2ND ABU RAYHAN BIRUNI
INTERNATIONAL
CHEMISTRY OLYMPIAD

THEORETICAL EXAM SOLUTIONS

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Physical constants and equations

In this booklet, we assume the activities of all aqueous species to be well approximated by their respective concentration in mol L^{-1}. To further simplify formulae and expressions, the standard concentration $c° = 1$ mol L^{-1} is omitted.

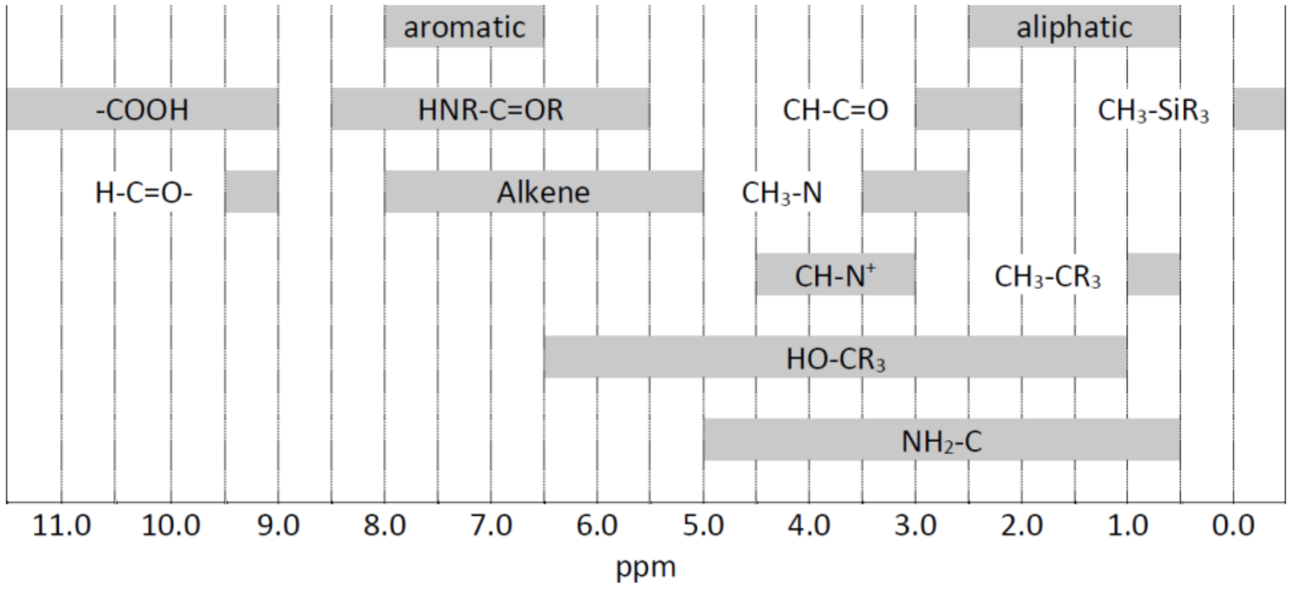
Avogadro's constant:	$N_A = 6.022 \cdot 10^{23}$ mol^{-1}
Universal gas constant:	$R = 8.314$ J mol^{-1} K^{-1}
Standard pressure:	$p° = 1$ bar $= 10^5$ Pa
Atmospheric pressure:	$P\mathrm{atm} = 1$ atm $= 1.013$ bar $= 1.013 \cdot 10^5$ Pa $= 760$ Torr
Zero of the Celsius scale:	273.15 K
Faraday constant:	$F = 9.6485 \cdot 10^4$ C mol^{-1}
Ideal gas equation:	$pV = nRT$
Gibbs free energy:	$G = H - TS$ $\Delta_r G° = -RT \ln K°$ $\Delta_r G° = -nFE_{\mathrm{cell}}°$ $\Delta_r G = \Delta_r G° + RT \ln Q$
Reaction quotient Q for a reaction a A(aq) + b B(aq) = c C(aq) + d D(aq):	$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$
Nernst–Peterson equation:	$E = E^0 - \frac{RT}{zF} lnQ$
where Q is the reaction quotient of the reduction half-reaction	at $T = 298$ K, $\frac{RT}{F} ln10 \approx 0.059$ V
Faraday's law:	$m = \frac{ItM}{Fv}$
Clausius-Clapeyron equation:	$ln\frac{P_2}{P_1} = -\frac{\Delta_{vap}H^0}{R}(\frac{1}{T_2} - \frac{1}{T_1})$
Arrhenius equation:	$k = A\, e^{-\frac{E_a}{RT}}$
Rate laws in integrated form:	
Zero order:	$[A] = [A]_0 - kt$
First order:	$\ln[A] = \ln[A]_0 - kt$
Second order:	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$
Half-life for a first order process:	$t_{1/2} = \frac{ln2}{k}$
The activity of radionuclide:	$A = kN$

Periodic table

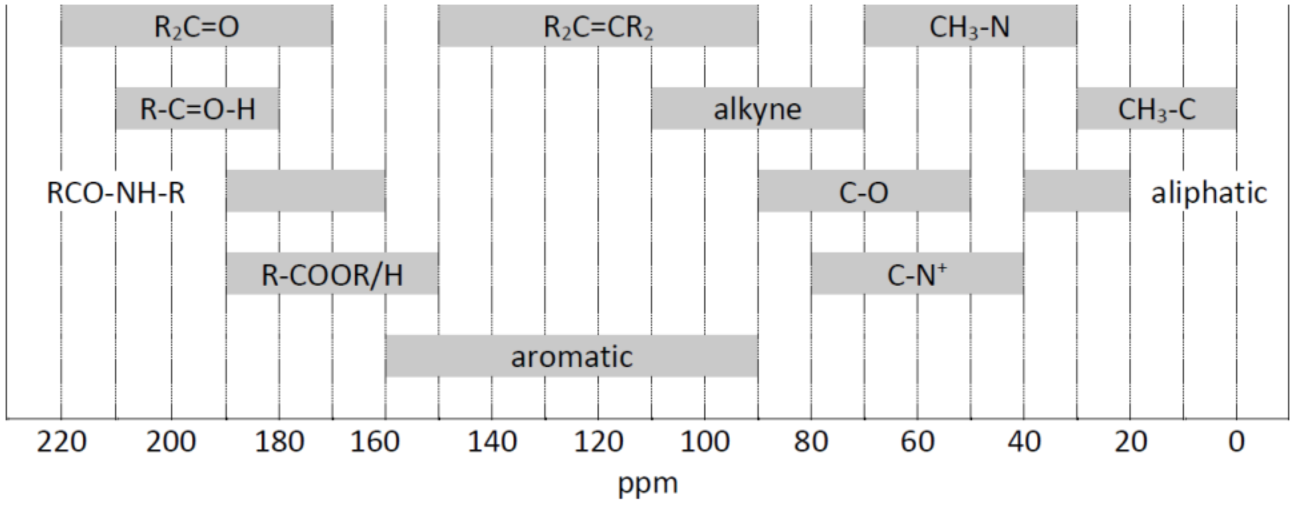
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H 1.008																	2 He 4.003
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.63	33 As 74.92	34 Se 78.97	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.95	43 Tc -	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57-71	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po -	85 At -	86 Rn -
87 Fr -	88 Ra -	89-103	104 Rf -	105 Db -	106 Sg -	107 Bh -	108 Hs -	109 Mt -	110 Ds -	111 Rg -	112 Cn -	113 Nh -	114 Fl -	115 Mc -	116 Lv -	117 Ts -	118 Og -

57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm -	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
89 Ac -	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np -	94 Pu -	95 Am -	96 Cm -	97 Bk -	98 Cf -	99 Es -	100 Fm -	101 Md -	102 No -	103 Lr -

^{1}H NMR chemical shifts



^{13}C NMR chemical shifts



Content

Problem 1. "The densest" (Azimjon Jamolov, Alexander Koronatov)

Question	1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.8	Total
Points	18	8	4	4	6	12	3	8	63
Result									

1.1. (18 pt.)

During the transition A - B, an exchange reaction most likely occurs, with the formation of water-insoluble **E**. Then **B** reacts with hydrochloric acid to give acid **C**. This reaction can also be considered an exchange reaction with the formation of a water-insoluble acid. Consider the residual mass as Y,

$$M_r(B) = n * 23 + Y$$
$$M_r(C) = n + Y$$
$$\frac{102.0845}{23n + Y} = \frac{86.8}{n + Y}$$

$$1.176Y + 1.176n = 23n + Y$$
$$0.176Y = 21.824n$$
$$Y = 123.937n \approx 124n$$

Let, $M_r(A) = a + Y$, where a is the mass of the cation. Then:

$$\frac{100}{a + 124n} = \frac{86.8}{n + 124n}$$

$$20n = a$$

Since **A** occurs naturally, the cation is most likely a metal. Substituting different values:

n	A
1	10
2	20
3	30
4	40

At n=2 a=20, which fits the calcium atom. This answer is also confirmed by the value of n, since salt **B** and acid **C** contain 2 atoms of sodium and hydrogen, respectively.

Then:

$$\boldsymbol{A} - CaY$$
$$\boldsymbol{B} - Na_2Y$$
$$\boldsymbol{C} - H_2Y$$

M(**Y**)=123.937*2=247.874 g/mol

The diagram shows that when heated, **C** turns into **D**, which is then reduced by hydrogen. Based on this, we can assume that **D** is an oxide, and **C** is an oxygen-containing acid.

Then:

$$\boldsymbol{Y} - XO_n^{2-}$$

M(**X**)= 247.874-16n

n	M	
1	231.874	-
2	215.874	-
3	199.874	-

4	183.874	W

Meaning, $\boldsymbol{A} - CaWO_4$ $\boldsymbol{B} - Na_2WO_4$ $\boldsymbol{C} - H_2WO_4$

$\boldsymbol{A} - CaWO_4$ mineral scheelite.

$\boldsymbol{B} - Na_2WO_4$

$\boldsymbol{C} - H_2WO_4$

$\boldsymbol{D} - WO_3$

$\boldsymbol{E} - CaCO_3$

X – W

For each compound: 3 points. No points given if the calculations are missing.

1.2. (8 pt.)

$CaWO_4 + Na_2CO_3 = Na_2WO_4 + CaCO_3 \downarrow$

$Na_2WO_4 + 2HCl = H_2WO_4 \downarrow + 2NaCl$

$H_2WO_4 = WO_3 + H_2O$

$WO_3 + 3H_2 = W + 3H_2O$

For each reaction equation: 2 points (1 point for the reaction and 1 point for the coefficients).

1.3. (4 pt.)

$$Z = \frac{\rho * a^3}{\frac{183.84}{N_a}} = \frac{19.3 * (0.316 * 10^{-7})^3}{\frac{183.84}{N_a}} = 2$$

A cubic unit cell having Z=2 – BCC

Unit cell type of metal **X**:

[ ] SC [x] BCC [ ] FCC

4 points. No points given if the calculations are missing.

1.4. (4 pt.)

$$r = a\frac{\sqrt{3}}{4} = 0.137\ nm$$

1.5. (6 pt.)

The spectra show that the molecule has 4 types of H atoms in a ratio of 1:1:1:1. Then the molecule has at least 4 hydrogen and 5 carbon atoms, C_5H_4, which corresponds to a mass of 64 g. 158-64=94 g/mol. Since this is a precursor for the ligand, the molecule must contain atoms capable of binding to tungsten: for example, nitrogen or oxygen.

94-16=78 – no suitable atom

94-14=80 – corresponds to bromine.

E: C_5H_4NBr

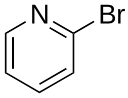
2 points for getting C_5H_4.

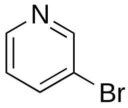
2 points for getting Bromine (Br).

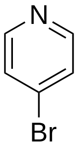
2 points for getting Nitrogen (N).

1.6. (12 pt.)

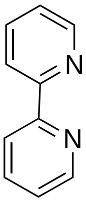
The spectra show that hydrogen atoms are aromatic. Then, there are several possible options for **E**, and only first and second will provide four different types of hydrogen atoms.

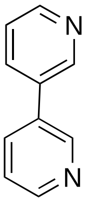


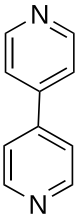




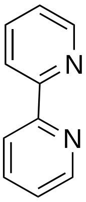
The Ullmann reaction is used to form aryl-aryl bonds.:

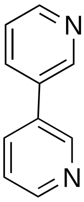




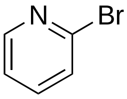
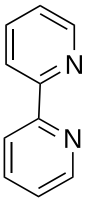


Only the hereunder two of the above structures contain 5 types of C and 4 types of H atoms.





To be a bidentate ligand, the nitrogen atoms must be closer together, so the correct answers for **E** and **F** are:

E (6 pt.)	**F** (6 pt.)
 4 points if the other option chosen.	 4 points if the other option chosen.

1.7. (3 pt.)

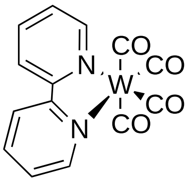
$\boldsymbol{G} - W(CO)_6$

1.8. (8 pt.)

a) $W(CO)_6 + bipy = W(bipy)(CO)_4 + 2CO$

(2 pt.) For the reaction: 1 point; For the coefficients: 1 point.

b) **H** (6 pt.)



Acknowledgements:

We thank “Enamine Ltd.” (Kyiv, Ukraine) and Dr. Dmytro Volochnyuk for providing high quality pictures of the NMR spectra presented in the task.

Problem 2. Radioisotope dating (Bekhzod Boltaev, Vadim Eremin)

Question	2.1	2.2	2.3	2.4	2.5	2.6	2.7	2.8	Total
Points	2	3	2	1	4	3	2	6	23
Result									

2.1. (2 pt.)

$^{14}C = {}^{14}N + \beta^- + \overline{\nu}_e$ or $^{14}C = {}^{14}N + \beta^-$

$^{14}N + {}^{1}n = {}^{14}C + {}^{1}p$

For each correct reaction equation: 1 point.

2.2. (3 pt.)

$\lambda = \frac{ln2}{5700} = 1.22\cdot10^{-4}$ years^{-1}

$N_t = N_0\cdot e^{-\lambda t} = N_0\cdot \exp(-1.22\cdot10^{-4}\cdot2336) = 0.752\cdot N_0$

$A = 0.752\cdot226 = 170$ Bq per kg of carbon

For calculation of λ: 1 point.

For calculation of specific activity: 2 points.

2.3. (2 pt.)

1850-1900 years ⇒ B

1900-1950 years ⇒ C (*burning of organic fossil fuels dilutes ^{14}C in the atmosphere, "Suess effect"*)

1950-2000rs ⇒ A (*nuclear tests increased ^{14}C concentration in the atmosphere*)

For correct matching 2 points. 0 point for any incorrect matching.

2.4. (1 pt.)

^{87}Rb ⇒ F

^{87}Sr ⇒ E

^{86}Sr ⇒ D

For correct matching: 1 point. 0 point for any incorrect matching.

2.5. (4 pt.)

$$\frac{N(^{87}Rb)}{N(^{86}Sr)} = \frac{N_0(^{87}Rb)}{N(^{86}Sr)}e^{-\lambda t} \qquad \text{(eq. 1)}$$

$$\frac{N(^{87}Sr)}{N(^{86}Sr)} = \frac{N_0(^{87}Sr)}{N(^{86}Sr)} + \frac{N_0(^{87}Rb)}{N(^{86}Sr)} - \frac{N(^{87}Rb)}{N(^{86}Sr)} = \frac{N_0(^{87}Sr)}{N(^{86}Sr)} + \frac{N(^{87}Rb)}{N(^{86}Sr)}(e^{\lambda t} - 1) \qquad \text{(eq. 2)}$$

$$\begin{cases} 0.780 = \frac{N_0(^{87}Sr)}{N(^{86}Sr)} + 18.5(e^{\lambda t} - 1) \\ 0.716 = \frac{N_0(^{87}Sr)}{N(^{86}Sr)} + 2.0(e^{\lambda t} - 1) \end{cases} \qquad (eq.\ 3)$$

$\lambda = \frac{ln2}{48.81 \cdot 10^9} = 1.42 \cdot 10^{-11}$ years^{-1}

t = $273 \cdot 10^6$ years.

For each equation (1, 2, and 3): 1 point.

For the correct value of the gold deposit's age: 1 point.

2.6. (3 pt.)

From "equation 3" in question 5 we obtain:

$$\frac{N_0(^{87}Sr)}{N(^{86}Sr)} = 0.780 - 18.5(e^{\lambda t} - 1) \ or \ \frac{N_0(^{87}Sr)}{N(^{86}Sr)} = 0.716 - 2.0(e^{\lambda t} - 1)$$

$$\frac{N_0(^{87}Sr)}{N(^{86}Sr)} = 0.708 \ (\textit{same for samples 1 and 2})$$

From "equation 1" in question 5 we obtain:

$$\frac{N_0(^{87}Rb)}{N(^{86}Sr)} = \frac{N(^{87}Rb)}{N(^{86}Sr)} e^{\lambda t}$$

$$\frac{N_0(^{87}Rb)}{N(^{86}Sr)} = 18.5e^{\lambda t} = 18.57 \ (\textit{for sample 1})$$

$$\frac{N_0(^{87}Rb)}{N(^{86}Sr)} = 2.0e^{\lambda t} = 2.008 \ (\textit{for sample 2})$$

$\frac{N_0(^{87}Sr)}{N(^{86}Sr)}$ = _0.708_ (*for samples 1 and 2*)

$\frac{N_0(^{87}Rb)}{N(^{86}Sr)}$ = _18.57_ (*for sample 1*)

$\frac{N_0(^{87}Rb)}{N(^{86}Sr)}$ = _2.008_ (*for sample 2*)

For each correct value: 1 point.

2.7. (2 pt.)

$^{235}U \Rightarrow$ _^{207}Pb_ ($A_r = 4n + 3$, *where "n" positive integer*)

$^{238}U \Rightarrow$ _^{206}Pb_ ($A_r = 4n + 2$, *where "n" positive integer*)

For correct matching: 2 points. 0 point for any incorrect matching.

2.8. (6 pt.)

$$\frac{N(^{206}Pb)}{N(^{204}Pb)} = \frac{N_0(^{206}Pb)}{N(^{204}Pb)} + \frac{N_0(^{238}U)}{N(^{204}Pb)} - \frac{N(^{238}U)}{N(^{204}Pb)} = \frac{N_0(^{206}Pb)}{N(^{204}Pb)} + \frac{N(^{238}U)}{N(^{204}Pb)}(e^{\lambda_{238} t} - 1) \qquad (eq.\ 4)$$

$$\frac{N(^{207}Pb)}{N(^{204}Pb)} = \frac{N_0(^{207}Pb)}{N(^{204}Pb)} + \frac{N_0(^{235}U)}{N(^{204}Pb)} - \frac{N(^{235}U)}{N(^{204}Pb)} = \frac{N_0(^{207}Pb)}{N(^{204}Pb)} + \frac{N(^{235}U)}{N(^{204}Pb)}(e^{\lambda_{235}t} - 1) \qquad (eq.\ 5)$$

$$\frac{\frac{N(^{206}Pb)}{N(^{204}Pb)} - \frac{N_0(^{206}Pb)}{N(^{204}Pb)}}{\frac{N(^{207}Pb)}{N(^{204}Pb)} - \frac{N_0(^{207}Pb)}{N(^{204}Pb)}} = \frac{N(^{238}U)(e^{\lambda_{238}t}-1)}{N(^{235}U)(e^{\lambda_{235}t}-1)} = 137.88\frac{(e^{\lambda_{238}t}-1)}{(e^{\lambda_{235}t}-1)} \qquad (eq.\ 6)$$

$$\frac{N(^{206}Pb)}{N(^{204}Pb)} = 137.88\frac{(e^{\lambda_{238}t}-1)}{(e^{\lambda_{235}t}-1)}\frac{N(^{207}Pb)}{N(^{204}Pb)} - 137.88\frac{(e^{\lambda_{238}t}-1)}{(e^{\lambda_{235}t}-1)}\frac{N_0(^{207}Pb)}{N(^{204}Pb)} + \frac{N_0(^{206}Pb)}{N(^{204}Pb)}$$

$\frac{N_0(^{207}Pb)}{N(^{204}Pb)}$ *and* $\frac{N_0(^{206}Pb)}{N(^{204}Pb)}$ *are constants, so we obtain a linear dependence:*

$$\frac{N(^{206}Pb)}{N(^{204}Pb)} = 137.88\frac{(e^{\lambda_{238}t}-1)}{(e^{\lambda_{235}t}-1)}\frac{N(^{207}Pb)}{N(^{204}Pb)} + const \qquad (eq.\ 7)$$

$$\begin{cases} 50.28 = 137.88\frac{(e^{\lambda_{238}t}-1)}{(e^{\lambda_{235}t}-1)}34.86 + const \\ 9.46 = 137.88\frac{(e^{\lambda_{238}t}-1)}{(e^{\lambda_{235}t}-1)}10.34 + const \end{cases}$$

$$\frac{(e^{\lambda_{238}t}-1)}{(e^{\lambda_{235}t}-1)} = \frac{50.28-9.46}{137.88(34.86-10.34)} = 0.01207 \qquad (eq.\ 8)$$

$\lambda_{238} = \frac{ln2}{4.47\cdot 10^9} = 1.55\cdot 10^{-10}$ years^{-1}

$\lambda_{235} = \frac{ln2}{0.704\cdot 10^9} = 9.85\cdot 10^{-10}$ years^{-1}

$t = 4.5\cdot 10^9$ years, variant d.

For each equation (4, 5, 6, 7 and 8): 1 point.

For correct choice: 1 point.

For correct choice without calculations: 0 point.

Problem 3. Natural source of "brown carbon" (Khamidulla Tukhtaev, Yunus Turmen)

Question	3.1	3.2	3.3	3.4	3.5	3.6	3.7	3.8	3.9	Total
Points	5	6	12	2	6	6	6	6	23	72
Result										

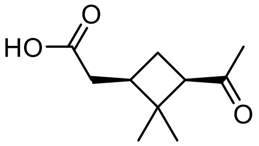
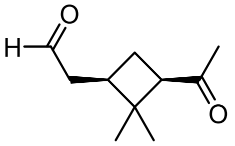
3.1. (5 pt.)

Overall: $2SO_2 + O_2 + 2H_2O \rightarrow 2H_2SO_4$ (1 pt.)

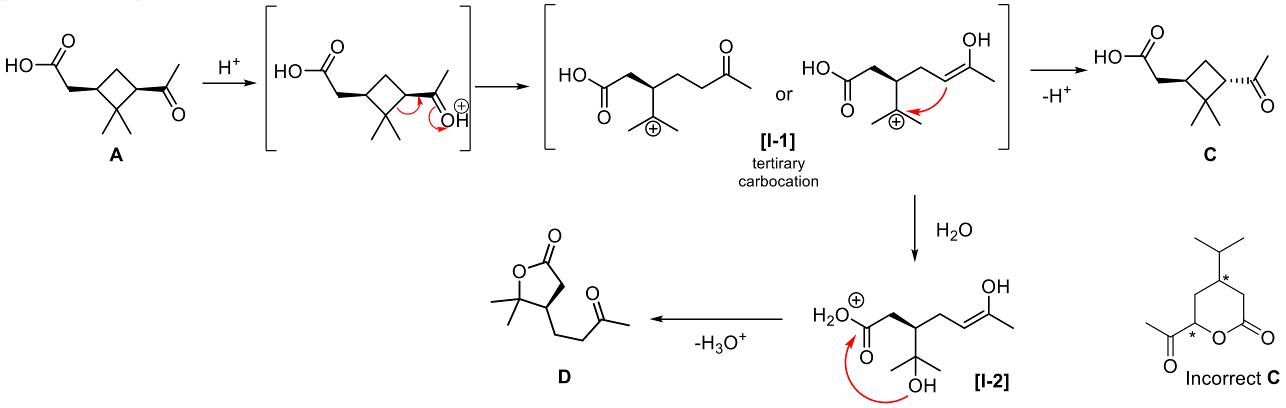
a) $SO_2 + {\bullet}OH \rightarrow HSO_3{\bullet}$ (1 pt.)
b) $HSO_3{\bullet} + O_2 \rightarrow SO_3 + HO_2{\bullet}$ (1 pt.)
c) $HO_2{\bullet} + SO_2 \rightarrow SO_3 + {\bullet}OH$ (1 pt.)
d) $SO_3 + H_2O \rightarrow H_2SO_4$ (1 pt.)

(1 point for each reasonable reaction at the given conditions)

3.2. (6 pt.) There is no information in the task whether it was oxidative or reductive ozonolysis. Therefore, we can assume both of them. Additionally, the mass difference is 16, which corresponds to one additional oxygen. (3 points for each structure, 2 point for a structure without correct configuration)

A (3 pt)	**B** (3 pt)
 **A** *cis*-pinonic acid $C_{10}H_{16}O_3$, MW 184.11	 **B** *cis*-pinonaldehyde $C_{10}H_{16}O_2$, MW 168.12

3.3. (12 pt.) **I-1** is a tertiary carbocation. Thus, it should be formed by decoupling C-C bond connected to quaternary carbon in cyclobutane fragment. Correct C-CH bond to break can be determined according to structure of **D**. The compound **C** has the same Mw as **A** and two stereogenic centers, which refers to **A**'s isomer – trans-pinonic acid. This isomer also can be formed due to cationic isomerization. (4 points for each structure, 2 point for a structure without correct configuration, 2 points for given incorrect structure of **C**)



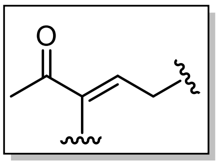
3.4. (2 pt.)

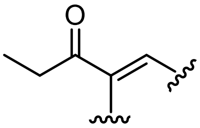
According to M_w, molecular formula is $C_{10}H_{14}O$.

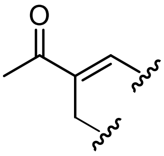
The degree of unsaturation $= \frac{(10*2+2)-14}{2} = 4$.

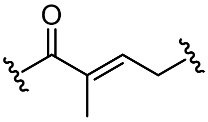
3.5. (6 pt.) Let us consider 3 carbon signals 140.9, 146.3, 197.1. The two former signals correspond to a double bond, whereas the latter one to the carbonyl atom of a ketone group. Signal 7.16 ppm belongs to an H at a double bond, and the other two to aliphatic groups. From possible structures, only one matches the given data, because signal 2.33 ppm neighboring with 197.1 and 146.3 belongs to CH_3 group. (2 point for the incorrect structure, which matches with 1D NMR data)

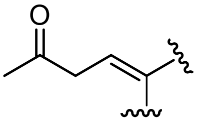
Fragment 1





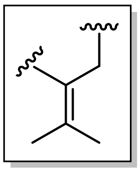


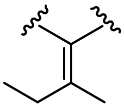


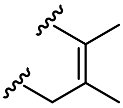


3.6. (6 pt.) The 2nd fragment contains three aliphatic groups (CH_2, CH_3, CH_3) and two sp^2 hybridized carbons which correspond to fully substituted double bond. Taking into account the structure of α-pinene and the fact that there are no neighboring signals between the signals of CH_2 and CH_3 group in addition with neighboring signals for all aliphatic groups at signal 133.1 ppm, the hereunder structure can be suggested. (2 point for the incorrect structure, which matches with 1D NMR data)

Fragment 2

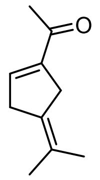




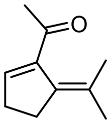


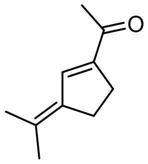
3.7. (6 pt.) Taking into account that the degree of unsaturation is 4 and that there are only 3 double bonds in the fragments 1 and 2, one can conclude that the fragments are connected forming a cycle. The fact that the signal at 2.63 ppm for 133.1 ppm carbon signal and 2.53 ppm for 146.3 ppm carbon signal are neighbors suggests the correct structure of **E**. (3 points for wrong assembly of correct fragments 1 and 2; 3 points for the logical assembly of incorrect fragments 1 and 2; 1 point for the any assembly of the fragments which do not correspond any given data)

E



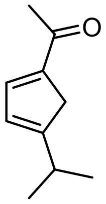
Compound **E**



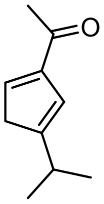


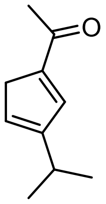
3.8. (6 pt.) **G** has the same structure skeleton but differs in the position of double bond(s) (according to hydrogenation data). 1.14 (d, 6H) and 2.72 (m, 1H) signals correspond to isopropyl group, while 7.24 (d, 1H), 6.21 (d, 1H) signals for vicinal H signals at double bonds. From three possible structures, only one matches the above data. (6 points if structure G is similar to drawn by student E and matches with NMR data, 2 points for given 2 incorrect structures)

G



Compound **G**



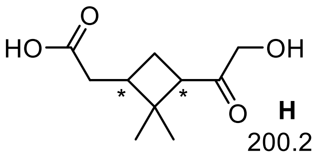
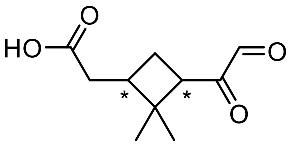
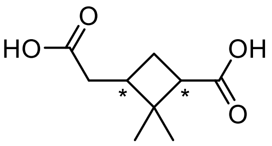


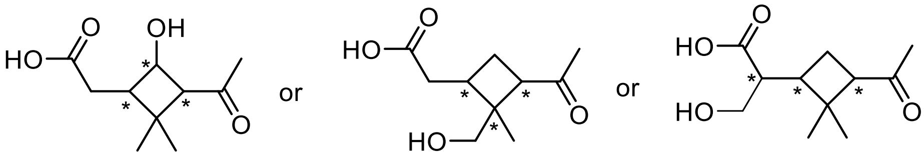
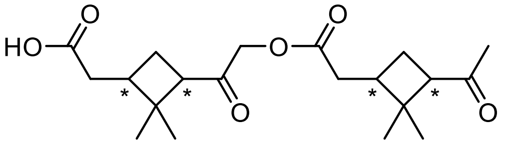
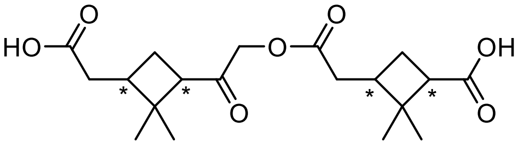
3.9. (23 pt.) From **A** to **J**, M_w increases by 16, then decreases by 2 in **I**, then by 12 in **J.** Thus, this process includes insertion of oxygen, dehydrogenation/oxidation and fragmentation by losing one carbon atom. This may happen only with -COCH$_3$- or -CH$_2$COOH groups. Oxidation of a -CH$_2$COOH group will lead to a symmetric dicarboxylic acid, which is not chiral. Thus, transformations occur with a -COCH$_3$ group.

There are 2 prochiral atoms in **A**. Thus, 2 structures are possible for **K**.

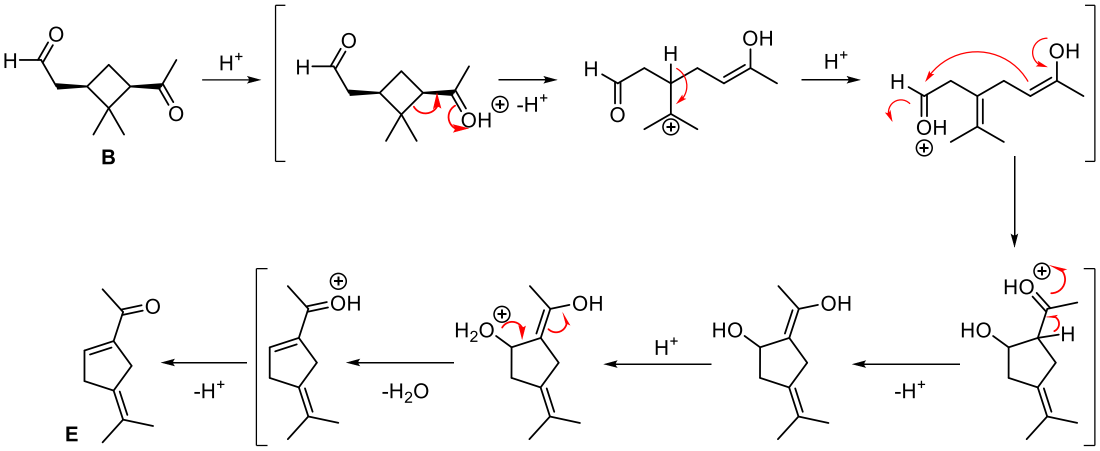
L and **M** are esters that contain 4 chiral atoms – 2 for each fragment (acid and alcohol). Therefore alcohol part can be only **H**. M_W of acid fragments are: 366.45 - 200.23 + 18 = 184.22 (matches **A**) and 368.43 - 200.23 + 18 = 186.20 (matches **J**)

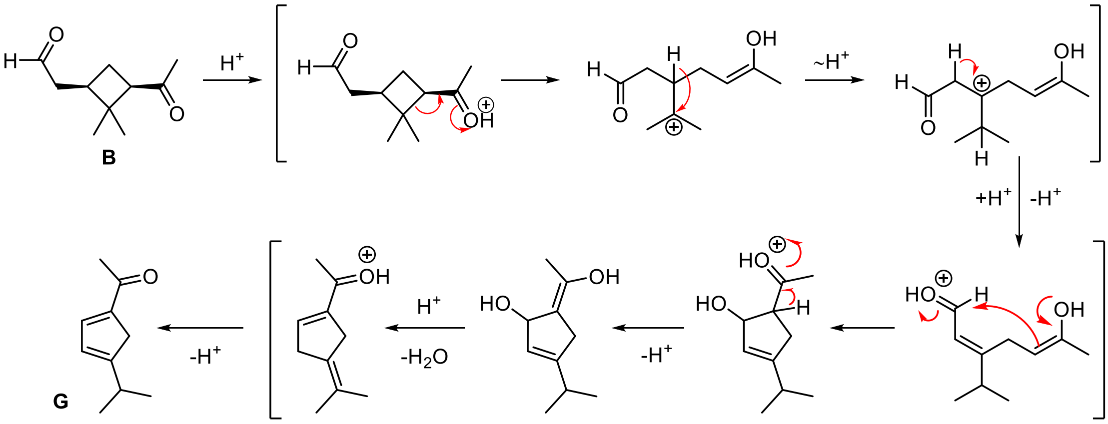
(3 points for H and I if structure matches with given data (Mw and stereochemistry and the transformation sequence)

H (3 pt.)	**I** (3 pt.)	**J** (3 pt.)
 **H** 200.23	 **I** 198.22	 **J** 186.21
K (each 3 pt.)		

<table>
<tr><td colspan="2">
K
200.23</td></tr>
<tr><td>L (4 pt.)

L
366.45</td><td>M (4 pt.)

M
368.43</td></tr>
</table>

Suggested formation mechanisms of **E** and **G**





Problem 4. The Many Faces of Arsenic: A Redox Journey (Bobur Boltaev, Andrei Shved)

Question	4.1	4.2	4.3	4.4	4.5	4.6	4.7	4.8	4.9	Total
Points	2	2	4	2	1	2	1	3	6	23
Result										

4.1. (2 pt.)

a) $H_3AsO_4 + 5e^- + 5H^+ = As + 4H_2O$

b) $H_3AsO_4 + 8e^- + 8H^+ = AsH_3 + 4H_2O$

1 point for each balanced reduction half-reaction.

0.5 points if the reaction is written as the oxidation half-reaction.

0 point if the half-reaction is not balanced.

4.2. (2 pt.)

$$E_1^o = \frac{2 \cdot 0.560 + 3 \cdot 240}{2 + 3} = 0.368 \text{ V}$$

$$E_2^o = \frac{5 \cdot 0.368 + 3 \cdot (-0.225)}{8} = 0.146 \text{ V}$$

$E°_1 = 0.368$ V

$E°_2 = 0.146$ V

1 point for each value. -0.5 points for miscalculations.

4.3. (4 pt.)

a) $2As + 3H_3AsO_4 + 3H_2O = 5H_3AsO_3$ (reaction 1)

$\Delta E°_1 = 0.560 – 0.240 = 0.320 \text{ V} \Rightarrow \Delta G°_1 < 0$ or

$-RT\ln K_1 = -6F(0.560 - 0.240) \Rightarrow K_1 = 2.97 \cdot 10^{32}$

Therefore, H_3AsO_4/As pair comproportionation reaction is spontaneous.

☑ Y

☐ N

b) $AsH_3 + H_3AsO_3 = 2As + 3H_2O$ (reaction 2)

$\Delta E°_2 = 0.240 – (–0.225) = 0.465 \text{ V} \Rightarrow \Delta G°_1 < 0$ or

$-RT\ln K_2 = -3F(0.240 - (-0.225)) \Rightarrow K_1 = 3.92 \cdot 10^{23}$

Therefore, H_3AsO_3/AsH_3 pair comproportionation reaction is spontaneous.

☑ Y

☐ N

1 point for each balanced reaction equation.
-0.5 points if the reaction equation is not balanced.
1 point for each correct decision with corresponding calculations.
-0.5 points if there is no tick for each.
0 points if the decision is correct, but no calculations are shown.

4.4. (2 pt.)

$As + 3H^+ + 3e^- = AsH_3$

$$E_{As/AsH_3} = -0.225 + \frac{0.059}{3}\lg[H^+]^3 = -0.225 - 0.059\cdot pH$$

$pH = 14 \Rightarrow E = -0.225 - 0.059\cdot 14 = -1.051$ V
(This value can be obtained from the Pourbaix diagram as well)

$E_{As/AsH_3}(pH = 14) = -1.051$ V

1 point for the dependence of E_{As/AsH_3} on pH.
1 point for the value of E_{As/AsH_3} at pH = 14.

4.5. (1 pt.)

From the graph it is visible that:
$[H_3AsO_3] = [H_2AsO_3^-] \Rightarrow K_a = [H^+] \Rightarrow pK_a \approx 9.2$.

$pK_a(H_3AsO_3) = 9.2$

1 point for the correct value.

4.6. (2 pt.)

$H_3AsO_4 + 2H^+ + 2e^- \rightarrow H_3AsO_3 + H_2O$

$$E = 0.560 + \frac{0.059}{2}\lg[H^+]^2 = 0.560 - 0.059\cdot pH \geq 0.536$$

The pH value(s) at which an H_3AsO_4 solution can oxidize I^-:

$pH \leq 0.41$

1 point for the value of 0.41.
1 point for the indication of the range below or equal to 0.41.

4.7. (1 pt.)

Based on the Pourbaix diagram, AsH_3 should be the most stable in a highly acidic environment with an electrode potential value of −0.76 V. Therefore, it is the arsenic-containing compound formed during the Marsh test:

Y: AsH_3

1 point for the compound.
No points if Y is given as a mixture.

4.8. (3 pt.)

X: As

a) $H_3AsO_3 + 3Zn + 6H^+ \rightarrow AsH_3 + 3Zn^{2+} + 3H_2O$ or
$H_3AsO_3 + 3Zn + 3H_2SO_4 \rightarrow AsH_3 + 3ZnSO_4 + 3H_2O$

b) $2AsH_3 \rightarrow 2As + 3H_2$

1 point for identifying **X**.
1 point per balanced reaction equation.

4.9. (6 pt.)

a) $8Cu(OH)_2 + AsH_3 + 3OH^- \rightarrow 4Cu_2O + AsO_4^{3-} + 11H_2O$

b) From the Pourbaix diagram we obtain: $pK_{a1} = 2.2$, $pK_{a2} = 6.8$, $pK_{a3} = 11.6$.

$$\begin{aligned}
&H_3AsO_4 + 8e^- + 8H^+ \rightarrow AsH_3 + 4H_2O && \Delta G^\circ_1 = -8F\cdot(0.146)\\
&H_3AsO_4 \rightleftharpoons H^+ + H_2AsO_4^- && \Delta G^\circ_2 = -RT\ln K_{a1}\\
&H_2AsO_4^- \rightleftharpoons H^+ + HAsO_4^{2-} && \Delta G^\circ_3 = -RT\ln K_{a2}\\
&HAsO_4^{2-} \rightleftharpoons H^+ + AsO_4^{3-} && \Delta G^\circ_4 = -RT\ln K_{a3}\\
&H_2O \rightleftharpoons H^+ + OH^- && \Delta G^\circ_5 = -RT\ln K_w\\
&AsO_4^{3-} + 8e^- + 7H_2O \rightarrow AsH_3 + 11OH^- && \Delta G^\circ_6 = \Delta G^\circ_1 - (\Delta G^\circ_2 + \Delta G^\circ_3 + \Delta G^\circ_4) + 11\,\Delta G^\circ_5
\end{aligned}$$

$\Delta G^\circ_6 = 648\ 328.7$ J/mol
$E^\circ_6 = -0.840$ V

Alternative solution:
From the Pourbaix diagram, one can construct a Latimer diagram at pH = 14:

$$\begin{tikzcd}
AsO_4^{3-} \arrow[r, "-0.72\ V"] \arrow[rrr, bend left, "E^\circ(AsO_4^{3-}/AsH_3)"] & H_2AsO_3^- \arrow[r, "-0.76\ V"] & As \arrow[r, "-1.0\ V"] & AsH_3
\end{tikzcd}$$

$$E^\circ(AsO_4^{3-}/AsH_3) = \frac{2\cdot(-0.72) + 3\cdot(-0.76) + 3\cdot(-1.0)}{2+3+3} = -0.84\ V$$

$$\begin{aligned}
&Cu^{2+} + e^- \rightarrow Cu^+ && \Delta G^\circ_7 = -1F\cdot(0.153)
\end{aligned}$$

$Cu(OH)_2 \rightleftharpoons Cu^{2+} + 2OH^-$ $\Delta G°_8 = -RT\ln(4.8\cdot10^{-20})$
$Cu_2O + H_2O \rightleftharpoons 2Cu^+ + 2OH^-$ $\Delta G°_9 = -RT\ln(4.0\cdot10^{-30})$
$2Cu(OH)_2 + 2e^- \rightarrow Cu_2O + 2OH^- + H_2O$ $\Delta G°_{10} = 2\Delta G°_7 + 2\Delta G°_8 - \Delta G°_9$

$\Delta G°_{10} = 23\ 185.6$ J/mol
$E°_{10} = -0.120$ V

For the overall reaction: $\Delta E° = E°_{10} - E°_6 = -0.120 - (-0.840) = 0.720$ V

$$K = \exp\left(\frac{8\cdot F\cdot 0.720}{RT}\right) = 2.6\cdot10^{97}$$

$K = 2.6\cdot10^{97}$

1 point for the balanced ionic equation for the reverse Marsh reaction.
2 points for each value of $\Delta G°_6$ or $E°_6$ and $\Delta G°_{10}$ or $E°_{10}$.
1 point for the value of K.

Problem 5. Water and the Aral Sea (Azimjon Jamolov, Vadim Eremin)

Question	5.1	5.2	5.3	5.4	5.5	5.6	5.7	5.8	5.9	Total
Points	6	4	3	2	4	4	6	2	2	33
Result										

5.1. (6 pt.)

a) (4 pt.)

$$H_2O(l) \rightleftarrows H_2O(g)$$

$\Delta H°_r = -241.8 - (-285.8) = 44.00\ kJ\ mol^{-1}$ (1 pt.)

$\Delta S° = 188.8 - 69.95 = 118.8\ J\ mol^{-1}\ K^{-1}$ (1 pt.)

$K_p = p_{H_2O}$ (bar)

$$\Delta G° = \Delta H°_r - T\Delta S = -RTln(K_p) = -RTln(p_{H_2O})$$

$$\ln(p_{H_2O}) = -\frac{\Delta H°_r}{RT} - (-\frac{T\Delta S}{RT})$$

$$\ln(p_{H_2O}) = -\frac{\Delta H°_r}{RT} + \frac{\Delta S}{R} == -\frac{\Delta H°_r}{R} \times \frac{1}{T} + \frac{\Delta S}{R}$$

$$\ln(p_{H_2O}) = -\frac{44.00 * 10^3}{8.314} \times \frac{1}{T} + \frac{118.8}{8.314}$$

$$\ln(p_{H_2O}) = -5292 \times \frac{1}{T} + 14.29$$

$$\ln(1) = -5292 \times \frac{1}{T} + 14.29$$

$T = \frac{5292}{14.29} = 370\ K$ (2 pt.)

b) $p = e^{-5292\times\frac{1}{298}+14.29} = 0.0312\ bar = 23.4\ Torr$ (2 pt.)

5.2. (4 pt.)

For adiabatic process: $q = 0$

$pV^{\gamma} = \text{const}$;

From ideal gas law: $PV = nRT$, $V = \frac{nRT}{P}$

$$P\left(\frac{RT}{P}\right)^{\gamma} = const \Rightarrow P^{1-\gamma} * T^{\gamma} = const$$

$$\left(\frac{P_1}{P_2}\right)^{1-\frac{C_p}{C_v}} = \left(\frac{T_2}{T_1}\right)^{\frac{C_p}{C_v}}$$

$$\left(\frac{0.802}{0.602}\right)^{1-\frac{28.86}{28.86-8.314}} = \left(\frac{T_2}{288}\right)^{\frac{28.86}{28.86-8.314}}$$

$$\Rightarrow T_2 = 265.16\,K \ \approx 265\,K$$

Calculation of γ – 1 pt

Derivation of correct relation from pV^{γ} = const – 2 pts

Calculation of T_2 – 1 pt

5.3. (3 pt.)

$\gamma(T, RH) = 0.3217$; $T_d = 4.52$ °C , if $T_0 = 14.85$°C

$\gamma(T, RH) = 0.3314$; $T_d = 4.66\,°C$, if $T_0 = 15$°C

Clouds will not form (1 pt.)

$\gamma(T, RH) =$ __0.3217 ______ (1 pt.)

$T_d =$ __4.52 °C_______ $°C$ (1 pt.)

5.4. (2 pt.)

Yes, clouds will form, as $T < T_d$. It will snow as T < 0$°C$ (1 pt.)

It will snow. (1 pt.)

If T_d and T at 3500 m are not found, no points given for the question.

If T_d and T are wrong, but the chosen answer is correct based on their values,1pt. for each question. If “No” option is chosen, no point is given for question **5.4b**

5.5. (4 pt.)

$$\underset{-10°C}{H_2O_{(s)}} \longrightarrow \underset{+3°C}{H_2O_{(l)}} \longrightarrow \underset{-5°C}{H_2O_{(l)}} \longrightarrow \underset{-5°C}{H_2O_{(s)}}$$

-1 point deduction if phase/temperature indicated incorrectly

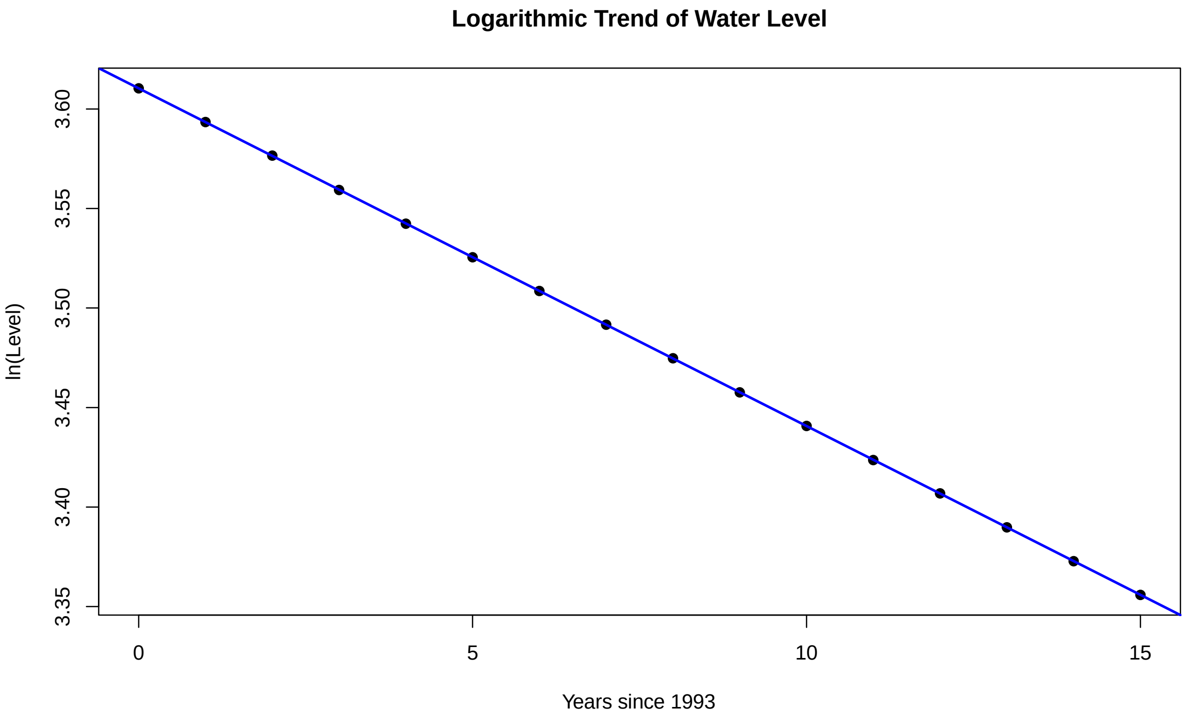
5.6. (4 pt.)

1 → 4: $H_2O_s\ (263.15\ K) \rightarrow H_2O_s(268.15K)$ (2 pt.)

$\Delta S = nC_p \ln\left(\frac{T_2}{T_1}\right) = 1 * 37.94 * \ln\left(\frac{-5+273.15}{-10+273.15}\right) = 0.714\,J$ (2 pt.)

Alternative way of calculation: overall change in entropy may be derived by calculating change in entropy for each step from the scheme. 1 pt. for each step and 1 pt. for the total entropy change.

5.7. (6 pt.)



4 points for the correct graph

$$\ln(level) = \ln(level_0) - kt$$

$$\ln(level) = 3.61 - 0.017 * t$$

$k = 0.017\ year^{-1}$ (2 pt.)

5.8. (2 pt.)

$$ln36.98 = lnl_{1960} - 0.017 * 33$$

$$l_{1960} = 64.8\ m$$

5.9. (2 pt.)

$$ln2 = ln36.98 - 0.017 * t$$

t= 171.6 approx. 172 years. It will dry out in year 2165.

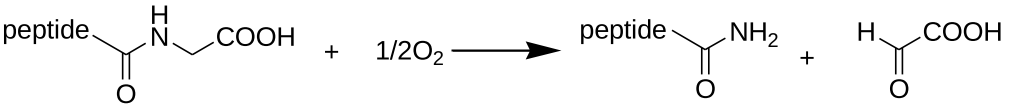
Problem 6. Functional peptides (Azizbek Nazarov, Bulat Garifullin)

Question	6.1	6.2	6.3	6.4	6.5	6.6	6.7	6.8	Total
Points	1.5	0.5	5	3	4	0.5	1.5	2	18
Result									

6.1. (1.5 pt.)

Note that for peptides **D** and **E**, the number of amide bonds exceeds expectations. Indeed, linear tetrapeptides should contain three amide bonds. It is possible to hypothesize that these compounds are cyclic peptides, but it remains unclear how a cyclic tetrapeptide formed from neutral amino acids (lacking additional amino or carboxyl groups) could originate from a pentapeptide. For a cyclic peptide, the number of NH and CO groups must be equal. However, during the biosynthesis of **D**, one CO group is lost (see the second reaction product), while the NH group formally remains intact.

Thus, **D** is a linear tetrapeptide with an amidated carboxylic group. Based on the product structures, oxidation targets the glycine (Gly) residue at the C-terminus of **D1**:



0.5 points for glycine, 0.5 points for the possibility of identifying the position, 0.5 points for the correct position. If Gly is not found in 6.1a 6.1b task will not be graded.

6.2. (0.5 pt.)

$NH_2\text{-}CH(R_1)\text{-}C(O)\text{-}NH\text{-}CH(R_2)\text{-}C(O)\text{-}NH\text{-}CH(R_3)\text{-}C(O)\text{-}NH\text{-}CH(R_4)\text{-}CONH_2$

6.3. (5 pt.)

a) (3 pt.) There are no chemical clues for identifying the sulfur-containing peptide. Thus, we must be based solely on the data provided in the table.

The molar masses of the peptides are given to two decimal places, and their hundredths are close, ranging from 0.62 to 0.71. To achieve such precision, the following atomic masses (g/mol) must be used in calculations: C – 12.01, N – 14.01, H – 1.008, O – 16.00. Considering the ratio of these elements in canonical amino acids, incorporating each average atom into the molecule will add approximately 0.0085 thousandths to the molar mass of the peptide. Verification of the assumption comes if the hundredths of the molecular masses are divided by the number of atoms in the peptides:

peptide	**A**	**B**	**C**	**D**	**E**
ratio	0.0081	0.0089	0.0083	0.0085	0.0085

B significantly differs in the value from the others, clearly indicating the presence of a sulfur atom (Ar = 32.**07**). Moreover, it resembles **A** structurally, and if the contribution of the sulfur atom (0.07) is subtracted from its molar mass, the remaining ratio for the 76 atoms matches that of **A**.

3 points if work shown

b) (1 pt.) Based on the calculations above, pentapeptide **B** can contain only one residue of a sulfur-containing amino acid. If 6.3a task is not solved the answer will not be graded.

c) There are two sulfur-containing canonical amino acids (Cys and Met), so we cannot even partially determine the amino acid composition of **B**. Thus, additional considerations are needed. Note that the **D**, composed of four different amino acids, has an anomalously large molar mass. The average molar mass of the amino acids in it is 166.4 g/mol [(610.7 + 3·18 + 1)/4]. Only two amino acids have a larger molar mass than this value: tyrosine and tryptophan, and at least one of them must be part of **D** for arithmetic reasons.

Suppose **D** contains tyrosine but not tryptophan: the average molar mass of the remaining three amino acids would then be 161.5 g/mol. Only phenylalanine has a larger molar mass than this value. Another iteration brings us to the average molar mass of the two remaining amino acids: 159.7 g/mol. The molar masses of all remaining amino acids are less than this value, which is a contradiction. Therefore, **D** contains a tryptophan residue.

1 point if work shown

6.4. (3 pt.)

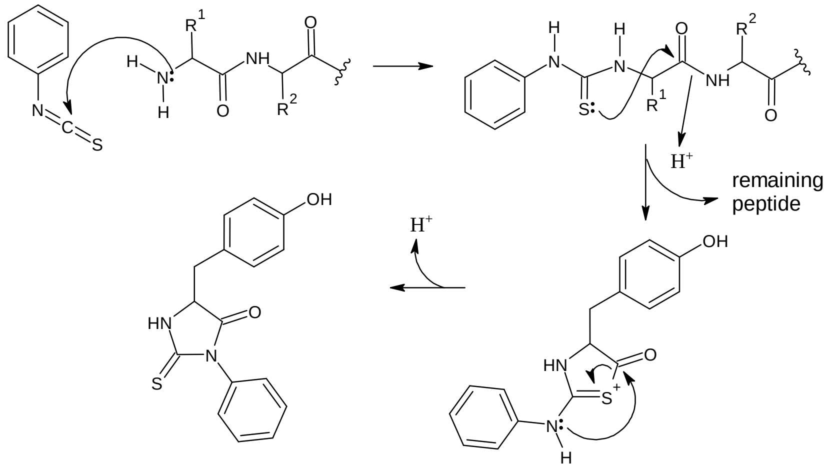
Further analysis of the structure of **D** using the average masses is sum up in the table:

Derivative of **D**	$\sum M_r$(amino acids)	M_{avg}(amino acids)	Possible amino acids
tetrapeptide	665.7	166.4	Trp
tripeptide	461.5	153.8	**Phe**, Tyr
dipeptide	296.3	148.2	**Tyr,** Met
The 4th amino acid	115.1	115.1	Pro

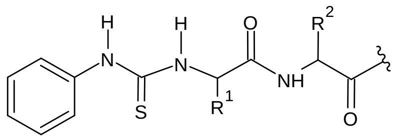
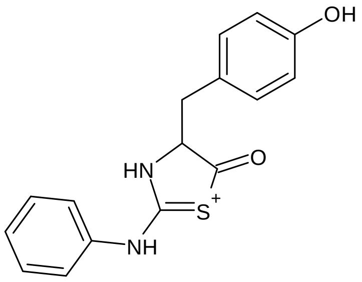
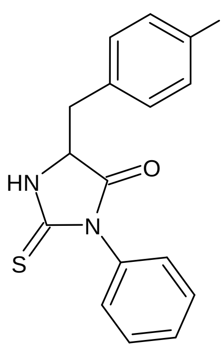
Bold indicates the amino acids selected at the branching point, with no need for exhaustive enumeration: in the case of the tripeptide, selecting either Phe or Tyr ultimately leads to the same answer; for the dipeptide, Met is excluded due to the absence of sulfur in **D**. The amino acid composition of **D** is: $Trp_1Phe_1Tyr_1Pro_1$. 0.75 pts for each correct aminoacid

6.5. (4 pt.)

The mechanism of the process is:

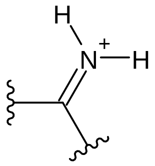


1 point for **X**, 1.5 point for each of **Y** and **Z**.

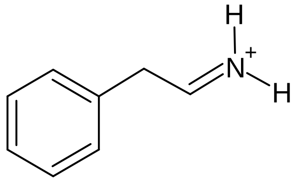
X	Y	Z
		

6.6. (0.5 pt.)
Looking at the results of TLC, the Rf value of the yellow spot is the same as that of glycine. This shows that the peptide has N-terminal Gly

6.7. (1.5 pt.)
The formula of the immonium ion is:



Possible options of the emitted gas include ammonia, carbon dioxide, and hydrogen disulfide. By calculation, the molar mass corresponds only to the derivative of phenylalanine:



6.8. (2 pt.)
N-Tyr-Gly-…-Met-C and Phe between Gly and Met.
The remaining molar mass: since 574.2 is the protonated mass => Mr=574.2-1=573.2

573.2-Mr(Tyr)-Mr(Gly)-Mr(Met)-Mr(Phe)+4x18=Mr(Gly)

There should be the bond between two identical amino acids => Gly-Gly
Amino acid sequence in the tetrapeptide(**Q** fragment) is:

N-Tyr-Gly-Gly-Phe-C

0.5 points for each correct amino acid position.

Problem 7. Legends about X (Islomjon Karimov, Maftuna Badalova, Andrei Shved)

Question	7.1	7.2	7.3	7.4	7.5	7.6	Total
Points	14	5	4	17	8	12	60
Result							

7.1. (14 pt.)

Since different amounts of hydrogen gas are produced from the same mass of **X** allotropes, we can assume that **X** forms two stable chlorides.

$$pV = nRT$$

$$101.325 \cdot 0.1887 = n \cdot 8.314 \cdot 273.15$$

Solving for n:

n = 0.00842 mol

General equation:

$$\mathbf{X} + x\mathrm{HCl} \rightarrow \mathbf{X}\mathrm{Cl_x} + \frac{x}{2}\mathrm{H_2}$$

$$A_r(\mathbf{X}) = \frac{1.00}{0.00842} \cdot \frac{x}{2} = 59.4x$$

If **X** has the oxidation state $x = +1$, then $A_r(\mathbf{X}) = 59.4$. No matches.

If **X** has the oxidation state $x = +2$, then $A_r(\mathbf{X}) = 118.8$. This corresponds to Sn.

Other oxidation states do not provide reasonable solutions.

X – Sn

For the second allotrope, the amount of hydrogen is twice as much. Therefore, two allotropes are α-Sn and β-Sn, forming $SnCl_2$ (or $H[SnCl_3]$, $H_2[SnCl_4]$) and $SnCl_4$ (or $H_2[SnCl_6]$), respectively.

Reaction equations:

1) α-Sn + 2HCl → $SnCl_2 + H_2$

2) β-Sn + 4HCl → $SnCl_4 + 2H_2$ or β-Sn + 6HCl → $H_2SnCl_6 + 2H_2$

6 points for **X** (no points are given if the calculations are missing).

4 points for reaction 1 (2 points deduction if the reaction is not balanced).

4 points for reaction 2 (2 points deduction if the reaction is not balanced).

7.2. (5 pt.)

$\Delta G° = \Delta H° - T\Delta S°$

The transition becomes spontaneous when $\Delta G° = 0$, therefore:

$(-2016) - 0 - T\cdot(44.14 - 51.18) = 0$

$T = 286.4$ K = 13°C

1 point for using the Gibbs equation.

1 point for choosing $\Delta G°$ as 0.

1 point for $\Delta H°$.

1 point for $\Delta S°$.

1 point for T *(full point for this question if the T is correct, but no solution is shown)*.

7.3. (4 pt.)

$$\Delta V/V = \frac{V_\alpha - V_\beta}{V_\beta} = \frac{\frac{1}{\rho_\alpha} - \frac{1}{\rho_\beta}}{\frac{1}{\rho_\beta}} = \frac{\rho_\beta - \rho_\alpha}{\rho_\alpha} = \frac{7.3-5.8}{5.8} \cdot 100\% = 26\%$$

$\Delta V/V = 26\%$

2 points for the equation.

2 points for the final answer (full points if the answer is correct, but no equation is shown).

7.4. (17 pt.)

From the lattice structure, it is possible to count the number of atoms per unit cell:

$$N = 8 \cdot \frac{1}{8} + 6 \cdot \frac{1}{2} + 4 \cdot 1 = 8 \text{ atoms per unit cell}$$

The volume is calculated using density, N of atoms per unit cell, and the atomic mass of Sn:

$$V = a^3 \text{ and } V = \frac{m}{\rho}$$

$$V = \frac{N \cdot M_{Sn}}{\rho \cdot N_A} = 2.72 \cdot 10^{-22} cm^3$$

$$a = \sqrt[3]{\frac{8 \cdot 118.8}{5.8 \cdot 6.022 \cdot 10^{23}}} \cdot 10^{10}$$

a = 648 pm or a = 650 pm (if **X** was not found)

Assuming that atoms located in tetrahedral voids “touch” the atoms surrounding it, it is possible to calculate the radius through the following steps:

1) Find the distance between two neighboring atoms located along the face diagonally: $\frac{\sqrt{2}}{2}a$;

2) Using trigonometry, find the distance between the atom in the tetrahedral void and the atom in the corner, which is $2r$. Therefore, $\sin\left(\frac{109.5°}{2}\right) = \frac{\frac{\sqrt{2}}{4}a}{2r}$

r = 140 pm or r = 141 pm (if **X** was not found)

9 points for the lattice parameter a.

(1 point for each location of the atoms and their respective sharing with other lattices; 0.5 points for each volume equation, 2 points for the relationship between density, N atoms, and the atomic mass of Sn, 3 points for the calculation).

8 points for the atomic radius (2 points for step 1, 4 points for step 2, 2 points for the final answer, or 6 points if there are no steps 1 and 2, but the ***r*** is correct).

7.5. (8 pt.)

$Sn^{2+} + 2e^{-} \rightarrow Sn$

$$n(e^-) = 2n_{\text{Sn}} = 2 \cdot \frac{\rho_\beta \cdot S \cdot d}{M_{\text{Sn}}}$$

$$I = j \cdot S$$

$$n(e^-) = \eta \cdot \frac{I \cdot t}{F} = \eta \cdot \frac{j \cdot S \cdot t}{F}$$

Therefore,

$$t = 2 \cdot \frac{\rho_\beta \cdot d \cdot F}{M_{\mathrm{Sn}} \cdot j \cdot \eta}$$

$$t = 2 \cdot \frac{7.3 \cdot 21 \cdot 10^{-4} \cdot 96485}{118.8 \cdot 2 \cdot 0.90} = 13.85\ \mathrm{s}$$

$t = 13.85$ s

1 point for the relationship between Sn and electrons.

2 points for substituting I with j·S (1 point for the half reaction only).

2 points for the final formula (1 point deduction if the yield was not included).

3 points for the required time.

7.6. (12 pt.)

Based on the described crystal structures, **Y** and **Z** consist of a metal cation and a non-metal anion in a 1:1 ratio. Since their lattice parameters are similar to that of α-Sn, the elements in **Y** and **Z** are likely to be of comparable size to Sn, hence, located in the same period. By examining the elements closest to Sn and considering the given mass fractions, one can identify:

Y – InSb

Z – CdTe

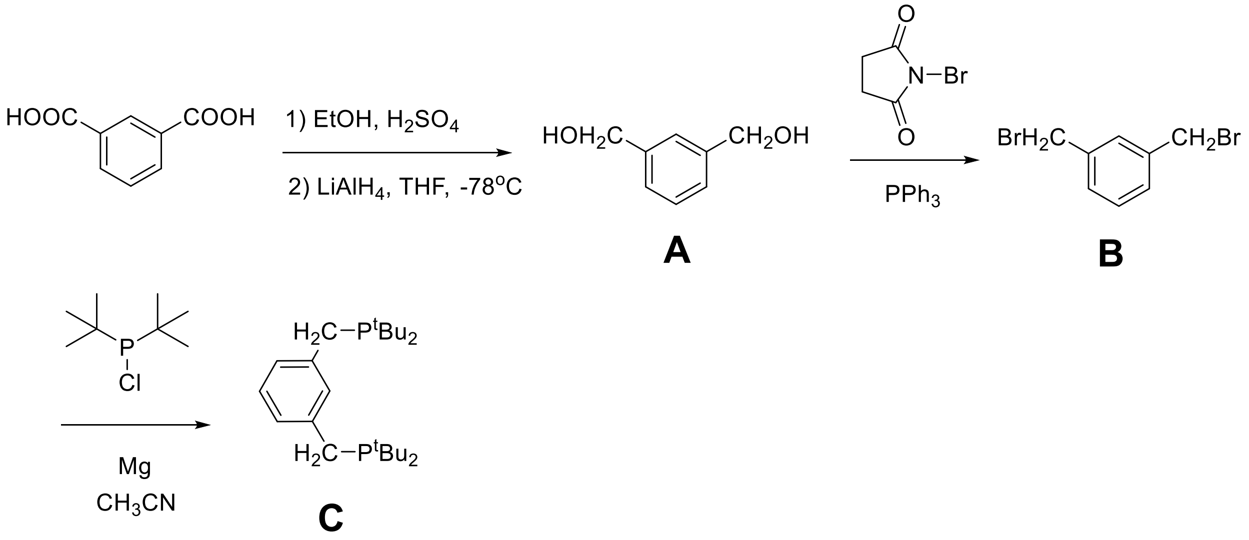
6 points for each compound (3 points for the right stoichiometry, 2 points for the one right element, and 1 point for the second right element).

Problem 8. Metal as a workhorse catalyst (Mirumid Mirakbarov, Alexander Koronatov)

Question	8.1	8.2	8.3	8.4	8.5	8.6	8.7	8.8	8.9	Total
Points	32	8	8	8	8	4	4	12	16	100
Result										

8.1. (32 pt.)

Reaction of ethanol with isophtalic acid in the acidic media is an esterification reaction. Further reduction with $LiAlH_4$ produces **A** – 1,3-di(hydroxymethyl)benzene. Next, a modified Appel reaction takes place, yielding in **B** –- di(brommethyl)benzene. And, at last magnesium-mediated coupling occurs with formation of 2 C-P bonds:



Let us find the metal **X**. Using the information above we can calculate

$$M(X) = \frac{80n}{0{,}1505} \times 0{,}1104 = 58{,}68n\ g/mol$$

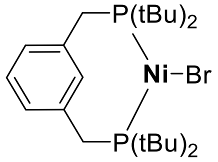
So, for n=1 we get Ni or Co (further investigation is preferred); for n=2 M(X)=117,37 g/mol – no metal with such molar mass; n=3 M(X)=176,04 g/mol – also no such metal. That is why for the only Ni and Co should be further considered.

Next, huge easter egg is metal **F** which is a neighbor of **X** in the Periodic table:

$$M(\mathbf{F}) = \frac{16n}{0{,}1408} \times (1 - 0{,}1408) = 97{,}63n$$

n=1 gives Tc – not a neighbor neither for Ni nor for Co. Moreover, Tc is in the group 7 of Periodic table, so TcO does not seem to be a substance stable enough to be used very often as a catalyst. n=2 gives M=195,3, which is **F**=Pt and **G**=PtO_2. Platinum dioxide is known as Adams' catalyst and is actually used in organic reactions as hydrogenation catalyst. Pt is in the same group as Ni so we finally conclude that **X** is Ni.

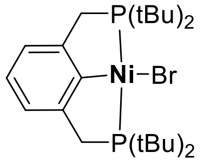
So, we have Ni as a metal and Ni:Br =1:1 in **D**. As the transformation from **C** to **D** does not seem to have any oxidants or reductants, we conceivably have Ni^{+2} in **D**. Since we have only Br^- and a neutral ligand **C**, the first approximation for **D** might be:



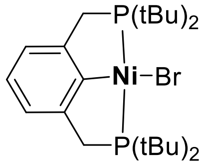
Yet this structure does not match the oxidation state of Ni, so let’s calculate the exact mass of the residue:

$$\Delta M = \frac{58,68}{0,1104} - 58,68 - 80 = 392,84 g/mol$$

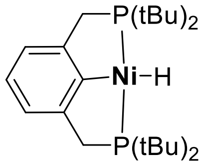
which corresponds to:



This hypothesis can be verified by the further reaction with $NaBH_4$, where bromine is substituted by hydrogen atom, thus yielding in Ni-H bond with the strong shielding in NMR and thus providing us the signal with the negative-value -10.29 ppm:



D

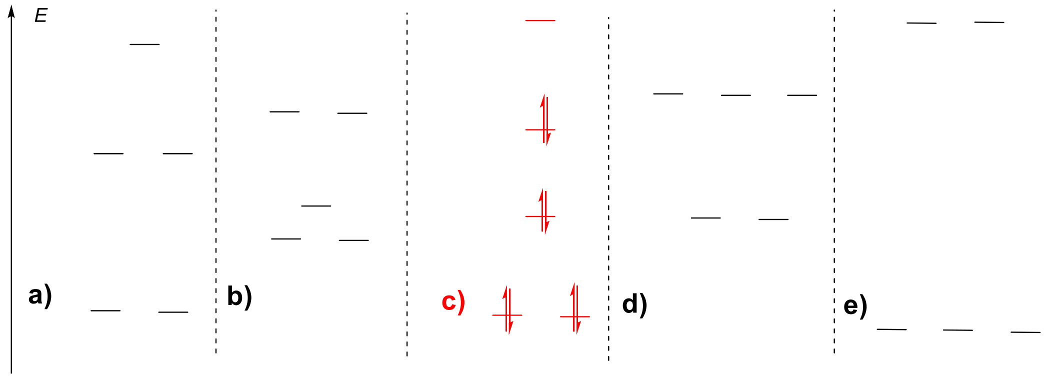


E

Subpoints:
For each correct structure of A-E – 4 pt.
For each correct formula of X, F, G – 4 pt.

8.2. (8 pt.)

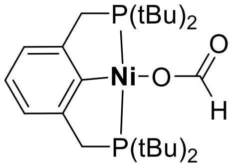
Ni, d8, CN 4, square-planar geometry, therefore **c** is the appropriate splitting of orbitals by energy due to crystal-field theory:

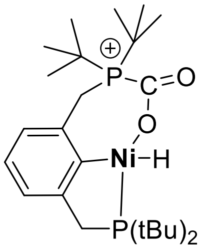


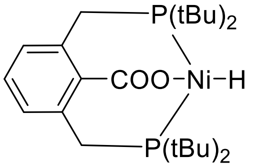
Subpoints:
Coordination number of Ni – 2 pt.
Correct energy diagram picking (without filling) – 4 pt.
Correct energy diagram filling – 6 pt.

8.3. (8 pt.)

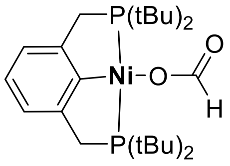
As the coordination number in **E** and **H** are the same, it could be proposed that carbon dioxide is inserted into ligand in this or that way:





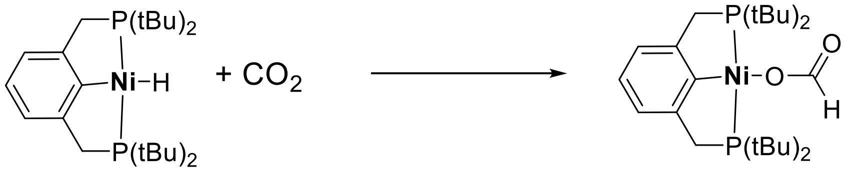


Moreover, the disappearance of the negative-value signal in NMR suggests that this insertion might be through Ni-H bond:



H

Equation of the reaction:



E **H**

Subpoints:

Correct structure of compound H – 4 pt.

Correct reaction equation – 4 pt.

8.4. (8 pt.)

E is a catalyst here. Due to conservation of matter we might assume, that 1 Na, 1 H, 2 O, 1 C are left for the formula of **Z**. As we found in **8.3.**, the catalytic cycle must include formation of formate moiety, so **Z**=HCOONa.

The corresponding reaction equation:

$NaHCO_3+H_2=HCOONa+H_2O$

Subpoints:

Compound Z – 4 pt.

Correct reaction equation – 4 pt.

8.5. (8 pt.)

The mass *m* of nickel is:

$$m = \frac{3215*3,6*10^{6}*365*1,25*10^{-4}}{393,5} * 58,7 = 78,77\ ton/year,$$

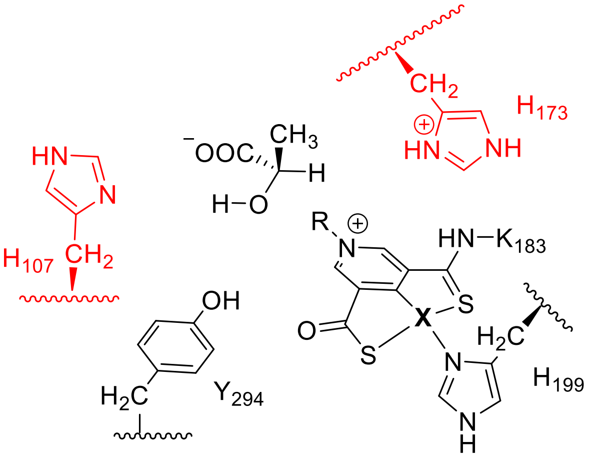
Note. Real numbers might be far less due to catalyst recycling

Subpoints:

- *Correct nickel mass in tons/year with correctly executed calculations – 8 pt.(full)*
- *For the correct calculation of total energy production per year without calculation of mass of nickel – 4 pt.*
- *For the correct calculation of nickel amount in incorrect units – 6 pt.*

8.6. (4 pt.)

From the picture given below we can see that only two nearby histidine fragments can play pivotal role in deprotonation due to the lone pair of nitrogen:



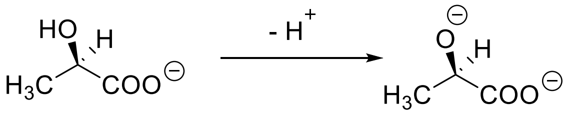
Number of amino acid residue: 107

8.7. (4 pt.) The same way as in (6) we can identify only one nearby fragment that could protonate formed **I1** intermediate, and it is H173 histidine fragment

Number of amino acid residue: 173

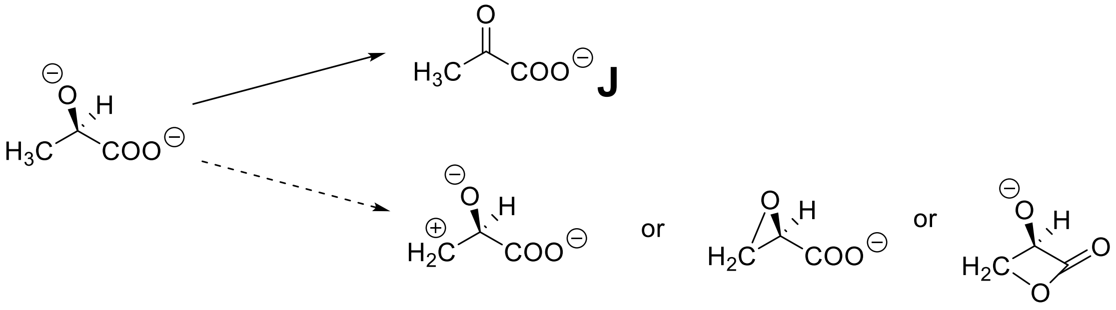
8.8. (12 pt.)

As the first step of the process is deprotonation, we might assume that it touches the most acidic proton:



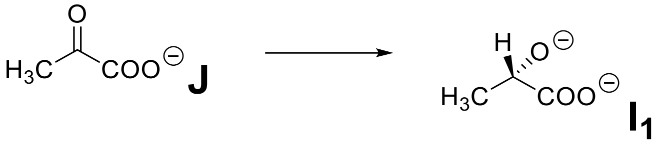
I

The next hydride removal might happen either from methyl or CH moiety:



As the hydride removal from methyl moiety doesn't yield in plane of symmetry, we conclude that **J** is pyruvate-ion.

Because we are dealing with the racemization process, it seems reasonable to draw the opposite configuration of **I**:

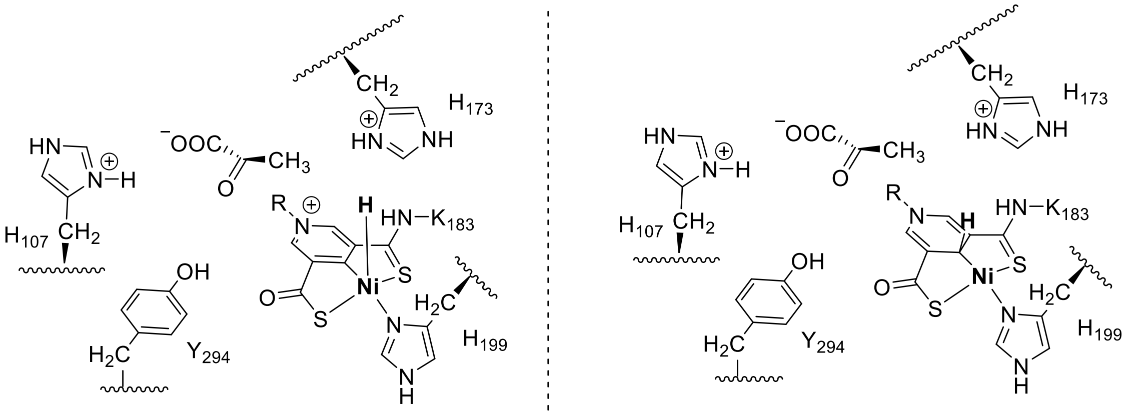


Subpoints:

Each compound (I, J, I_1) – 4 pt.

8.9. (16 pt.)

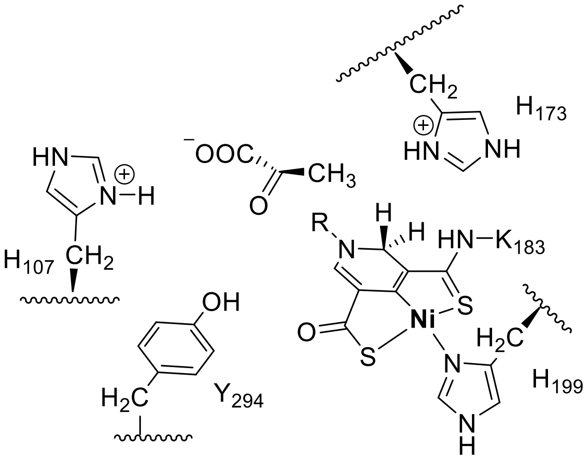
Because there are few aromatic moieties that could be broken, we might assume attacking of the pyridinium core. The change of the metal geometry suggests that the hydride migrates to the metal center in **K_2**:



hydride to metal (**K_2**)

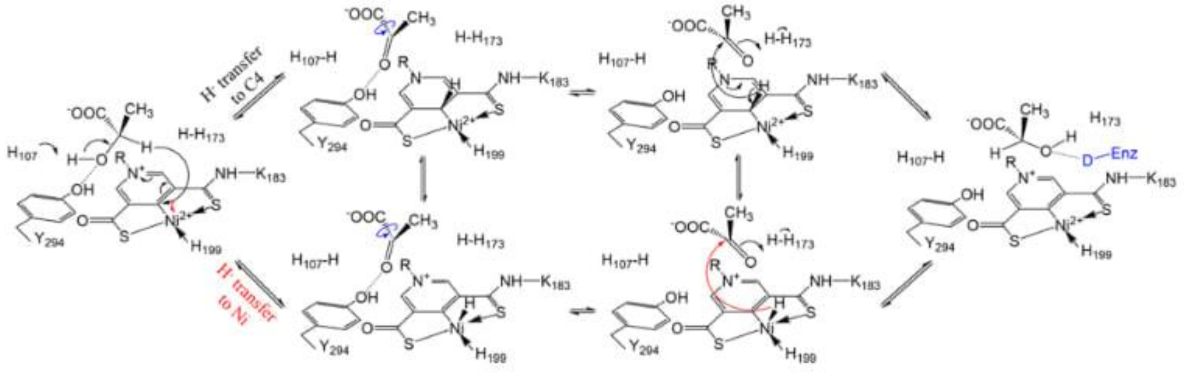
hydride to pyridinium (**K_1**)

Another option for the structure of **K_1** (which is also correct) can be assumed when the hydride is also bound to the 2nd position (C2) in the pyridine ring (makes also some sense, since the metal bound to sp^2 carbon should yield a more stable complex; this means that conjugation between one N-lone pair and C=O is lost, but the C=O-C=C conjugation is retained). It is known that pyridinium salts can be reduced regioselectively depending on a reducing agent and a substitution pattern:



another possible **K_1** structure

Full mechanism[2,3]:



Subpoints:

Each correct mechanism with depiction of key reactants/intermediates – 8 pt.

Literature:

1. Enthaler, S. *et al.* Exploring the Reactivity of Nickel Pincer Complexes in the Decomposition of Formic Acid to CO2/H2 and the Hydrogenation of NaHCO3 to HCOONa. *ChemCatChem* **7**, 65–69 (2015).

2. Rankin, J. A. *et al.* Lactate Racemase Nickel-Pincer Cofactor Operates by a Proton-Coupled Hydride Transfer Mechanism. *Biochemistry* **57**, 3244–3251 (2018).

3. Gatreddi, S., Urdiain-Arraiza, J., Desguin, B., Hausinger, R. P. & Hu, J. Structural Basis for the Catalysis and Substrate Specificity of a LarA Racemase with a Broad Substrate Spectrum. *ACS Catal.* **15**, 2857–2866 (2025).