO_4{\cdot}xH_2O$ (123334-20-3)	Toxic Environmental hazard	H301, H411 P264, P270, P273, P301+P310, P391, P405
Potassium permanganate solution, $KMnO_4$, 1 wt% (7722-64-7)	Oxidizing Corrosive Harmful Health hazard Environmental hazard	H272, H302, H314, H361d, H373, H410 P210, P260, P273, P280, P303+P361+P353, P305+P351+P338

*It is recommended to prepare 1–5 wt% solutions (at least 20 ml per student) of the encoded compounds. The 5 wt% solutions of salts containing WO_4^{2-}, Al^{3+}, Cd^{2+}, Ca^{2+}, Cu^{2+}, and VO^{2+} ions provide more clear observations in comparison with 1 wt% solutions. Some ions that do not participate in identification reactions could be substituted with other inert ions (see suggestions further). Solutions of some encoded compounds could be simulated using a mixture of compounds of targeted ions with inert counterions (see suggestions further). Warn the students about the implemented changes. Recommended amount for Zn dust – at least 100 mg per student.

Glassware and Equipment

Item	**Quantity**
Test tube rack	1
Permanent marker	1
Closed vials with solutions **1–5**	5
Closed vials with solutions **CH-1**, **CH-2**, **CH-3**	3
Closed vials with solutions **A**, **B**	2
Closed vials with NH_3, H_2SO_4, $KMnO_4$ solutions	3
Closed vial with Zn dust	1
Test tubes	At least 20
Plastic Pasteur pipettes	13
Wash bottle with distilled water	1
Small spatula for Zn dust	1

Part A

Note: the chemistry of tungsten (W) and titanium (Ti) won't be a part of the practical exam.

*The tungstate (WO_4^{2-}) could be substituted with phosphate (PO_4^{3-}). In this case, proceed as if it would correspond to the second letter **W** in the canton's code. Warn the students which anion they are working with.

2.1.

Anion	**Canton code(s)**	**Example of the compound**
formate (**H**COO^-)	**ZH** **SH**	$Zn(HCOO)_2$ $Sr(HCOO)_2$
hydroxide (**O**H^-)	**SO**	$Sr(OH)_2$
iodide (**I**$^-$)	**AI** **TI**	AlI_3 TiI_3 (violet solution)
sulphide (**S**$^{2-}$)	**BS** **VS**	BaS no example of soluble salt
tungstate (**W**O_4^{2-}) or *phosphate* (PO_4^{3-}, letter **W**)	**NW** **OW**	Na_2WO_4 or Na_3PO_4 no example of soluble salt

2.2.

Solution	**1** $Zn(HCOO)_2$	**2** Na_2WO_4 or Na_3PO_4	**3** $Sr(OH)_2$	**4** BaS	**5** AlI_3
+1 $Zn(HCOO)_2$		white ↓	white ↓ (no dissolution in excess of **1**)	white ↓	–
+2	white ↓		white ↓	white ↓	white ↓

Na_2WO_4 or Na_3PO_4					
+3 $Sr(OH)_2$	white ↓ (no dissolution in excess of **3**)	white ↓		white ↓ (small amount of precipitate)	white ↓, then solution (excess of **3**)
+4 BaS	white ↓	white ↓	white ↓ (small amount of precipitate)		white ↓ (opacity) (+ odorous ↑)*
+5 AlI_3	–	white ↓	solution, then white ↓ (excess of **5**)	white ↓ (+ odorous ↑)*	
+NH_3	white ↓, then solution (excess of NH_3)	–	–	–	white ↓
+H_2SO_4	–	If Na_2WO_4: yellow ↓ (opacity, can be slow if low concentrations of WO_4^{2-} are used) If Na_3PO_4: –	white ↓	white ↓ (+ odorous ↑)*	–

*The formation of H_2S as a gas is hardly observable. However, it can be confirmed by the characteristic smell or a test with paper soaked in Pb^{2+}, Ag^{+}, or Cd^{2+} salt solution.

2.3.

1	**2**	**3**	**4**	**5**
$Zn(HCOO)_2$	Na_2WO_4	$Sr(OH)_2$ Saturated solution. Filtration may be required. Use it freshly prepared and store it in a closed bottle.	BaS Filtration may be required depending on the quality of the chemical. Use it freshly prepared and store it in a closed bottle.	AlI_3 Carefully dissolve the salt in small portions. It may form a pale yellow solution due to contamination with iodine.

* If these chemicals are not available, the following substitutes can be used:

1	**2**	**3**	**4**	**5**
$Zn(CH_3COO)_2$ $Zn(NO_3)_2$ $ZnCl_2$ $Na(HCOO)$ can also be added, but formate ion is not necessary here.	Na_3PO_4 Analogous to Na_2WO_4, it gives white precipitates with Zn^{2+}, Sr^{2+}, Ba^{2+}, and Al^{3+}, but no precipitate with H^{+}.	$Sr(CH_3COO)_2$ + NaOH $Sr(NO_3)_2$ + NaOH $SrCl_2$ + NaOH (filtration may be required)	$Ba(CH_3COO)_2$ + Na_2S $Ba(NO_3)_2$ + Na_2S $BaCl_2$ + Na_2S	$Al(NO_3)_3$ $AlCl_3$ KI can also be added, but iodide ion is not necessary here.

2.4.

Combination	**Ionic equation(s)**
1+2	$Zn^{2+} + WO_4^{2-} = ZnWO_4\downarrow$ If Na_3PO_4 is used as **2**: $3Zn^{2+} + 2PO_4^{3-} = Zn_3(PO_4)_2\downarrow$ (or hydroxyphosphate)
1+3	$Zn^{2+} + 2OH^- = Zn(OH)_2\downarrow$ (saturated solution of $Sr(OH)_2$ is not basic enough to completely dissolve $Zn(OH)_2$ and form the hydroxo complex: $Zn(OH)_2 + 2OH^- = [Zn(OH)_4]^{2-}$)
1+4	$Zn^{2+} + S^{2-} = ZnS\downarrow$
1+5	–
2+3	$Sr^{2+} + WO_4^{2-} = SrWO_4\downarrow$ If Na_3PO_4 is used as **2**: $3Sr^{2+} + 2PO_4^{3-} = Sr_3(PO_4)_2\downarrow$ (or hydroxyphosphate)
2+4	$Ba^{2+} + WO_4^{2-} = BaWO_4\downarrow$ If Na_3PO_4 is used as **2**: $3Ba^{2+} + 2PO_4^{3-} = Ba_3(PO_4)_2\downarrow$ (or hydroxyphosphate)
2+5	$2Al^{3+} + 3WO_4^{2-} = Al_2(WO_4)_3\downarrow$ If Na_3PO_4 is used as **2**: $Al^{3+} + PO_4^{3-} = AlPO_4\downarrow$ (or hydroxyphosphate)
3+4	$Sr^{2+} + S^{2-} = SrS\downarrow$ (small amount of precipitate as it is slightly soluble)
3+5	$Al^{3+} + 3OH^- = Al(OH)_3\downarrow$ In excess of **3**: $Al(OH)_3 + OH^- = [Al(OH)_4]^-$ (or $[Al(OH)_6]^{3-}$)
4+5	$2Al^{3+} + 3S^{2-} + 6H_2O = 2Al(OH)_3\downarrow + 3H_2S\uparrow$
1+NH_3	$Zn^{2+} + 2NH_3 + 2H_2O = Zn(OH)_2\downarrow + 2NH_4^+$ In excess of NH_3: $Zn(OH)_2 + 4NH_3 = [Zn(NH_3)_4]^{2+} + 2OH^-$
1+H_2SO_4	–
2+NH_3	–
2+H_2SO_4	$2H^+ + WO_4^{2-} = WO_3{\cdot}H_2O\downarrow$ If Na_3PO_4 is used as **2**: $H^+ + PO_4^{3-} = HPO_4^{2-}$ (or $H_2PO_4^-$, or H_3PO_4) – no visible observations
3+NH_3	–
3+H_2SO_4	$H^+ + OH^- = H_2O$ $Sr^{2+} + SO_4^{2-} = SrSO_4\downarrow$
4+NH_3	–
4+H_2SO_4	$2H^+ + S^{2-} = H_2S\uparrow$ $Ba^{2+} + SO_4^{2-} = BaSO_4\downarrow$
5+NH_3	$Al^{3+} + 3NH_3 + 3H_2O = Al(OH)_3\downarrow + 3NH_4^+$ (no dissolution in excess of NH_3)
5+H_2SO_4	–

Part B

2.5.

Colourless	$Ca(HCOO)_2$	$Cd(HCOO)_2$	$CsHCOO$
Coloured	$Cr(HCOO)_3$	$Co(HCOO)_2$	$Cu(HCOO)_2$

2.6.

Vial	Compound	Ionic equation(s) with observations
CH-1	CsHCOO	–
CH-2	$Cd(HCOO)_2$	$Cd^{2+} + 2NH_3 + 2H_2O = Cd(OH)_2\downarrow + 2NH_4^+$ (white precipitate or opacity if lower concentrations of Cd^{2+} are used) $Cd(OH)_2 + 6NH_3 = [Cd(NH_3)_6]^{2+} + 2OH^-$ (dissolution in the excess of ammonia)
CH-3	$Ca(HCOO)_2$	$Ca^{2+} + SO_4^{2-} = CaSO_4\downarrow$ (white precipitate, slow)

* If these chemicals are unavailable, other soluble salts of Cs^+ (or any other alkali metal), Cd^{2+}, and Ca^{2+} can be used, for example, acetates, nitrates, and chlorides.

* If Cs salt (but not formate) is available, you can demonstrate to the students the reaction of $CsMnO_4$ precipitation upon it reaction with $KMnO_4$. Purple crystals are formed.

2.7.

Chosen anions	S^{2-}	WO_4^{2-} or PO_4^{3-}

Vial	Ionic equation(s) with observations
CH-1	–
CH-2	$Cd^{2+} + S^{2-} = CdS\downarrow$ (yellow precipitate) and $Cd^{2+} + WO_4^{2-} = CdWO_4\downarrow$ (white precipitate) or $3Cd^{2+} + 2PO_4^{3-} = Cd_3(PO_4)_2\downarrow$ (or hydroxyphosphate, white precipitate)
CH-3	$Ca^{2+} + S^{2-} = CaS\downarrow$ (small amount of precipitate as it is slightly soluble, may not be spotted instantly) and $Ca^{2+} + WO_4^{2-} = CaWO_4\downarrow$ (white precipitate) or $3Ca^{2+} + 2PO_4^{3-} = Ca_3(PO_4)_2\downarrow$ (or hydroxyphosphate, e.g., $Ca_5(PO_4)_3OH$, white precipitate)

Part C

2.8.

Vial	Cation	Associated code(s)
A	Cu^{2+}	**CH**
B	VO^{2+}	**VD** **VS**

Combination	**Ionic equation(s)**
A+NH_3	$Cu^{2+} + 2NH_3 + 2H_2O = Cu(OH)_2\downarrow + 2NH_4^+$ (blue precipitate) $Cu(OH)_2 + 4NH_3 + 2H_2O = [Cu(NH_3)_4(H_2O)_2]^{2+} + 2OH^-$ (dark blue solution)
A+Zn(H^+)	$Cu^{2+} + Zn = Cu\downarrow + Zn^{2+}$ (solution turns from blue to colourless)
B+NH_3	$VO^{2+} + 2NH_3 + 2H_2O = VO(OH)_2\downarrow + 2NH_4^+$ (brown precipitate) No dissolution in excess of NH_3
B+Zn(H^+)	$2VO^{2+} + Zn + 4H^+ = 2V^{3+} + Zn^{2+} + 2H_2O$ (green solution) $2V^{3+} + Zn(H^+) = 2V^{2+} + Zn^{2+}$ (violet solution)

2.9. **A** (**CH**) – $Cu(HCOO)_2$, test with $KMnO_4$ (without or with H_2SO_4). **B** (**VS**) – $VOSO_4$, test with $Ca(HCOO)_2$ (**CH-3**).

Vial	**Anion**	**Reaction equation(s) with observations**
A	$HCOO^-$	$6Cu(HCOO)_2 + 8KMnO_4 + H_2O = 8MnO_2\downarrow + 3(CuOH)_2CO_3\downarrow + 8KHCO_3 + CO_2\uparrow$ (disappearance of purple colour, green to brown precipitate, gas evolution not observable) or $5Cu(HCOO)_2 + 4KMnO_4 + 11H_2SO_4 = 5CuSO_4 + 2K_2SO_4 + 4MnSO_4 + 10CO_2\uparrow + 16H_2O$ (disappearance of purple colour, slow)
B	SO_4^{2-}	$VOSO_4 + Ca(HCOO)_2 = VO(HCOO)_2 + CaSO_4\downarrow$ (white precipitate, slow)

*If $Cu(HCOO)_2$ is not available, either use a mixture of $Cu(CH_3COO)_2$ or $Cu(NO_3)_2$ and $Na(HCOO)$ solutions, or dissolve $Cu(OH)_2$ in a solution of HCOOH.

2.10. *Bonus question:*

☐ polyethylene
☐ proteins
☐ fats
☐ starch
☑ cellulose

Solution: A Simple Aldol Condensation

3.1. Answer depends on the student's TLC and should be consistent with their observations.

3.2. Answer depends on the student's TLC and should be consistent with their observations.

3.3. The used 1.3 mL of cinnamaldehyde correspond to

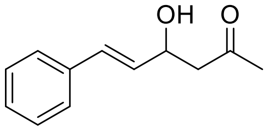
$1.3\ \mathrm{mL} \cdot 1.05 \frac{\mathrm{g}}{\mathrm{mL}} = 1.37\ \mathrm{g}$, i. e. $\frac{1.37\ \mathrm{g}}{132.16 \frac{\mathrm{g}}{\mathrm{mol}}} = 0.0103\ \mathrm{mol}$ of the compound.

Theoretically, they yield an equimolar amount of product, i. e.

$0.0103\ \mathrm{mol} \cdot 172.23 \frac{\mathrm{g}}{\mathrm{mol}} = 1.8\ \mathrm{g}$ of product.

3.4. NaOH is not consumed in the reaction, which works also with 3 equivalents of NaOH.

3.5. Structure of the aldol intermediate:



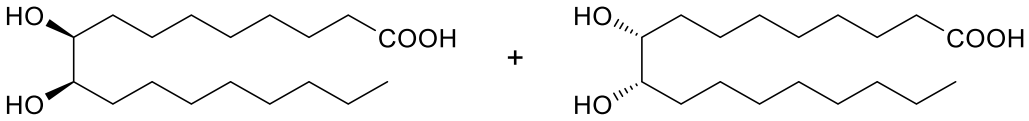
Solution: Dihydroxylation of Oleic Acid

4.1. Answer depends on the student’s TLC and should be consistent with their observations.

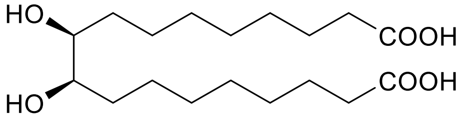
4.2. The product of the above reaction does not contain any UV-active functional group (functional group absorbing UV light in the wavelength range of a typical UV lamp). Therefore, it does not show under the UV lamp. On the other hand, $KMnO_4$ (purple) from the staining solution oxidizes the product (and other oxidizable compounds) and its consumption leaves whitish spots on a purple background.

4.3. In the above reaction, 1.6 equivalents of $KMnO_4$ are used in relation to oleic acid. After dihydroxylation of the latter, the excess of permanganate is reduced by sodium sulfite, first to manganese dioxide (basic solution), then to Mn(II) (acidic solution). The elimination of excess $KMnO_4$ prevents the product from being further oxidized (cleavage of the CC-bond of the diol unit under formation of carboxy termini).

4.4. The permanganate ion can approach the double bond from either side of the plane defined by the double bond unit of oleic acid to effectuate the *cis*-transfer of two O-atoms. This results in the formation of two product enantiomers.



4.5. The *cis*-dihydroxylation product of the shown dicarboxylic acid is achiral and it is formed as a single stereoisomer.



Solution: Synthesis of Lidocaine

5.1. Answer depends on the student's TLC and should be consistent with their observations.

5.2. Answer depends on the student's TLC (if applicable) and should be consistent with their observations.

5.3. Answer depends on the student's TLC (if applicable) and should be consistent with their observations.

5.4. After completion of the reaction, the reaction mixture is washed multiple times with water in order to remove the side product diethylammonium chloride and excess diethylamine.

5.5. a) Amount of *N*-(2,6-dimethylphenyl)chloroacetamide used in the reaction:

$$\frac{1\ \mathrm{g}}{197.66\,\frac{\mathrm{g}}{\mathrm{mol}}} = 5.06 \cdot 10^{-3}\ \mathrm{mol}$$

Amount of diethylamine used in the reaction:

$$\frac{2.1\ \mathrm{mL} \cdot 0.706\,\frac{\mathrm{g}}{\mathrm{mL}}}{73.14\,\frac{\mathrm{g}}{\mathrm{mol}}} = 20.27 \cdot 10^{-3}\ \mathrm{mol}$$

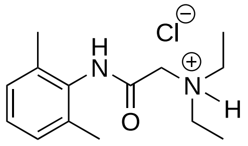
Consequently, the molar ratio *N*-(2,6-dimethylphenyl)chloroacetamide to diethylamine is:

$$\frac{20.27 \cdot 10^{-3}}{5.06 \cdot 10^{-3}} = 4.01$$

In other words, ca. 4 equivalents of diethylamine have been used in relation to *N*-(2,6-dimethylphenyl)chloroacetamide.

b) In the course of the reaction, a part of diethylamine, which acts as a nucleophile and a base at the same time, is protonated (the reaction formally generates one equivalent of HCl). The protonated part (= diethylammonium ion) is no longer available for the nucleophilic substitution with *N*-(2,6-dimethylphenyl)chloroacetamide. It needs to be compensated for by using an excess of diethylamine in the reaction.

5.6.



Solution: Transformation of Vanillin to Vanillyl Alcohol

6.1. Answer depends on the student's TLC and should be consistent with their observations.

6.2. In the above procedure, vanillin is reduced to vanillyl alcohol.

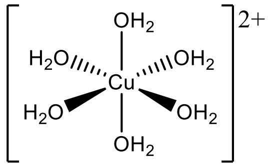
6.3. The gas evolving after the addition of HCl (aq) is hydrogen (H_2).

6.4. Yes, the reaction could still come to completion, because each equivalent of $NaBH_4$ can transfer more than one hydride to the carbonyl group of vanillin.

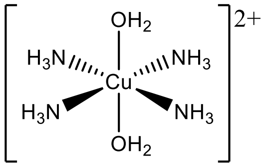
Solution: Colourful Copper

Complex	**A**	**B**	**C**	**D**	**E**
Colour	Light blue	Dark Blue	Light blue	Violet	Green
Molecular formula	$[CuH_{12}O_6]^{2+}$	$[CuH_{16}N_4O_2]^{2+}$	$K_2[CuC_4H_4O_{10}]$	$[CuC_{10}H_{18}O_6]$	$[CuC_{14}H_{12}N_2O_4]$

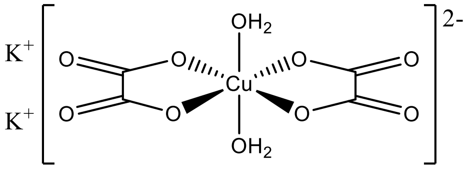
7.1.



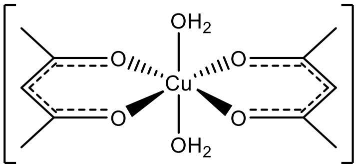
A



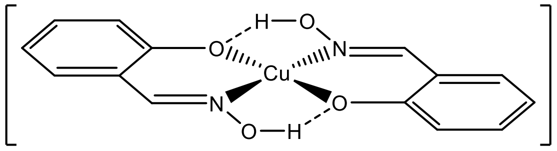
B



C



D



E

7.2. Correct answer: "Precipitation of $Cu(OH)_2$"

7.3. Calculation based on $m_{prep} = 225.0\ \text{mg}$ **X** ($CuCl_2$) being used:

$m_{isol} = 562.0\ \text{mg}$ expected

$$MW_{\text{Cu(C}_7\text{H}_6\text{NO}_2)_2} = MW_{\text{Cu}} + 14 * MW_{\text{C}} + 12 * MW_{\text{H}} + 2 * MW_{\text{N}} + 4 * MW_{\text{O}}$$

$$= 63.55\ \frac{\text{g}}{\text{mol}} + 14 * 12.01\ \frac{\text{g}}{\text{mol}} + 14 * 1.008\ \frac{\text{g}}{\text{mol}} + 2 * 14.07\ \frac{\text{g}}{\text{mol}} + 4 * 16.00\ \frac{\text{g}}{\text{mol}}$$

$$= 335.9\frac{\text{g}}{\text{mol}}$$

$$n_{\text{Cu},isol} = \frac{m_{solid}}{MW_{\text{Cu(C}_7\text{H}_6\text{NO}_2)_2}} = 1.67\ \text{mmol}$$

The initial mass of copper is therefore calculated as:

$$m_{\text{Cu},isol} = n_{\text{Cu},isol} * MW_{\text{Cu}} = 1.67\ \text{mmol} * 63.55\ \frac{\text{g}}{\text{mol}} = 106.1\ \text{mg}$$

The copper content is therefore calculated as:

$$wt\%_{\text{Cu},isol} = \frac{m_{\text{Cu},isol}}{m_{prep}} = 47.2\%$$

7.4. Calculation based on $m_{titr} = 100.0\ \text{mg}$ **X** ($CuCl_2$) being used:

$$n_{\mathrm{Cu},titr} = V_{sample} * \frac{V_{titr}}{V_{aliquot}} * [\mathrm{EDTA}]_{standard} = 0.500\ \mathrm{L} * \frac{7.44\ \mathrm{mL}}{50.00\ \mathrm{mL}} * 10.0\ \mathrm{mM} = 0.74\ \mathrm{mmol}$$

$$m_{\mathrm{Cu},titr} = n_{\mathrm{Cu},titr} * MW_{\mathrm{Cu}} = 0.74\ \mathrm{mmol} * 63.55\ \frac{\mathrm{g}}{\mathrm{mol}} = 47.0\ \mathrm{mg}$$

$$wt\%_{\mathrm{Cu},titr} = \frac{m_{\mathrm{Cu},titr}}{m_{titr}} = 47.0\%$$

7.5. Based on the provided information, the anion of an anhydrous Cu(II) salt needs to be identified:

$$wt\%_{\mathrm{Cu}} = \frac{MW_{\mathrm{Cu}}}{MW_{anion} + MW_{\mathrm{Cu}}}$$

$$MW_{anion} = MW_{\mathrm{Cu}} * \frac{1 - wt\%_{\mathrm{Cu}}}{wt\%_{\mathrm{Cu}}} = 63.55\ \frac{\mathrm{g}}{\mathrm{mol}} * \frac{1 - 0.473}{0.473} = 70.81\ \frac{\mathrm{g}}{\mathrm{mol}}$$

This corresponds to twice the molecular weight of chlorine ($MW = 35.45\ \mathrm{g/mol}$). Therefore, it can be concluded that the sample was anhydrous Cu(II) chloride, $CuCl_2$. Near misses such as carbonate ($MW = 60.01\ \mathrm{g/mol}$) or azide ($MW = 42.03\ \mathrm{g/mol}$) can be excluded by their Cu(II) salts being insoluble in water.

7.6. Answer depends on student's preformance and should be consistent with their observations.

Hard Water – Easy Titrations

Chemicals:

Chemical	**State**	**Comment**	**GHS Hazard Statements**
Water Sample **W**	Liquid	Prepared from $CaCl_2 \cdot 2H_2O$ (10035-04-8), $MgCl_2 \cdot 6H_2O$ (7791-18-6), and $NaHCO_3$ (144-55-8)	H319; P264, P280, P305+P351+P338, P337+P313
0.010 M HCl standard solution (7647-01-0)	Liquid		Not a hazardous substance or mixture according to Regulation (EC) No 1272/2008.
1.0 M HCl solution (7647-01-0)	Liquid	Corrosive	H290; P234, P390
Methyl orange solution (10 g/L in EtOH)	Liquid	Prepared from methyl orange (547-58-0) and EtOH (64-17-5) Flammable	H225, H301, H319; P210, P233, P240, P241, P242, P264, P270, P301+P310, P305+P351+P338, P405, P501
0.010 M EDTA standard solution	Liquid	Prepared from EDTA disodium salt dehydrate (6381-92-6)	H332, H373, H412; P260, P271, P273, P304+P340+P312, P314, P501
1.0 M NaOH (1310-73-2)	Liquid	Corrosive	H290; P234, P390
Buffer solution (pH = 10, $c_{HB+} + c_B = 8.8$ M)	Liquid	Prepared from NH_4Cl (12125-02-9) and NH_3 (25%, w/w, in H_2O) (1336-21-6)	H302, H314, H319, H335, H410; P261, P264, P270, P271, P273, P280, P303+P361+P353, P305+P351+P338, P310+P312, P337+P313

Eriochrome® Black T (1 wt% in NaCl)	Solid	Prepared from Eriochrome® Black T (1787-61-7) and NaCl (7647-14-5)	H319, H441; P264, P273, P280, P305+P351+P338, P337+P313, P391
Murexide (1 wt% in NaCl)	Solid	Prepared from Murexide (3051-09-0) and NaCl (7647-14-5)	Not a hazardous substance or mixture according to Regulation (EC) No 1272/2008.

Glassware and Equipment:

Item	**Count**	**Intended Use**
Volumetric flask, 500 mL	1	Distribution of **W** to students
Bottle, 200 mL	1	Distribution of EDTA standard soltution to students
Bottle, 100 mL	1	Distribution of HCl standard solution to students
Bottle, 50 mL	3	Distribution of 1.0 M HCl (1), 1.0 M NaOH (1), buffer solution (1) to students
Vial, 10 mL	3	Distribution of methyl orange solution (1), Eriochrome® Black T mixture (1), and murexide mixture (1) to students
Beaker, 50 mL	1	To check the pH value of **W** and to fill burette
pH indicator strips	10	To check the pH value of **W**, of neutralized sample in part II, and of alkalified sample in part III
Burette, 25 mL	1	For titrations

Laboratory stand with burette holder	1	For titrations
Funnel, fitting the burette	1	To fill the burette
Erlenmeyer flask, 250 mL	3	For titrations
Volumetric pipette, 25.00 mL	1	To aliquot samples
Pipette bulb	1	To aliquot samples
Plastic pipette	3	For addition of methyl orange (1), 1.0 M HCl (1), and 1.0 M NaOH (1)
Hot plate	1	For sample preparation in part II
Water bath	1	For sample preparation in part II
Thermometer	1	To monitor water bath temperature
Spatula	1	For addition of Eriochrome® Black T and Murexide
H_2O wash bottle	1	To clean glassware

Preparations:

Preparations are outlined to suffice for ~20 students.

Students' samples **W**:

1. Prepare individual stocks for $CaCl_2.2H_2O$, $MgCl_2.6H_2O$, and $NaHCO_3$ in 500 mL volumetric flasks:
    - 1800 mg $CaCl_2.2H_2O$ to 500 mL H_2O
    - 550 mg $MgCl_2.6H_2O$ to 500 mL H_2O
    - 1150 mg $NaHCO_3$ to 500 mL H_2O
2. Aliquot 25 mL of each stock solution to a student's 500 mL volumetric flask and dilute to the mark with H_2O. The corresponding solution contains $[Ca^{2+}]$ = 1.22 mM, $[Mg^{2+}]$ = 0.27 mM, and $[HCO_3^-]$ = 1.37 mM.

Methyl orange:

1. In a 100 mL volumetric flask, dissolve 1.00 g methyl orange in EtOH.
2. Distribute the solution to students' vials.

EDTA standard solution:

1. In a 1000 mL volumetric flask, dissolve 3.72 g in H_2O.
2. Distribute to the standard solution to students' bottles.

pH buffer (pH = 10, $c_{HB+} + c_B = 8.8$ M):

1. In a 1000 mL volumetric flask, add
   - 70 g NH_4Cl
   - 570 mL concentrated NH_3 (25% in H_2O)
2. Fill to the mark with H_2O.
3. Distribute to the buffer to students' bottles.

Eriochrome® Black T:

1. Grind 25 mg Eriochrome® Black T and 10 g NaCl to a fine powder.
2. Distribute to students' vials.

Murexide:

1. Grind 100 mg murexide and 10 g NaCl to a fine powder.
2. Distribute to students' vials.

0.010 M HCl solution, 1.0 M HCl solution, 1.0 M NaOH solutions are commercially available or can be prepared from simple dilution or dissolution.

Solutions (calculations based on preparations outlined above):

1. The pH value of **W** is about 8 depending on the used amount of $NaHCO_3$. Being 2 pH units below $pK_{a,2}$, it can be calculated that $[HCO_3^-]/[CO_3^{2-}] > 100$ and, therefore, the presence of CO_3^{2-} can be neglected:

   $HCO_3^- + HCl \rightarrow H_2CO_3 + Cl^-$

   or

   $HCO_3^- + HCl \rightarrow CO_2\,(aq) + H_2O + Cl^-$

2. Carbonate hardness (CH) includes all Ca^{2+} and Mg^{2+} balanced by HCO_3^- and CO_3^{2-} in solution. As established in task 1, the presence of CO_3^{2-} can be neglected:

$$([\mathrm{Ca}^{2+}] + [\mathrm{Mg}^{2+}])_{\mathrm{CH}} = \frac{1}{2} * [\mathrm{HCO}_3^-] + [\mathrm{CO}_3^{2-}] \cong \frac{1}{2} * [\mathrm{HCO}_3^-]$$

$$[\mathrm{HCO}_3^-] = \frac{V_1}{V_{sample,1}} * [\mathrm{HCl}]_{standard} = \frac{6.85\ \mathrm{mL}}{50.00\ \mathrm{mL}} * 10.0\ \mathrm{mM} = 1.37\ \mathrm{mM}$$

$$([\mathrm{Ca}^{2+}] + [\mathrm{Mg}^{2+}])_{\mathrm{CH}} = \frac{1}{2} * 1.37\ \mathrm{mM} = 0.69\ \mathrm{mM}$$

3. Total hardness (TH) can be calculated directly from the co-titration of both alkaline earth metals:

$$([\mathrm{Ca}^{2+}] + [\mathrm{Mg}^{2+}])_{\mathrm{TH}} = \frac{V_2}{V_{sample,2}} * [\mathrm{EDTA}]_{standard} = \frac{7.47\ \mathrm{mL}}{50.00\ \mathrm{mL}} * 10.0\ \mathrm{mM} = 1.49\ \mathrm{mM}$$

4. The ratio can be calculated from the titration of Ca^{2+} and the previous result:

$$[\mathrm{Ca}^{2+}] = \frac{V_3}{V_{sample,3}} * [\mathrm{EDTA}]_{standard} = \frac{6.12\ \mathrm{mL}}{50.00\ \mathrm{mL}} * 10.0\ \mathrm{mM} = 1.22\ \mathrm{mM}$$

$$\frac{[\mathrm{Ca}^{2+}]}{[\mathrm{Mg}^{2+}]} = \frac{[\mathrm{Ca}^{2+}]}{([\mathrm{Ca}^{2+}] + [\mathrm{Mg}^{2+}])_{\mathrm{TH}} - [\mathrm{Ca}^{2+}]} = \frac{1.22\ \mathrm{mM}}{1.49\ \mathrm{mM} - 1.22\ \mathrm{mM}} = 4.51$$

5. The correct answers are:
   - Addition of $Ca(OH)_2$: Lime softening, i.e. Ca^{2+} removal by $Ca^{2+} + 2\ HCO_3^- + Ca(OH)_2 \longrightarrow 2\ CaCO_3 \downarrow + 2\ H_2O$
   - Pass through ion exchange resin (NaCl-regenerated): Ca^{2+} and Mg^{2+} removal by $2\ (R\text{-}SO_3)Na + M^{2+} \longrightarrow 2\ (R\text{-}SO_3)_2M + 2\ Na^+$ using $R\text{-}SO_3^{2-}$ to abbreviated the resin
   - Boiling: Removal of carbonate hardness by HCO3⁻ auto-protonation by $M^{2+} + 2\ HCO_3^- \longrightarrow MCaCO_3 \downarrow + CO_2 \uparrow + H_2O$