Problems & Solutions

52nd IChO 2020

International Chemistry Olympiad

Istanbul, Turkey

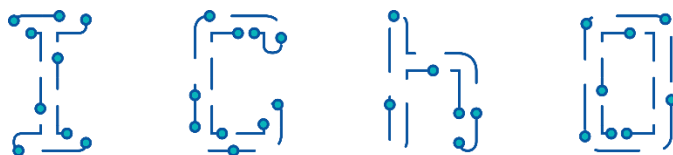**CHEMISTRY FOR A BETTER TOMORROW**

July 25, 2020

Instructions

- Only write with pen. Your calculator should be non-programmable.
- This examination has **9 problems**.
- You will have **5 hours** to solve the exam.
- **Begin** only when the **START** command is given.
- All results must be written in the appropriate boxes in pen in the designated areas on the **answer sheets**. Use the back of the exam sheets if you need scratch paper. Remember that answers written outside the answer boxes will not be graded.
- Write relevant calculations in the appropriate boxes when necessary. Full marks will be given for correct answers only when your work is shown.
- The invigilator will announce a **30-minute** warning before the Stop command.
- You **must stop** working when the **STOP** command is given. Failure to stop writing will lead to the nullification of your exam.
- The official English version of this examination is available on request only for clarification.

- You are not allowed to leave your working place without permission. If you need any assistance (broken calculator, need to visit a restroom, etc), raise hand and wait until an invigilator arrives.

GOOD LUCK!

Problems & Grading Information

Problem	Title	Total Score	% of Total Score
1	Two Beauties of Turkey: the Van Cat and the Ankara Cat	24	8
2	A Tale of a Reactive Intermediate	77	10
3	(±)-Coerulescine	51	8
4	Symmetry Does Matter!	66	10
5	Konya, Carrot, Beta-Carotene, Vitamin-A, Immune System, Vision	100	14
6	Thermodynamics through an Interstellar Journey	80	12
7	Phthalocyanines	85	12
8	Boron Compounds and Hydrogen Storage	58	14
9	Quantification of Heavy Metal Ions	100	12
	TOTAL	641	100

Table of Contents

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Physical Constants and Equations

Avogadro's number, $N_A = 6.0221 \times 10^{23} mol^{-1}$
Boltzmann constant, $k_B = 1.3807 \times 10^{-23} JK^{-1}$
Universal gas constant, $R = 8.3145 \, JK^{-1}mol^{-1} = 0.08205 \, atm \, L \, K^{-1}mol^{-1}$
Speed of light, $c = 2.9979 \times 10^8 ms^{-1}$
Planck's constant, $h = 6.6261 \times 10^{-34} J \, s$
Faraday's constant, $F = 9.6485 \times 10^4 \, C \, mol^{-1}$
Mass of electron, $m_e = 9.1093 \times 10^{-31} \, kg$
Standard pressure, $P = 1 \, bar = 10^5 \, Pa$
Atmospheric pressure, $P_{atm} = 1.01325 \times 10^5 \, Pa = 760 \, mmHg = 760 \, torr$
Zero of the Celsius scale, $273.15 \, K$
1 picometer (pm) $= 10^{-12} \, m$; $1Å = 10^{-10} \, m$; 1 nanometer (nm) $= 10^{-9} \, m$
$1 \, eV = 1.6 \times 10^{-19} J$
$1 \, cal = 4.184 \, J$
$1 \, amu = 1.6605 \times 10^{-27} \, kg$
Charge of an electron: $1.6 \times 10^{-19} \, C$

Ideal gas equation: $\quad PV = nRT$
Enthalpy: $\quad H = U + PV$
Gibbs free energy: $\quad G = H - TS$
$$\Delta G = \Delta G^0 + RTlnQ$$
$$\Delta_r G^0 = -RTlnK = -nFE^0_{cell}$$

Entropy change:

$$\Delta S = \frac{q_{rev}}{T}, \text{ where } q_{rev} \text{ is heat for the reversible process}$$

$$\Delta S = nRln\frac{V_2}{V_1} \text{ (for isothermal expansion of an ideal gas)}$$

Nernst equation: $\quad E = E^0 + \frac{RT}{nF} ln \frac{C_{oxidation}}{C_{reduction}}$

Energy of a photon: $\quad E = \frac{hc}{\lambda}$

Integrated rate law
Zeroth-order: $\quad [A] = [A]_0 - kt$
First-order: $\quad ln[A] = ln[A]_0 - kt$
Second order: $\quad \frac{1}{[A]} = \frac{1}{[A]_0} + kt$
Arrhenius equation: $\quad k = Ae^{-E_a/RT}$
Equation of linear calibration curve: $y = mx + n$
Lambert–Beer equation: $A = \varepsilon lc$

Periodic Table of Elements

1																	18
1 H 1.008	2		atomic number Symbol atomic weight									13	14	15	16	17	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	3	4	5	6	7	8	9	10	11	12	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 -

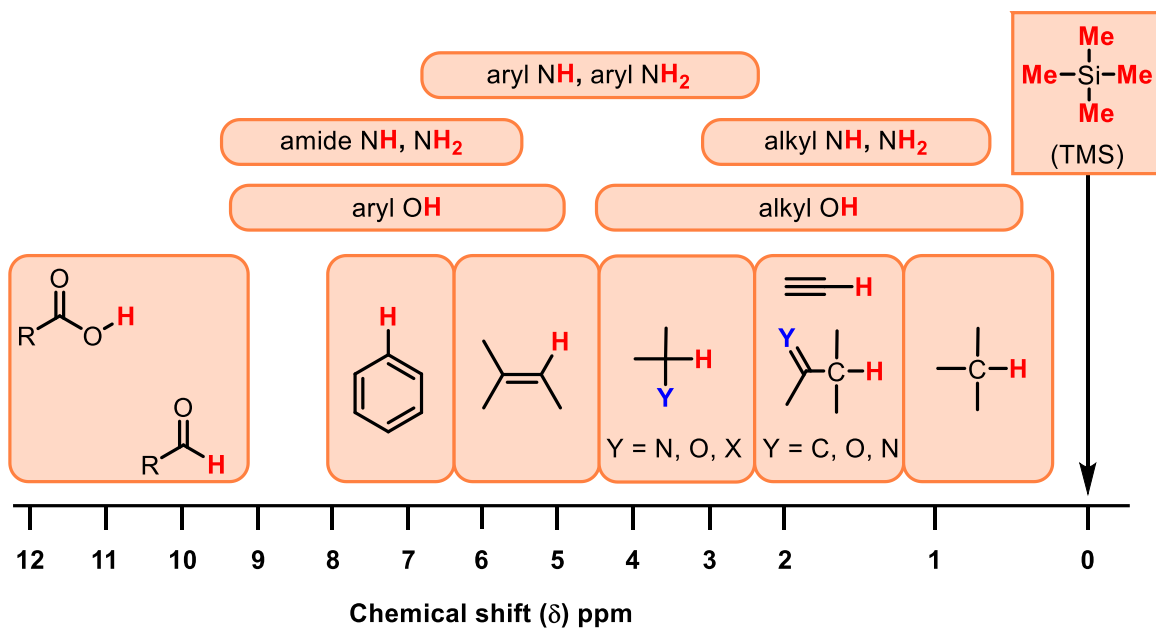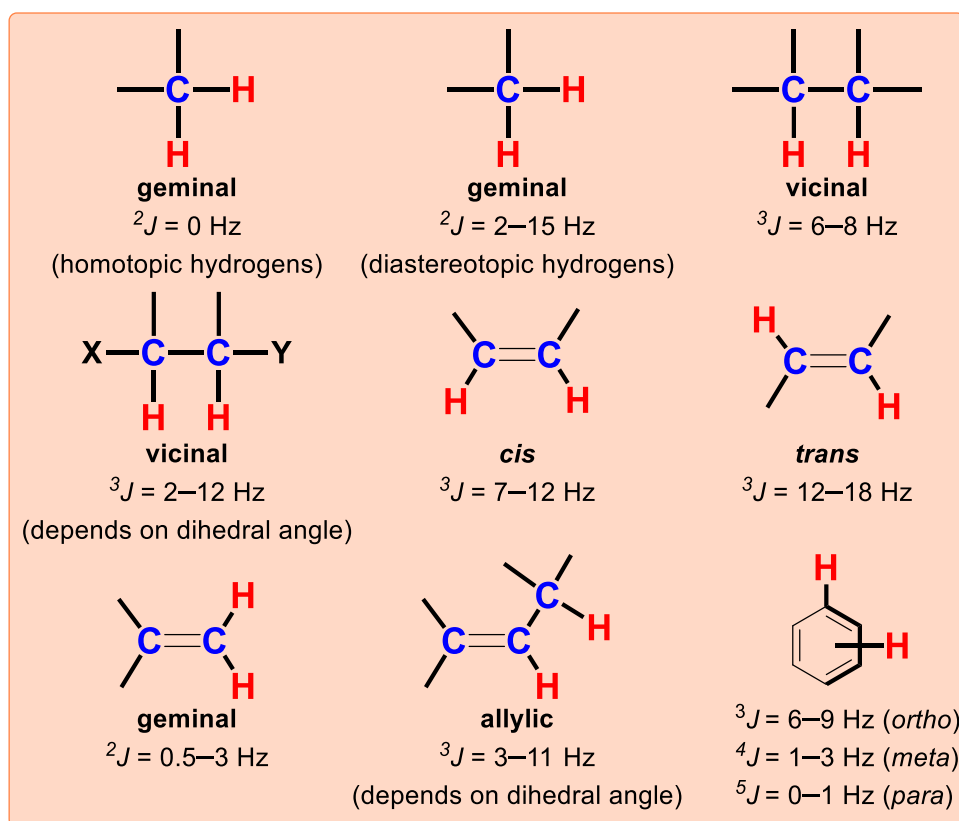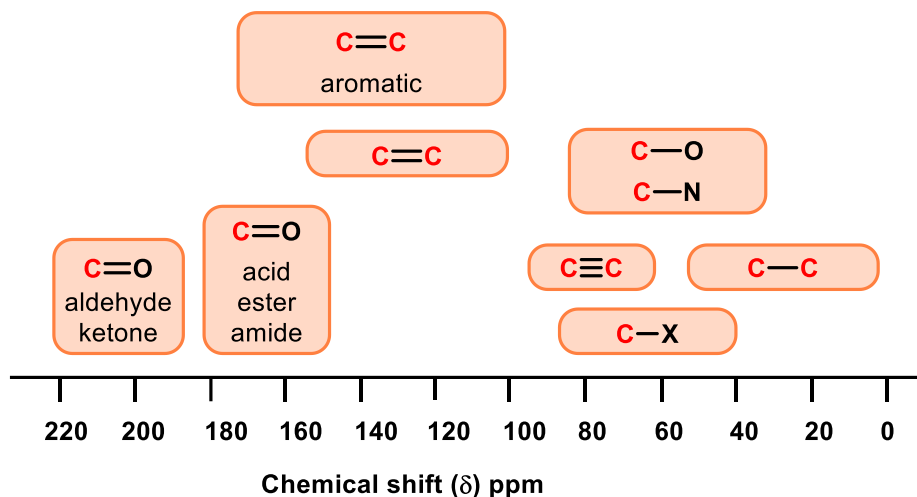| 57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm -	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
89 Ac -	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np -	94 Pu -	95 Am -	96 Cm -	97 Bk -	98 Cf -	99 Es -	100 Fm -	101 Md -	102 No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

2019 IYPT
International Year
of the Periodic Table
of Chemical Elements

IUPAC

^{1}H-NMR Chemical Shifts

aryl N**H**, aryl N**H$_2$**

amide N**H**, N**H$_2$**

alkyl N**H**, N**H$_2$**

aryl O**H**

alkyl O**H**

Me–Si–Me (TMS)

Y = N, O, X   Y = C, O, N

Chemical shift (δ) ppm

12 11 10 9 8 7 6 5 4 3 2 1 0

Typical Coupling Constants

geminal
^2J = 0 Hz
(homotopic hydrogens)

geminal
^2J = 2–15 Hz
(diastereotopic hydrogens)

vicinal
^3J = 6–8 Hz

vicinal
^3J = 2–12 Hz
(depends on dihedral angle)

cis
^3J = 7–12 Hz

trans
^3J = 12–18 Hz

geminal
^2J = 0.5–3 Hz

allylic
^3J = 3–11 Hz
(depends on dihedral angle)

^3J = 6–9 Hz (*ortho*)
^4J = 1–3 Hz (*meta*)
^5J = 0–1 Hz (*para*)

^{13}C-NMR Chemical Shifts

IR Absorption Frequency Table

Functional Group	Type of Vibration	Absorption Frequency Region (cm^{-1})	Intensity
Alcohol			
O–H	(stretch, H-bonded)	3600–3200	strong, broad
	(stretch, free)	3700–3500	strong, sharp
C–O	(stretch)	1150–1050	strong
Alkane			
C–H	stretch	3000–2850	strong
	bending	1480–1350	variable
Alkene			
=C–H	stretch	3100–3010	medium
	bending	1000–675	strong
C=C	stretch	1680–1620	variable
Alkyl Halide			
C–F	stretch	1400–1000	strong
C–Cl	stretch	800–600	strong
C–Br	stretch	600–500	strong
C–I	stretch	500	strong
Alkyne			
C–H	stretch	3300	strong, sharp
C≡C	stretch	2260–2100	variable, not present in symmetrical alkynes
Amine			
N–H	stretch	3500–3300	medium (primary amines have two bands; secondary amines have one band, often very weak)

C–N	stretch	1360–1080	medium-weak
N–H	bending	1600	medium
Aromatic			
C–H	stretch	3100–3000	medium
C=C	stretch	1600–1400	medium-weak, multiple bands
Carbonyl			
C=O	stretch	1820–1670	strong
Acid			
C=O	stretch	1725–1700	strong
O–H	stretch	3300–2500	strong, very broad
C–O	stretch	1320–1210	strong
Aldehyde			
C=O	stretch	1740–1720	strong
C–H	stretch	2850–2820 & 2750–2720	medium, two peaks
Amide			
C=O	stretch	1690–1640	strong
N–H	stretch	3500–3100	unsubstituted have two bands
	bending	1640–1550	
Anhydride			
C=O	stretch	1830–1800 &1775–1740	two bands
Ester			
C=O	stretch	1750–1735	strong
C–O	stretch	1300–1000	two bands or more
Ketone			
acyclic	stretch	1725–1705	strong
	stretch	3-membered - 1850	strong
	stretch	4-membered - 1780	strong
cyclic	stretch	5-membered - 1745	strong
	stretch	6-membered - 1715	strong
	stretch	7-membered - 1705	strong
α,β-unsaturated	stretch	1685–1665	strong
conjugation moves absorptions to lower wavenumbers			
aryl ketone	stretch	1700–1680	strong
Ether			
C–O	stretch	1300–1000 (1150–1070)	strong
Nitrile			
C≡N	stretch	2260–2210	medium
Nitro			
N–O	stretch	1560–1515 & 1385–1345	strong, two bands

Problem 1	Question	1.1	1.2	1.3	Total
8% of the total	Points	14	4	6	**24**

Problem 1. Two Beauties of Turkey: the Van Cat and the Ankara Cat
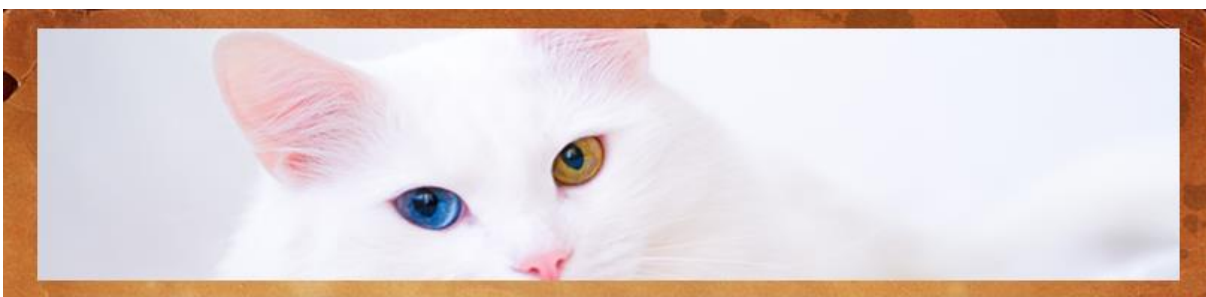
The most beautiful of cats, the Van cat is a pure breed living only in Lake Van basin. Another endemic cat breed is the Ankara cat. They are called Angora cats. Their most important feature is their two different eye colors.

Van cat	Ankara cat	*Nepeta cataria* (catnip)

Just like people, cats can sometimes be stressed and angry. Just as people are made happy by melatonin, the stress of cats can be reduced and they can be made happy thanks to a natural product. Nepetalactone is an organic compound isolated from the plant catnip (*Nepeta cataria*), which acts as a cat attractant. Nepetalactone is a ten-carbon bicyclic monoterpenoid compound derived from isoprene with two fused rings: a cyclopentane and a lactone.

Cat eating catnip in the garden   Cat's dream
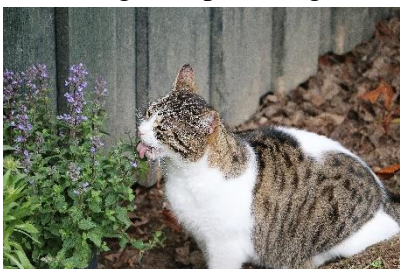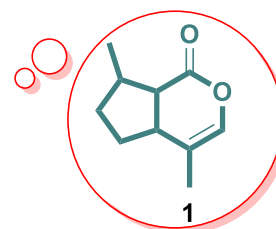
1
Nepetalactone
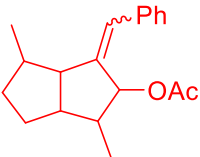
Total synthesis of nepetalactone:
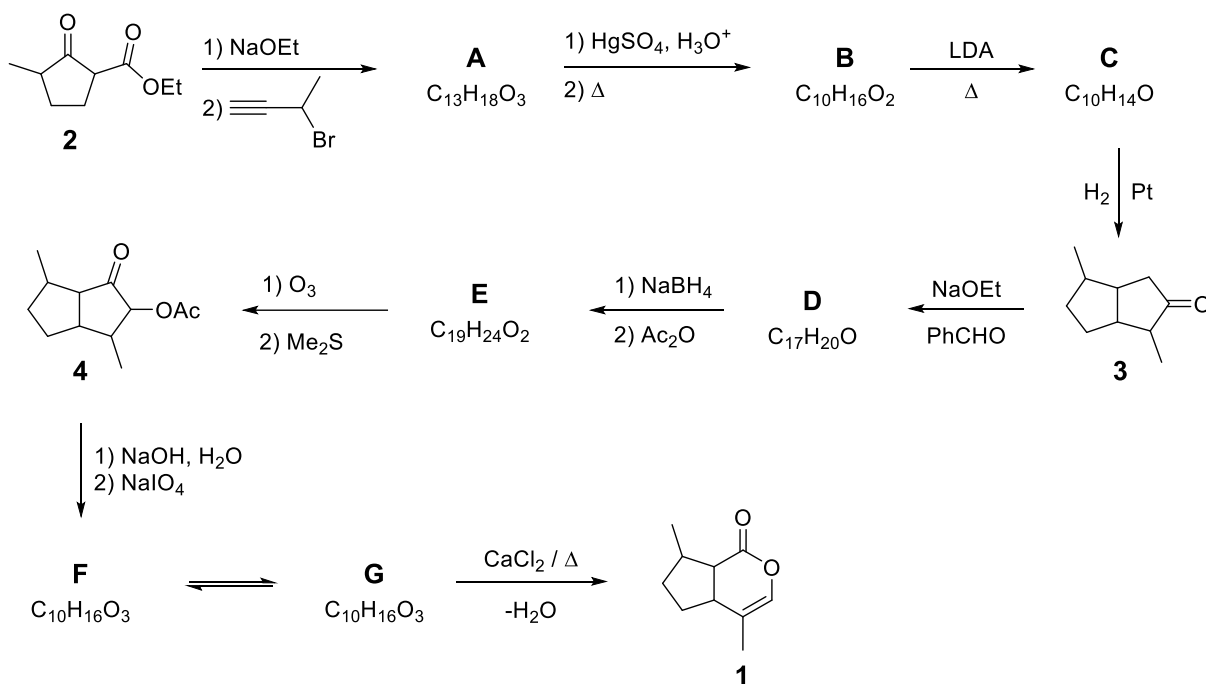
1.1. The above scheme describes the total synthesis of nepetalactone. **Draw** structures of **A–G**, without stereochemical details.

Hints:
- Compound **A** has strong and sharp band at 3300 cm^{-1} in the IR spectrum.
- **A**, **B,** and **F** are monocyclic, while **C**, **D**, **E**, and **G** are bicyclic compounds.
- **F** has one doublet at ~ 9.8 ppm in the ^{1}H-NMR spectrum.

Reactions of nepetalactone:
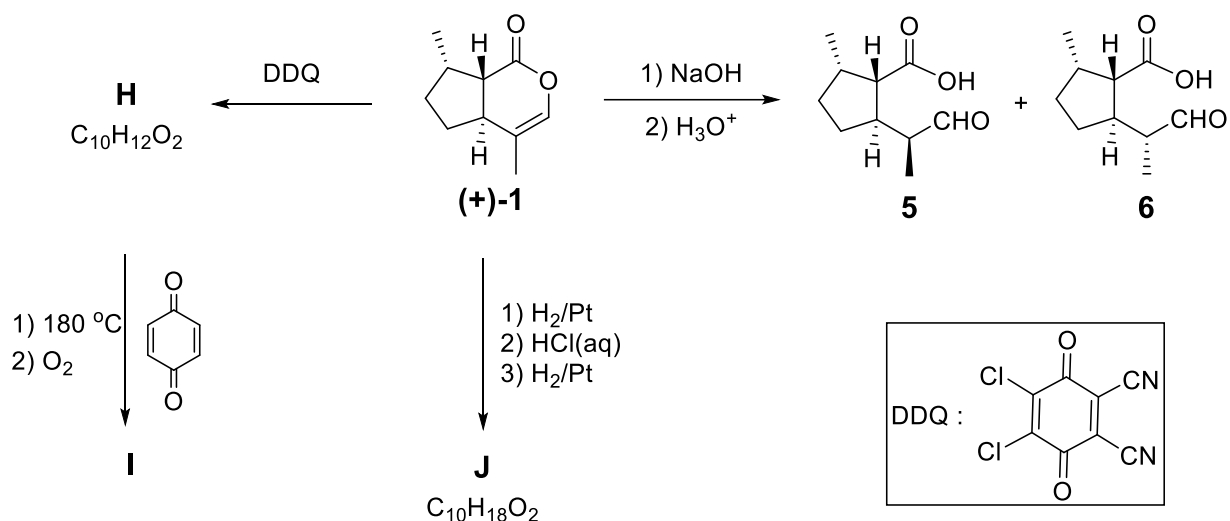
The above scheme includes a few reactions of one of the enantiopure nepetalactone **1** isomers. Three of the reaction products (**5**, **6**, and **J**) are used as insect repellents in industry.

1.2. For the relationship between **5** and **6**, which of the following is/are true? **Tick** the box next to the correct answer(s) on your answer sheets.

☐   Enantiomers
☐   Diastereomers
☐   Identical
☐   Stereoisomers

Reaction of **1** with DDQ gives highly conjugated compound **H**. Also, thermal reaction of compound **H** with *p*-quinone gives **I** with molar mass of 226.28 g/mol.

1.3. Draw the structures of **H**, **I**, and **J** indicating stereochemistry.

   Hints:
   - During the formation of **I**, sequential pericyclic reactions and an oxidation reaction (due to the presence of O_2) take place, and a well-known gas forms during the reaction.
   - **J** has a strong and very broad band between 3300 and 2500 cm^{-1} in the IR spectrum.
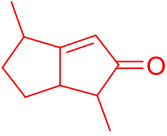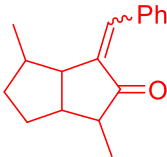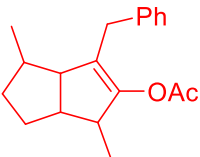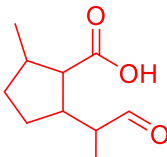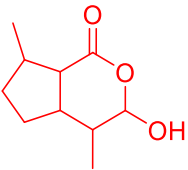
Solution:

Total synthesis of nepetalactone:

1.1. <u>Draw</u> the structures of **A–G** without stereochemical details.

A	B
2 points for correct answer. *1 point if propargylation position is not correct. Zero points for allene structure as it is not consistent with hints given.*	*2 points for correct answer.*

C

2 points for correct answer.
1 point for unconjugated enone.

D

2 points for correct answer.
Both E and Z isomers will receive full points
1 point if condensation position is not correct.

E

2 points for correct answer.

1 point for a product via 1,4-reduction.

F

2 points for correct answer.

G

2 points for correct answer.
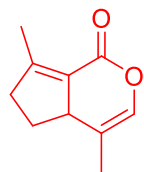*1 point for enol form of F.*

Reactions of nepetalactone:
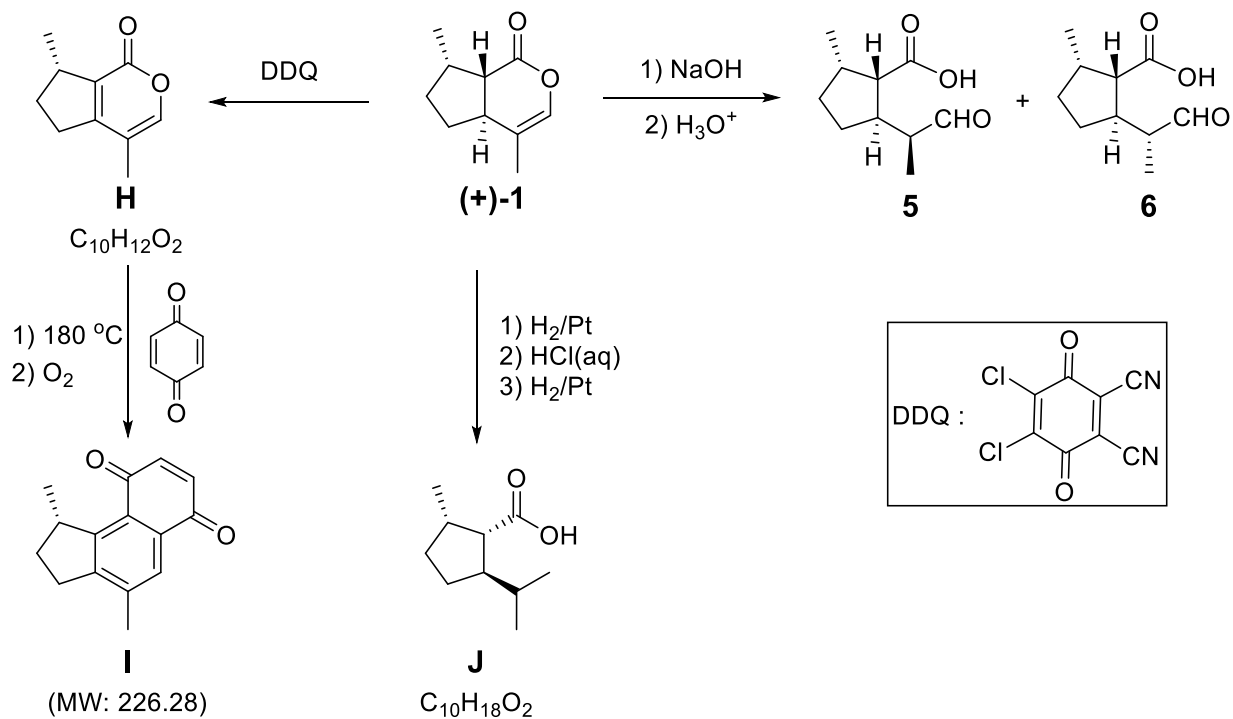
H
$C_{10}H_{12}O_2$

(+)-1

5

6

DDQ :

I
(MW: 226.28)

J
$C_{10}H_{18}O_2$

1.2. For the relationship between **5** and **6**, which of the following is/are true? __Tick__ the box next to the correct answer(s).

☐ Enantiomers	*4 points (total) for the two correct answers (2 points for each correct answer).*
☒ Diastereomers	
☐ Same compounds	*2 points (total) if there is one mistake.*
☒ Stereoisomers	*0 points if there are more than one mistakes.*

1.3. __Draw__ the structures of **H**, **I**, and **J** indicating stereochemistry.

H	I
2 points for correct answer.	*2 points for correct answer.*

1 point for a conjugated oxidation product via a five-membered ring.

J
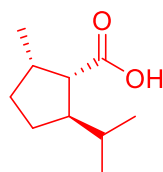
*2 points for correct answer.*
1 point without stereochemical detail.

Problem 2	Question	2.1	2.2	2.3	2.4	2.5	2.6	2.7	**Total**
10% of the total	Points	7	9	8	16	5	4	28	**77**

Problem 2. A Tale of a Reactive Intermediate

Arynes constitute a special class of reactive intermediates. The first experimental evidence for the structure of an aryne (benzyne) was demonstrated in 1953 via the elegant labeling experiments by John D. Roberts and coworkers.

In one such experiment, chlorobenzene, whose carbon at position 1 was labeled with radioactive ^{14}C, was reacted with KNH_2 in liquid NH_3 to give nearly equal amounts of isotopic isomers **A** and **B** along with the inorganic salt **C**. This reaction proceeds via the formation of aryne intermediate **D**.
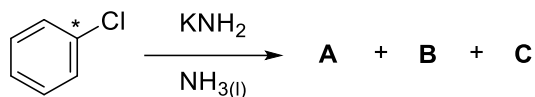
2.1. Draw the structure of **A**, **B** and **D**, and provide the formula of **C**. Indicate the position(s) of ^{14}C-labeled carbon(s) with an asterisk (*) whenever applicable."

Analysis of the ^{14}C-labeled product(s) was achieved via degradation experiments (the ^{14}C-labeled carbons are not shown on the structures). Radioactivities of the intermediates and final products were examined.
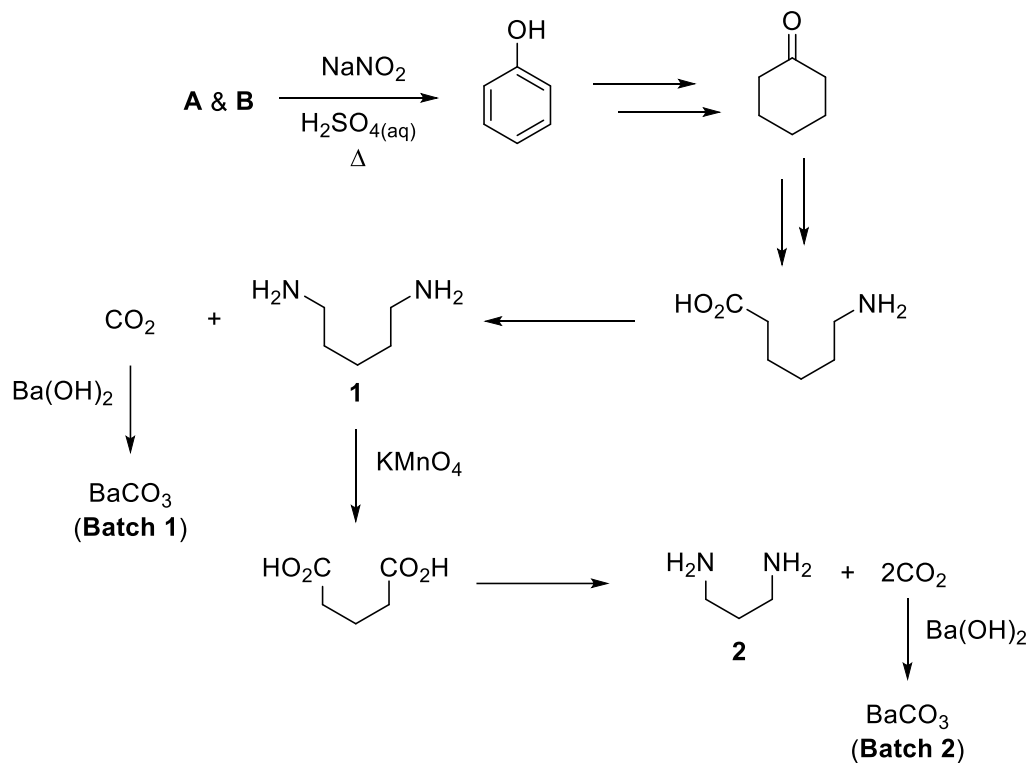
2.2. Tick the appropriate boxes on the answer sheet for the intermediates and products that you expect to exhibit radioactivity.

Considering only **A**:	Considering only **B**:
☐ Compound **1**	☐ Compound **1**
☐ BaCO₃ (Batch **1**)	☐ BaCO₃ (Batch **1**)
☐ Compound **2**	☐ Compound **2**
☐ BaCO₃ (Batch **2**)	☐ BaCO₃ (Batch **2**)

With the aim of facilitating aryne formation, Kobayashi and co-workers developed a fluoride-induced aryne generation protocol. Using this method, benzene derivative **3** is reacted with furan (**4**) in the presence of CsF, resulting in the formation of **E**, **F**, and **G**.
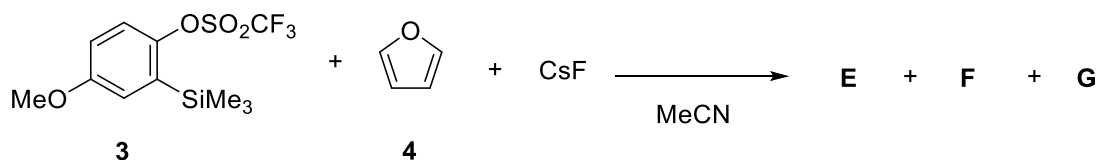
- Combustion analysis of **E** revealed the following atom content: 75.8% carbon, 5.8% hydrogen, and 18.4% oxygen.
- **E** does not have a proton that is exchangeable with D_2O in ^1H-NMR spectroscopy.
- **F** is an ionic compound.

**2.3. <u>Determine</u>** the structures of **E**, **F**, and **G** (without stereochemical details).

In the absence of a nucleophile or a trapping agent, arynes can undergo [2+2]-type cyclodimerization or [2+2+2]-type cyclotrimerization reactions under suitable conditions. The aryne derivative that is obtained when **3** is treated with one equivalent of CsF in MeCN can give, in principle, four different dimerization and trimerization products (**H–K**).

- **H** has two planes of symmetry.
- **I** is expected to exhibit 21 signals in its ^{13}C-NMR spectrum.
- **I** and **J** both exhibit an *m/z* value of 318.1 in their mass spectra.

2.4. <u>Determine</u> the structures of **H–K**.

When **5** is reacted with *β*-ketoester **6** in the presence of 2 equivalents of CsF at 80 °C, **L** is obtained as the major product. The ^1H-NMR and ^{13}C-NMR data for **L**, in CDCl$_3$, are as follows:

- ^1H-NMR: δ 7.79 (dd, J = 7.6, 1.5 Hz, 1H), 7.47–7.33 (m, 2H), 7.25–7.20 (m, 1H), 3.91 (s, 2H), 3.66 (s, 3H), 2.56 (s, 3H) ppm.

- ^{13}C-NMR: δ 201.3, 172.0, 137.1, 134.4, 132.8, 132.1, 130.1, 127.5, 51.9, 40.2, 28.8 ppm.
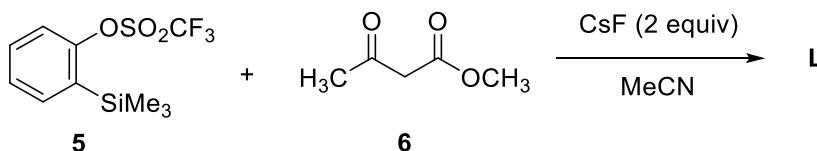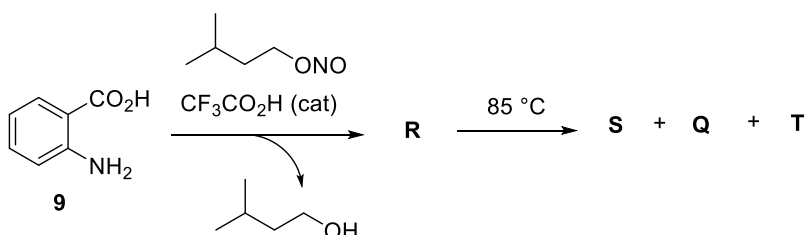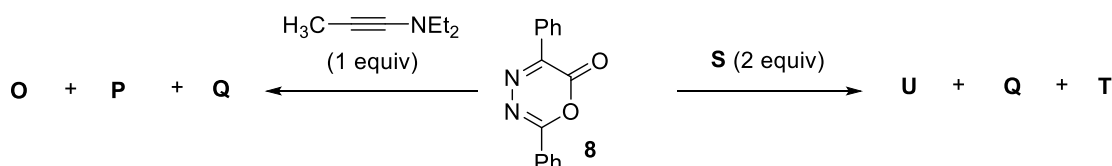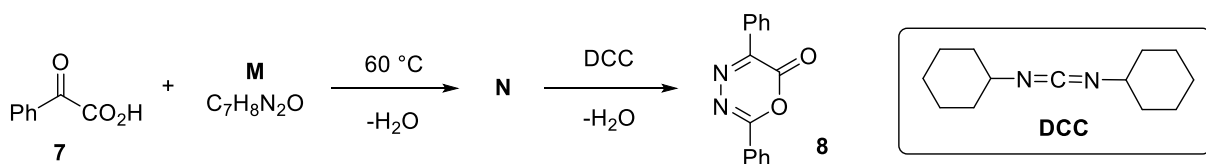

2.5. <u>Determine</u> the structure of **L**.

2.6. In the reaction shown in task **2.5**, which of the statement(s) in the answer sheet describe(s) the function of CsF?

- The pK_a values of HF and *β*-ketoester **6** in dimethyl sulfoxide (DMSO) are about 15 and 14, respectively.

☐ F⁻ hydrolyzes the trifluoromethanesulfonate (O_3SCF_3) group of **5**.

☐ F⁻ attacks the –SiMe₃ group of **5**.

☐ F⁻ acts as a base to deprotonate **6**.

☐ F⁻ acts as a nucleophile and attacks the ester group of **6**.

Diazapyrone derivative **8** was shown to be a useful reactant for the construction of a variety of cyclic frameworks. Its preparation from phenylglyoxylic acid (**7**) and its use in two different reactions are described below.

- **Q** and **T** are gases under ambient conditions.
- **O** and **P** are constitutional isomers.
- **Q** does not have any signals in its IR spectrum.
- Heating 1 mol of **R** at 85 °C generates 1 mol of reactive intermediate **S**.
- Reaction of **8** with two equivalents of **S** gives **U**, **Q**, and **T**.
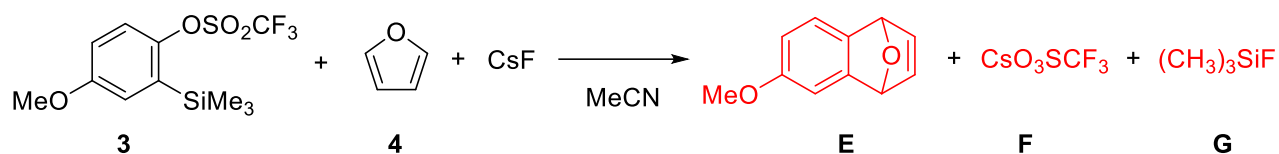

Note:

equiv= equivalent

cat= catalyst

2.7. **Determine** the structures of **M–U**.

Solution:

2.1. <u>Draw</u> the structures of **A–D**. Indicate the position(s) of ^{14}C-labeled carbon(s) with an asterisk (*) whenever applicable.

A	B
  2 points. *1 point if labeled carbon is not shown or if its position is incorrect.*	 **B** *2 points.* *1 point if labeled carbon is not shown or if its position is incorrect.* *If unlabeled aniline is given as an answer for both **A** and **B**, then only 1 point will be given in total for **A** and **B**.*
C KCl or K^+ : $\ddot{C}\ddot{l}$: $^-$ *1 point.* *0 points if only cation or anion is written.*	**D** *2 points.* *2 points for different resonance forms of **A** including the circle representation for aromaticity.* *1 point if labeled carbon is not shown or if its position is incorrect.*

2.2. <u>Tick</u> the appropriate boxes on the answer sheet for the intermediates and products that you expect to exhibit radioactivity.

Considering only **A**:	Considering only **B**:
☐ Compound **1** ☒ BaCO₃ (Batch **1**) ☐ Compound **2**	☒ Compound **1** ☐ BaCO₃ (Batch **1**) ☐ Compound **2**

☐ BaCO₃ (Batch **2**)	⊠ BaCO₃ (Batch **2**)
Solution: only BaCO₃ (Batch 1)	*Solution: Compound 1 and BaCO₃ (Batch 2)*
3 points for the correct answer. *0 points for one or more mistakes.*	*6 points (total) for the two correct answers (3 points for each correct answer).* *3 points (total) if there is one mistake.* *0 points if there are more than one mistakes.*

Note: *The answer to this task will depend on the student's structural assignment of compounds **A** and **B** in task **2.1***
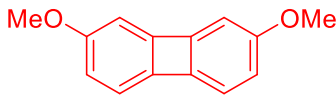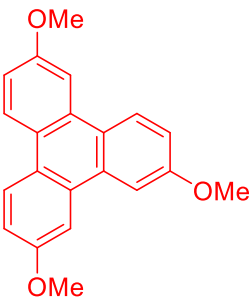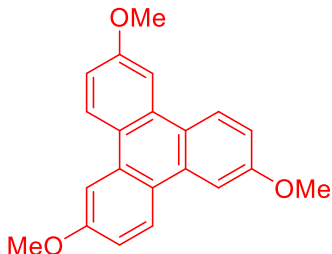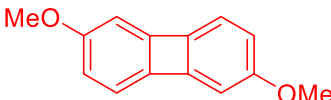
2.3. <u>Determine</u> the structures of **E**, **F**, and **G** (without stereochemical details).
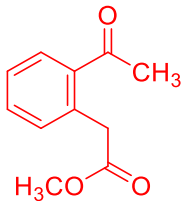
E	**F**
   4 points. *2 points if the product of [2+2] reaction between aryne and furan is written.* *0 points if ring-opened naphthol product is written.*	CsO₃SCF₃ or Cs⁺CF₃SO₃⁻ or CsOTf *2 points.*
G (CH₃)₃SiF or Me₃SiF *2 points.*	

2.4. Determine the structures of **H–K**.

H	I
MeO — OMe (structure) *4 points.*	OMe, OMe, OMe (structure) *4 points.*
J	**K**
OMe, OMe, MeO (structure) *4 points.*	MeO — OMe (structure) *4 points.*

2.5. Determine the structure of **L**.

L

(structure with C(=O)CH₃ and CH₂C(=O)OCH₃ groups on benzene)

5 points

The following isomer will also receive full points:
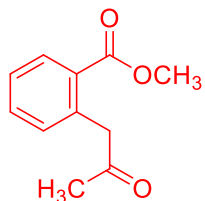
2 points for the following structures:

or
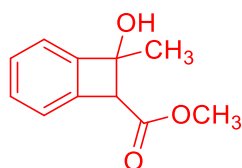
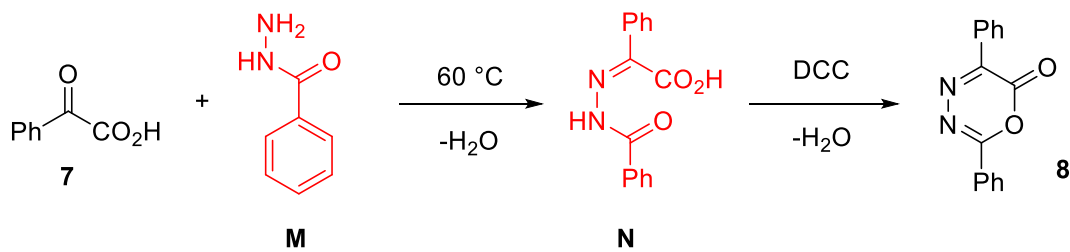**2.6.** In the reaction shown in task **2.5**, which of the statement(s) in the answer sheet describe(s) the function of CsF?

☐ F^- hydrolyzes the trifluoromethanesulfonate (O_3SCF_3) group of **5**.

☒ F^- attacks the $-SiMe_3$ group of **5**.

☒ F^- acts as a base to deprotonate **6**.

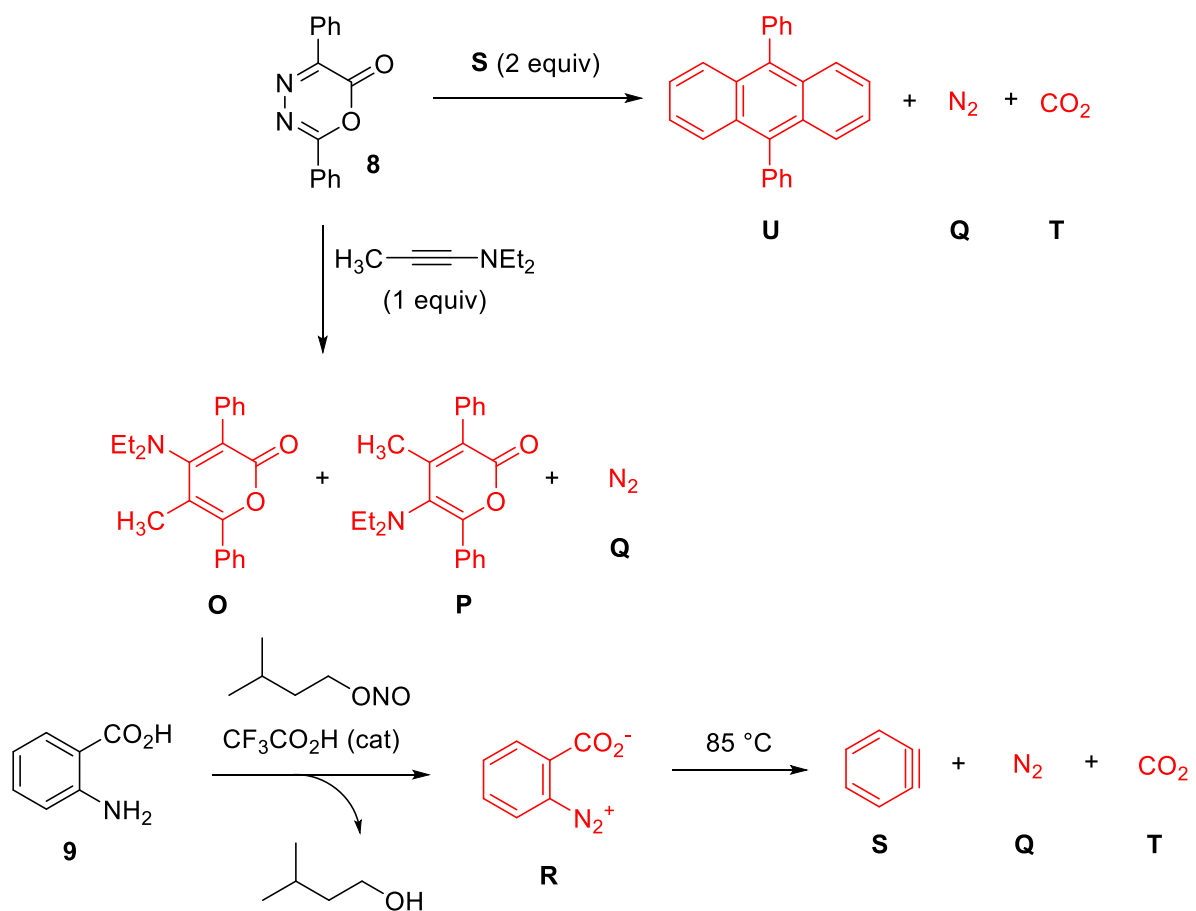☐ F^- acts as a nucleophile and attacks the ester group of **6**.

The correct statements are the 2nd and 3rd statements.

4 points (total) for the two correct answers (2 points for each correct answer).
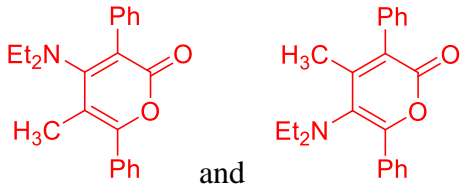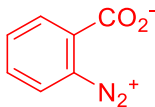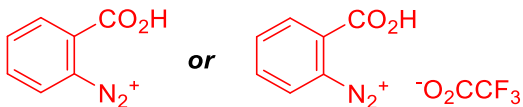*2 points (total) if there is one mistake.*
0 points if there are more than one mistakes.
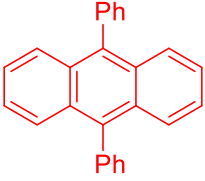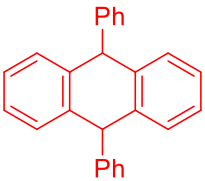
2.7. <u>Determine</u> the structures of **M–U**.

M	N
4 points.	*4 points.*
The following tautomer will receive full points:	*The following tautomer will receive full points:*

O and **P**

and

6 points (3 points for each isomer)

Q

N_2

2 points.

R

3 points.

3 points will be given for the following answers:

 or

S

3 points.

T

CO_2

2 points.

U

4 points.

2 points for the following answer:

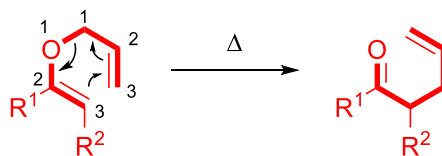| Problem 3	Question	3.1	3.2	3.3	3.4	3.5	3.6	3.7	Total
8% of the total	Points	8	16	4	8	5	5	5	51

Problem 3. (±)-Coerulescine

A spiro compound is typically an organic compound containing rings linked together by one common atom (spiroatom) as carbon atom with bold in figure below. The spiro[pyrrolidin-3,3′-oxindole] ring system is a structural framework incorporated in several cytostatic alkaloids and unnatural compounds. Coerulescine (**1**) and horsfiline are the simplest prototype members of this subfamily that can be synthesized by the route shown below.
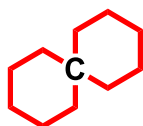
Claisen rearrangement, which is a [3,3]-sigmatropic rearrangement, is a powerful carbon–carbon bond-forming reaction in which an allyl vinyl ether is converted thermally to an unsaturated carbonyl compound as shown in the Scheme below. When compound **A** is heated, it undergoes Claisen rearrangement to give carbonyl compound **B**.

For this entire task, your answers can be given without any stereochemical details.

CHO / NO$_2$ benzaldehyde derivative

$CH_2=CHCH_2OCH_2PPh_3Cl$, t-BuONa →

A $C_{11}H_{11}NO_3$

139 °C →

B $C_{11}H_{11}NO_3$

1) CrO_3, H_2SO_4, H_2O
2) H_2SO_4, EtOH

C $C_{13}H_{15}NO_4$

Zn, NH_4Cl →

D $C_{11}H_{11}NO$

NaH, (Boc)$_2$O →

(3-allyl-oxindole with N-Boc)

NaH, Cl–C(=O)–O–Et (ethyl chloroformate) ↓

E $C_{19}H_{23}NO_5$

OsO_4 (cat.) / $NaIO_4$ →

F $C_{18}H_{21}NO_6$

$MeNH_2 \cdot HCl$ / $NaBH_3CN$ →

G $C_{17}H_{20}N_2O_4$

2.5 M HCl ↓

H $C_{12}H_{12}N_2O_2$

1) n-BuLi
2) $LiAlH_4$ →

(±)-coerulescine

1) NBS
2) NaOMe, CuI →

I (±)-horsfiline

Boc : (tert-butyl carbonate group)   NBS : (N-bromosuccinimide)

3.1. Draw the structures of **A** and **B**.

- **A** is an inseparable mixture of *cis/trans* isomers.
- **B** has IR absorption at 1726 cm^{-1}.

3.2. Draw structures for **C**, **D**, **E**, and **F**.

- **D–F** have a bicyclic structure.

3.3. Choose the correct order of steps for the transformation of **F** to **G**.

☐ Imine formation, then reduction, then amidation

☐ Amidation, then imine formation, then reduction

☐ Reduction, then amidation, then imine formation

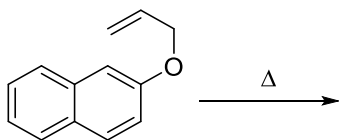**3.4. Draw** structures for **G** and **H** (both spiro compounds).

3.5. Draw the structure of the intermediate produced by treatment with *n*-BuLi in the step **H** → **coerulescine (1)**.

Coerulescine (1), on treatment with *N*-bromosuccinimide (NBS), gives the bromo derivative, which upon heating with sodium methoxide in the presence of cuprous iodide gives **horsfiline (I)** in 60% yield.

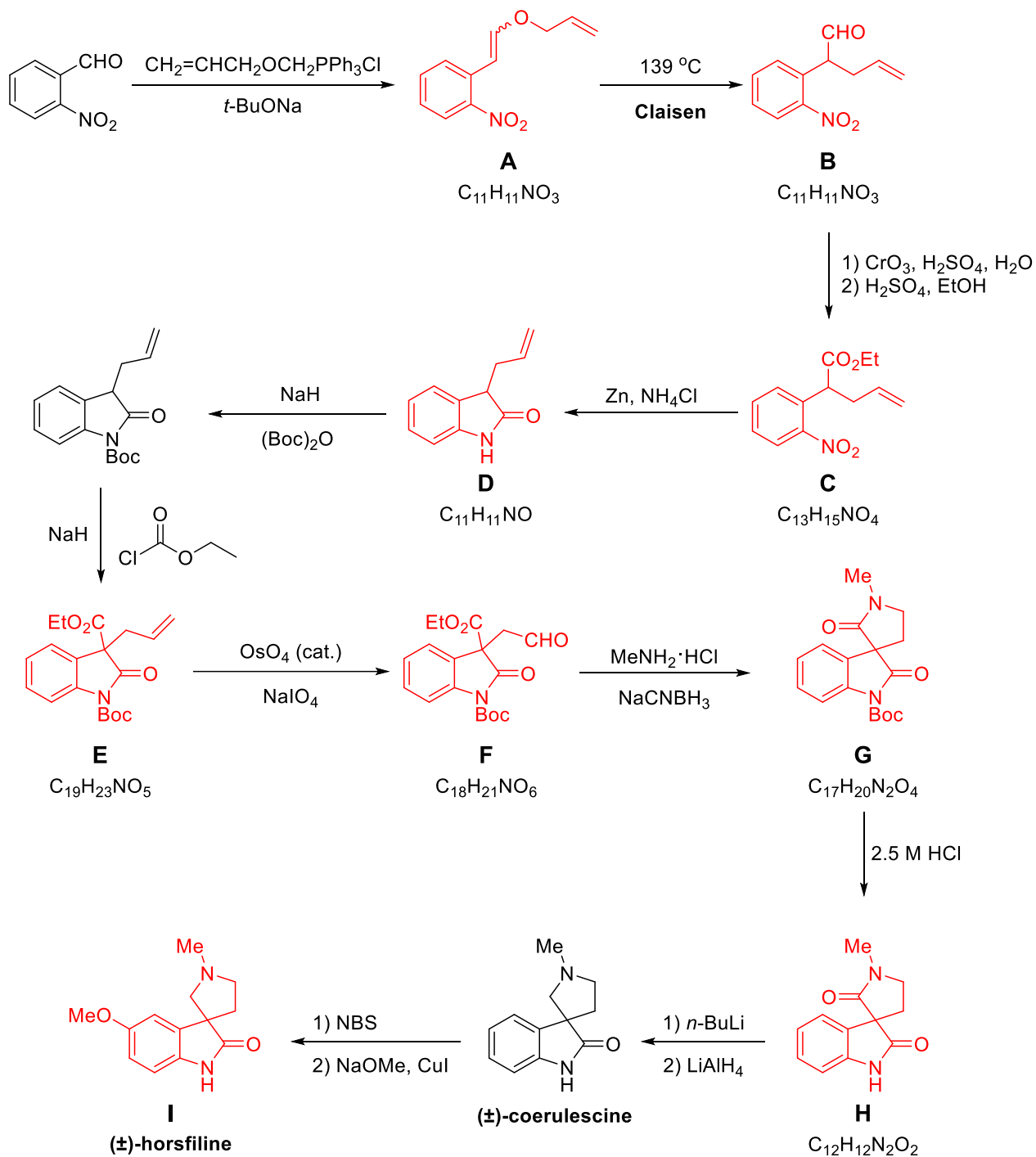**3.6. Choose** the correct structure for compound **I** consistent with the following selected ^{1}H-NMR data: δ 7.05 (d, $J = 1.4$ Hz, 1H), 6.78 (d, $J = 8.0$ Hz, 1H), 6.72 (dd, $J = 8.0, 1.4$ Hz, 1H) ppm.

☐   ☐   ☐   ☐
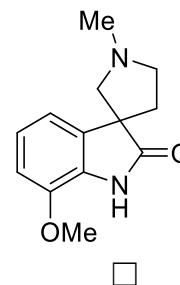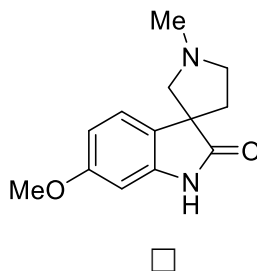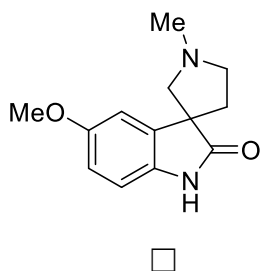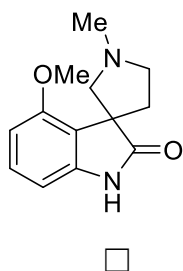
3.7. When the allyl ether of 2 naphthol is heated a sigmatropic rearrangement is initiated. **Write** the structure of major product isolated from this reaction.
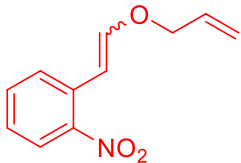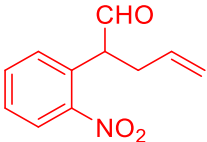
Solution:
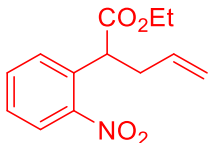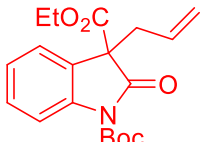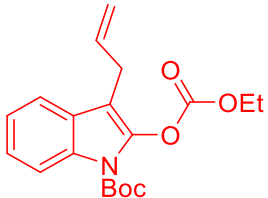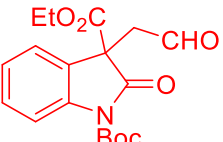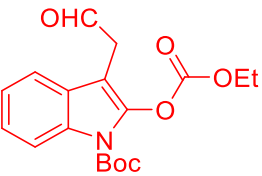
3.1. <u>Draw</u> the structures of **A** and **B**.

A	B
4 points.	*4 points.*
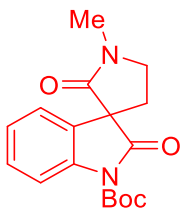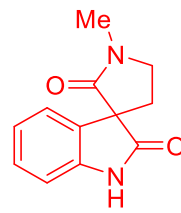
3.2. <u>Draw</u> structures for **C**, **D**, **E**, and **F**.

C	D
4 points.	*4 points.*

E	F
4 points. *3 points will be given for the following answer:* 	*4 points.* *The following tautomer will receive full points:*
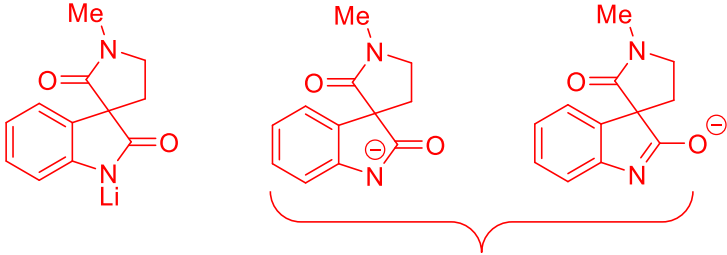
3.3. Choose the correct reaction order for the transformation of **F** to **G**.

☒ Imine formation, then reduction, then amidation	
☐ Amidation, then imine formation, then reduction	*4 points for correct answer.*
☐ Reduction, then amidation, then imine formation	*0 points for incorrect answer.*

3.4. Draw structures for **G** and **H**.

G	H
4 points.	*4 points.*

3.5. Draw the structure of the intermediate for the reaction with *n*-BuLi in the step **H → coerulescine**.

acceptable

Regioselective reduction of carbonyl group can be achieved via lithiation of free NH.

5 points for the correct structure.

3.6. **Choose** the correct structure for compound **I** consistent with the following selected ^{1}H-NMR data: δ 7.05 (d, J = 1.4 Hz, 1H), 6.78 (d, J = 8.0 Hz, 1H), 6.72 (dd, J = 8.0, 1.4 Hz, 1H) ppm.

7.05 ppm
(d, J = 1.4 Hz)

Weaker *ortho, para* director.

Stronger *ortho, para* director.
Since the nitrogen of amide is attached to the ring, it is *ortho*- and *para*-director. The unshared pair of electrons on the nitrogen activates the ring through resonance effects. Thus, bromination followed by methoxylation occurs in the *para*-position.

Ha and Hb protons show AB system
at 6.78 ppm (d, J = 8.0 Hz)
and 6.72 ppm (dd, J = 8.0, 1.4 Hz).

NMR data are compatible with this structure,
but not compatible with the possible *ortho*-substitute product.

5 points.

5 points for correct (second structure) answer.
2 points for third structure.
0 points for incorrect answer.

3.7. When the allyl ether of 2 naphthol is heated a sigmatropic rearrangement is initiated. **Write** the structure of major product isolated from this reaction.
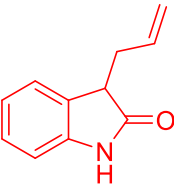
loss of aromaticity in one ring   major product

loss of aromaticity in two rings   minor product

The enone tautomer in which aromaticity lost in one ring for major product is less favored than the enol tautomer.

5 points for the correct identification of major product.

3 points for keto-form (enone) of major product structure.

2 points for minor product structure.

1 points for keto-form (enone) of minor product structure.
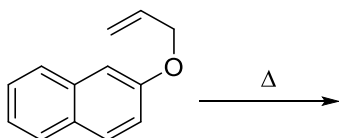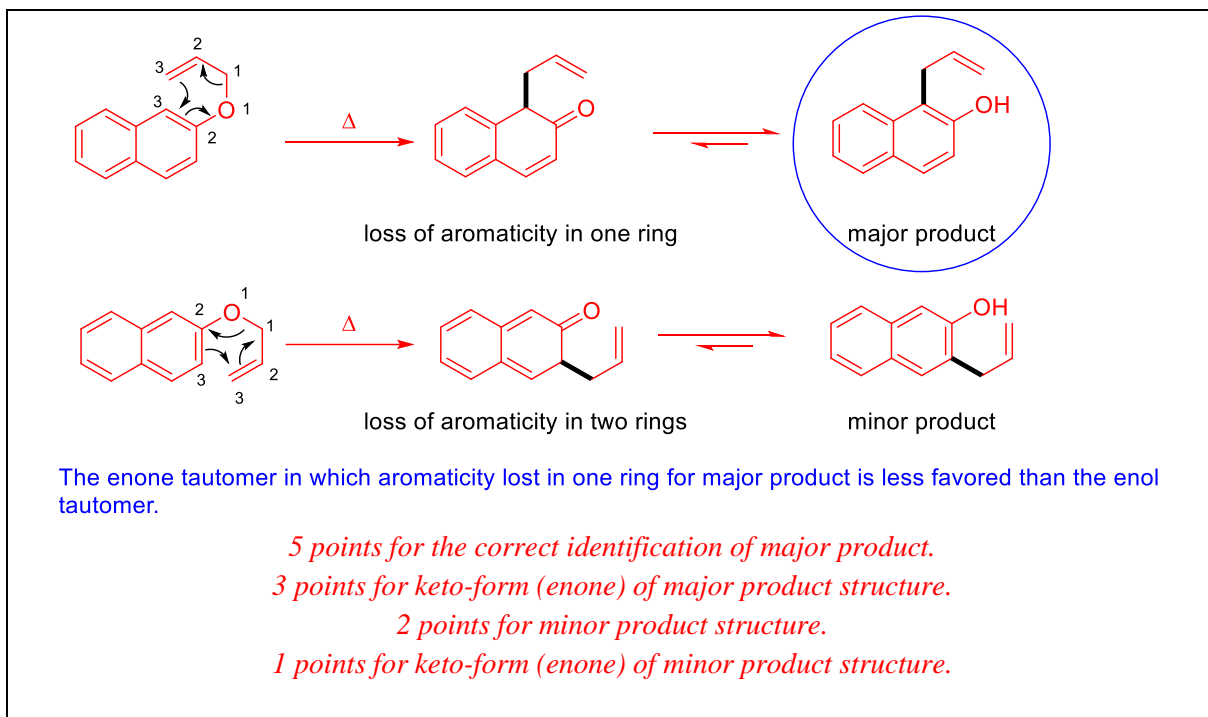
Problem 4	Question	4.1	4.2	4.3	4.4	4.5	4.6	4.7	Total
10% of the total	Points	12	6	6	16	9	9	8	64

Problem 4. Symmetry Does Matter!

There are numerous reactions in organic chemistry that proceed through cyclic transition states and these are classified as pericyclic reactions. Woodward–Hoffmann rules, developed by Robert B. Woodward and Roald Hoffmann, are used to rationalize stereochemical aspects and the activation energy of pericyclic reactions.
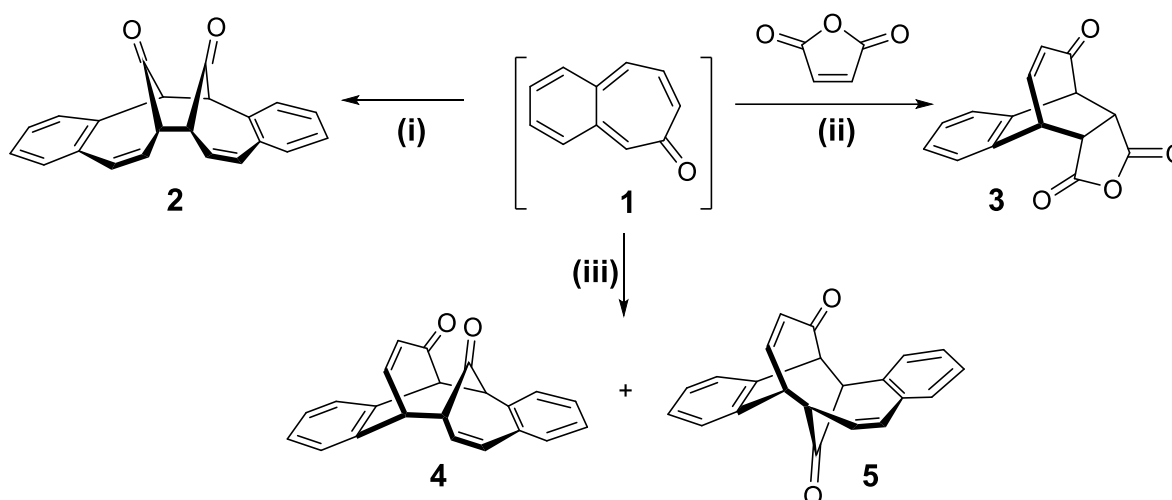
Woodward–Hoffmann rules				
	Electrocyclic reactions		**Cycloadditions**	
Number of electrons	Thermal (Δ)	Photochemical (hν)	Thermal (Δ)	Photochemical (hν)
$4n$ (n = 1, 2, ..)	Conrotatory (con)	Disrotatory	Disfavored	Favored
$4n+2$ (n = 1, 2, ..)	Disrotatory (dis)	Conrotatory	Favored	Disfavored

4.1. Fill in the table for reactions (**i**)–(**iii**) or products **2**–**5**:

Reaction	Product	[? + ?] cycloaddition	Δ or hν
i	2		
ii	3		
iii	4		
	5		

There are three possible benzotropone isomers. Although two of the benzotropone isomers were isolated, 3,4-benzotropone (**1**) has not been isolated. Its instability is attributed to the *o*-quinoidal structure of **1** because it has no sextet electron system in the benzene ring.

4.2. <u>Draw</u> the structures of stable benzotropone isomers **A** (with 6 signals in its ^{13}C-NMR) and **B** (with 11 signals in its ^{13}C-NMR).

4.3. When the following tetraene is reacted under photochemical conditions, symmetry-allowed product(s) of three different ring sizes can form according to the Woodward–Hoffmann rules. **<u>Tick</u>** the correct answer in each row.
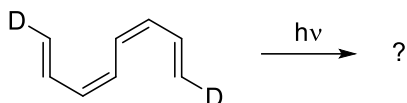
Prof. Dr. Aziz Sancar
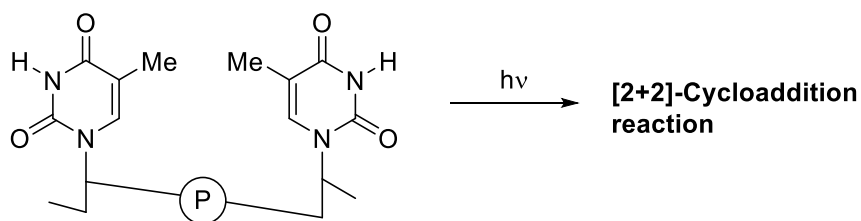
The Nobel Prize in Chemistry 2015 was awarded jointly to the Turkish scientist Aziz Sancar, Swedish scientist Tomas Lindahl, and American scientist Paul Modrich for their "mechanistic studies of DNA repair". Pyrimidine bases found in DNA may undergo a photochemical **[2+2]-cycloaddition reaction** (see above figure) with UV light that reaches a person's skin, causing

damage to DNA, which may ultimately lead to skin cancer. The research by Professor Aziz Sancar focused on the DNA repair mechanism for this type of damage.

Thymine (**T**) is one of the nucleobases that can undergo such a photochemical reaction with UV light. Let us assume that we have a solution of free thymine that was subjected to UV irradiation.
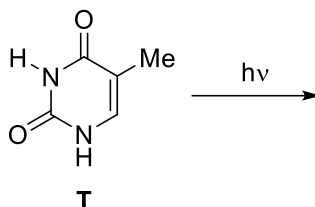
4.4. Considering stereochemistry, **draw** the structures of **all possible products** of this reaction between two free thymine (**T**) molecules. **Circle** the compound(s) which is/are chiral. Drawing only one enantiomer of an enantiomeric pair is sufficient. Please note that only C=C bonds participate in this reaction.

A broad range of halogenated derivatives of norbornadiene (**N**) are known in the literature. Tribromo-norbornadiene ($C_7H_5Br_3$) has six achiral isomers. Three of these isomers (**6**, **7**, and **8**) are given below.
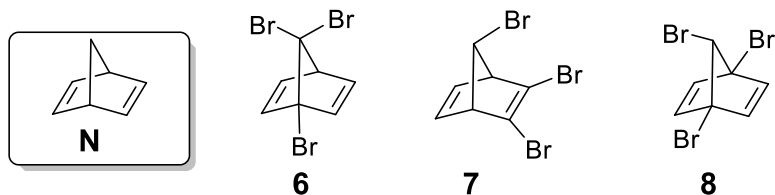
4.5. How many signals do you expect from the ^{13}C-NMR spectra of **6**, **7**, and **8**? **Fill in** the following boxes.

6	7	8
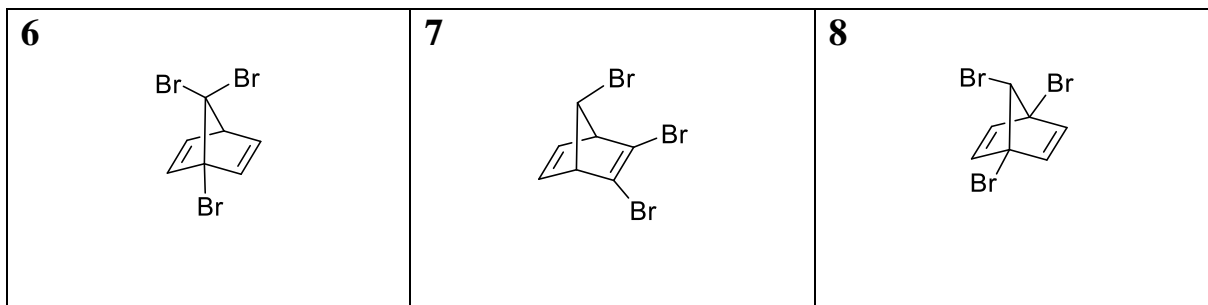
4.6. **Draw** structures of the remaining achiral tribromo-norbornadiene ($C_7H_5Br_3$) isomers (**C**, **D**, and **E**) in addition to **6–8** over the given figures in the boxes.

C	D	E
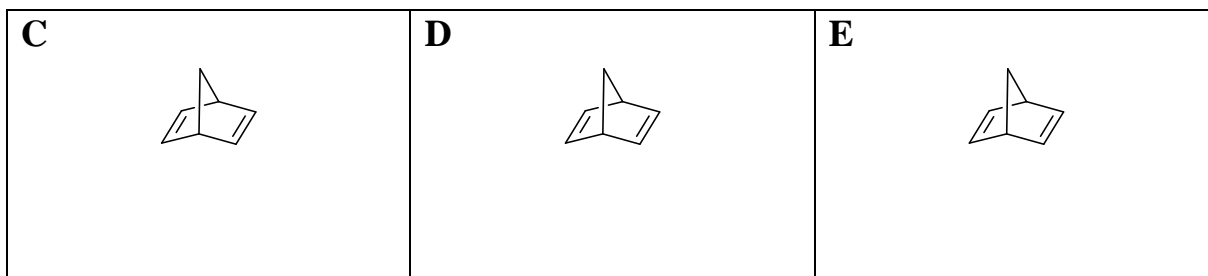
The NMR spectrum of ether **9** is complex. Two MeO– groups are different as are all the hydrogen atoms on the rings. However, diphenol **10** has a very simple NMR spectrum and there are only three types of protons (marked as a, b, and c). A reasonable average structure responsible for all resonance structures and its symmetry is shown as **11**.

9   **10**   **11**
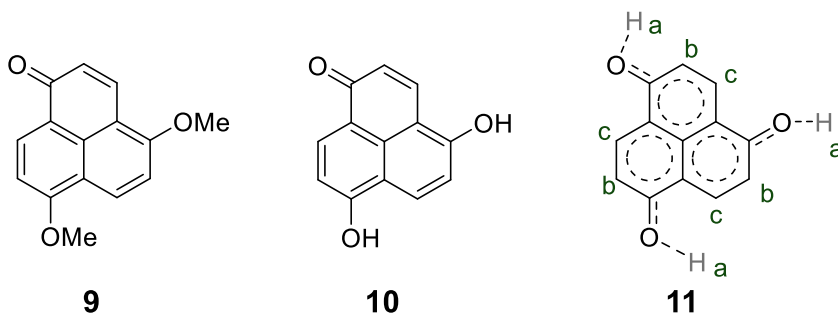
4.7. How many signals do you expect from the ^{13}C- and ^1H-NMR spectra of **12** and **13**?
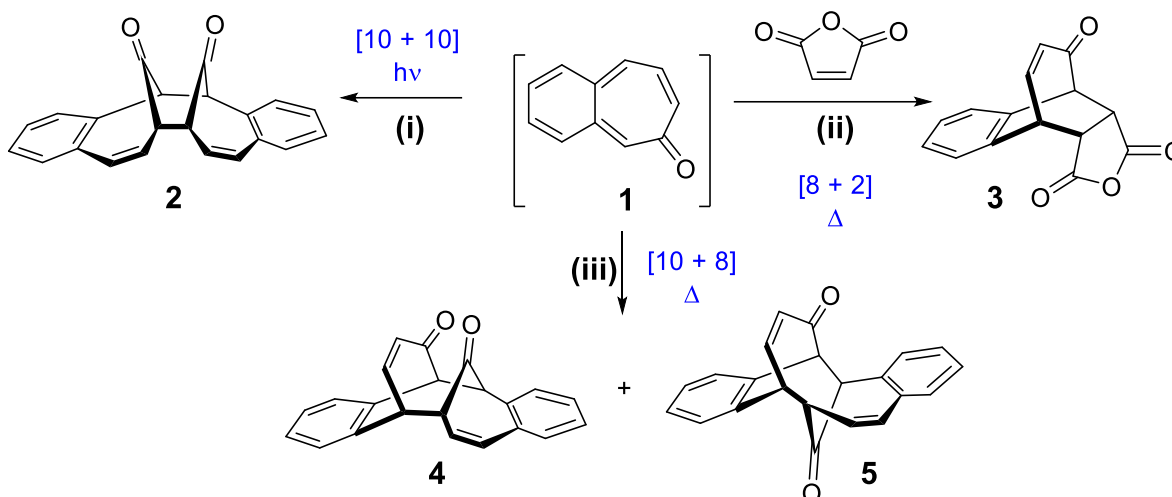
12   **13**

Solution:

4.1. <u>Fill</u> in the table for reactions (**i**)–(**iii**) or products **2**–**5**:

Reaction	Product	[? + ?] cycloaddition	Δ or hν
i	**2**	[10 + 10] ([6 + 6] is also acceptable). *2 points.*	hν *1 point.*
ii	**3**	[8 + 2] ([4 + 2] is also acceptable). *2 points.*	Δ *1 point.*
iii	**4**	[10 + 8] ([6 + 4] is also acceptable). *2 points.*	Δ *1 point.*
	5	[10 + 8] ([6 + 4] is also acceptable). *2 points.*	Δ *1 point.*

4.2. <u>Draw</u> the structures of stable benzotropone isomers **A** (with 6 signals in its ^{13}C-NMR) and **B** (with 11 signals in its ^{13}C-NMR).

A	B
3 points.	*3 points.*
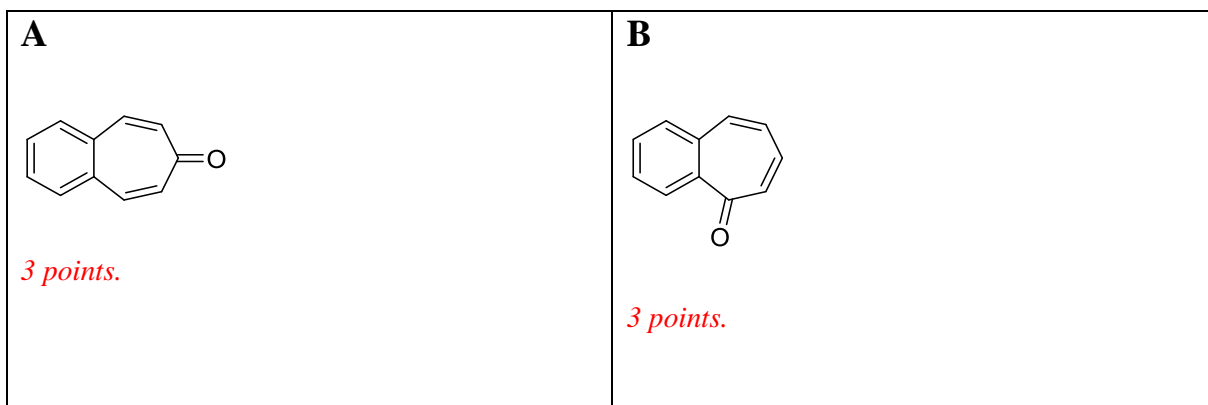
4.3. When the following tetraene is reacted under photochemical conditions, symmetry-allowed product(s) can form according to the Woodward–Hoffmann rules. **<u>Tick</u>** the correct answer(s).
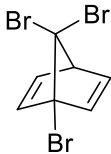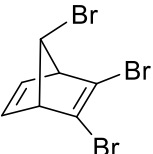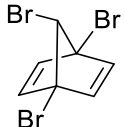
6 points if all the answers are correct.
2 points if there is one mistake.
0 points if there is more than one mistake.
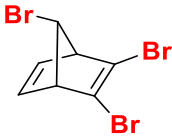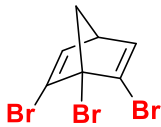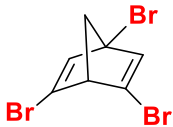
4.4. Considering stereochemistry, **draw** the structures of **all possible products** of this reaction. **Circle** the compound(s) which is/are chiral. Drawing only one enantiomer of an enantiomeric pair is sufficient. Please note that only C=C bonds participate in this reaction.


3 points for each correct structure (12 points in total).
0 points for each structure when there is missing stereochemical information.

4 points (in total) for the correct determination of chirality for the two chiral compounds (2 points each).
2 points if there is one mistake in the determination of chirality.
*0 points if there is more than one mistake in the determination of chirality.*
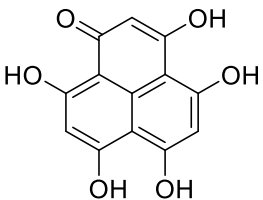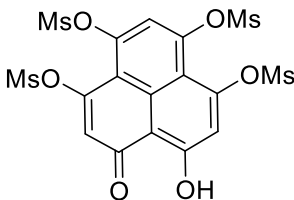
4.5. How many signals do you expect from the ^{13}C-NMR spectra of **6**, **7**, and **8**? **Fill in** the following boxes.

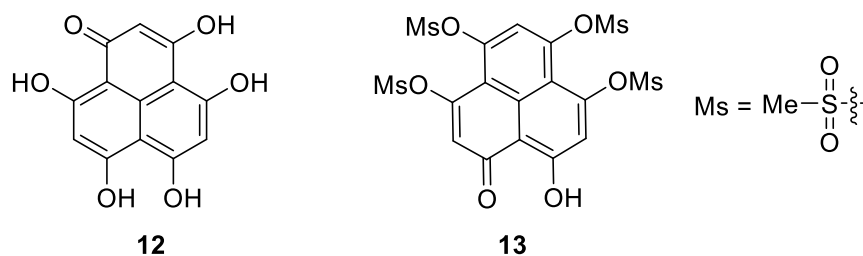| 6	7	8
5 signals in ^{13}C-NMR *3 points.*	4 signals in ^{13}C-NMR *3 points.*	4 signals in ^{13}C-NMR *3 points.*

4.6. **Draw** open structures of the remaining achiral (meso) tribromo-norbornadiene ($C_7H_5Br_3$) isomers (**C**, **D**, and **E**) in addition to **6**–**8** over the given figures in the boxes.

C	D	E
3 points.	*3 points.*	*3 points.*

**4.7**. How many signals do you expect from the ^{13}C- and ^{1}H-NMR spectra of **12** and **13**?

12	13
4 signals in ^{13}C-NMR *(2 points).* *2* signals in ^{1}H-NMR *(2 points).*	*10* signals in ^{13}C-NMR *(2 points).* *5* signals in ^{1}H-NMR *(2 points).*

Ms = MeSO$_2$

Problem 5	Question	5.1	5.2	5.3	5.4	5.5	5.6	5.7	5.8	Total
14% of the total	Points	13	13	15	8	12	10	17	12	100

Problem 5. Konya, Carrot, Beta-Carotene, Vitamin-A, Immune System, Vision
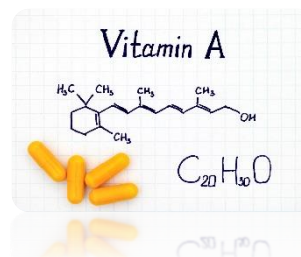
Mevlana (Rumi) was a great mystic and Sufi poet who lived out his days in Konya in the 13th century. The indirect relevance of Konya to chemistry is that the city provides 65% of the country's carrot production, from which one of the essential vitamins (vitamin A) is obtained.

Carrot is an important source of β-carotene, which gives the vegetable its orange color. This molecule is a red-orange pigment naturally found in plants and fruits and is a provitamin A carotenoid. It is converted to vitamin A, which is essential for normal growth and development, the immune system, and vision function.
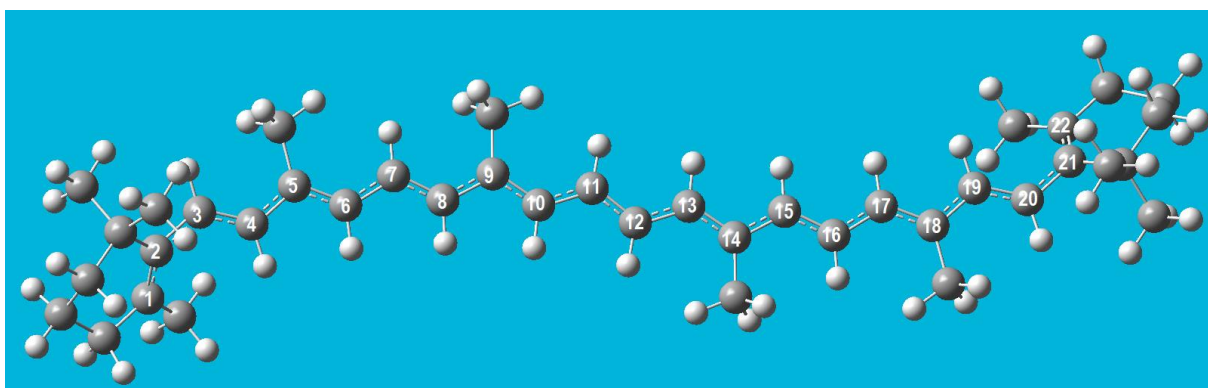
Figure 1. Ball and stick representation of the structure of β-carotene. The gray and white spheres represent the carbon and hydrogen atoms, respectively. The numbered carbon atoms belong to the linear conjugated π-segment of the molecule.

β-Carotene has an extended polyene chain of 22 carbon atoms. It is a conjugated π-system, having alternating single and double bonds. Its experimental maximum absorption wavelength (λ_{max}) is 455 nm. We assume that all the bonds between C_1 and C_{22} are conjugated bonds. There are 22 π-electrons in the molecule (Figure 1).

To a crude approximation, the electrons in the C-$2p_z$ orbitals, which are perpendicular to the molecular plane, are assumed to move along the entire molecule, without interacting with each other. They are like independent particles confined in a molecule moving along the x-axis in one dimension. These characteristics of π-electrons make them eligible for being treated by the simplest model called the **particle in one-dimensional box** model.

The wave function and the energies of the quantized levels for an electron moving in a one-dimensional box with infinite potential walls are given as follows:

$$\Psi_n(x) = \sqrt{\frac{2}{L}} \sin\frac{n\pi x}{L}$$ Eq.1

where n is the quantum number, n=1,2,3,4,…. ∞, and L is the box length.

$$E_n = \frac{n^2 h^2}{8m_e L^2}$$ Eq.2

In two dimension, within the framework of independent particle approximation, the wavefunction is expressed as a product of one-dimensional wavefunctions, and the energy is expressed as a sum of one-dimensional energies. The energy levels of the two dimensional rectangular box is given as follows:

$$E_{n_x,n_y} = \left[\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2}\right]\left\{\frac{h^2}{8m_e}\right\}$$ Eq. 3

where n_x, n_y are the quantum numbers and they are positive integers. L_x, L_y are the dimensions of the box in the 2D model. They are positive numbers.

5.1. Which two of the sentences given below are correct? **Tick** only one answer which includes correct sentences in your answer sheet.

The β-carotene molecule is orange in color because

i)   it absorbs in the visible region of the electromagnetic spectrum.

ii)   HOMO $\rightarrow$LUMO transition occurs by absorption of IR photon.

iii)   the spacing between the 22nd and the 23rd energy levels is equal to the energy of the IR photon at the orange wavelength.

iv)   it absorbs green/blue light and it transmits red/yellow color.

v)   it absorbs in the UV-Vis region since the molecule has no net dipole moment.

Although it is highly unrealistic, let us assume that the conjugated segment of the molecule is linear and treated with the particle in a one-dimensional box model as shown in figure 2. In

this case, the length of the box can be approximated as $L = 1.40 \times n_C$ (in Å), where n_C is the number of carbon atoms in the conjugated segment.

Use this information to answer the questions 5.2–5.6.
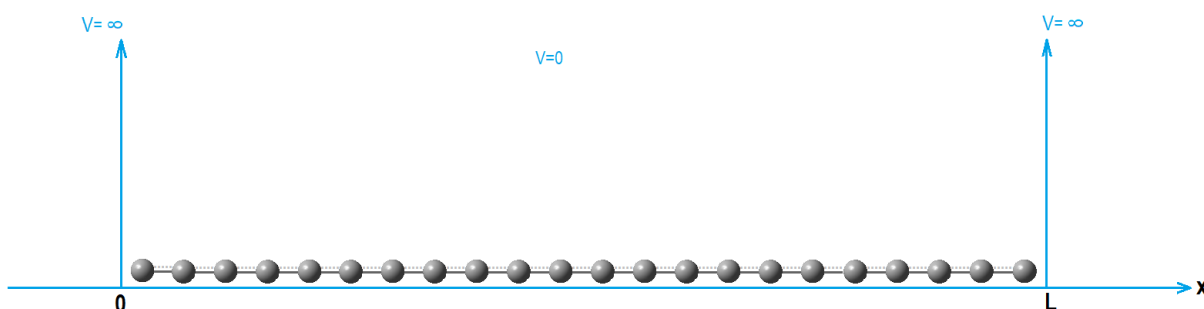
Figure 2. Schematic representation of the conjugated line segment made up carbon atoms of β-carotene in a one-dimensional box of length L.

5.2. <u>Calculate</u> the energies (in J) of the lowest two energy levels

5.3. <u>Draw</u> the wavefunctions of the lowest two energy levels with proper labelling the x-axis.

5.4. <u>Sketch</u> the energy level diagram up to n = 4 showing the relative spacing.

5.5. What is the total π-energy (in J) of the molecule?

5.6. <u>Calculate</u> the wavelength (in nm) at which the transition between the highest occupied and lowest unoccupied energy levels occurs.

Use the particle in a two-dimensional box model to answer questions 5.7–5.8.
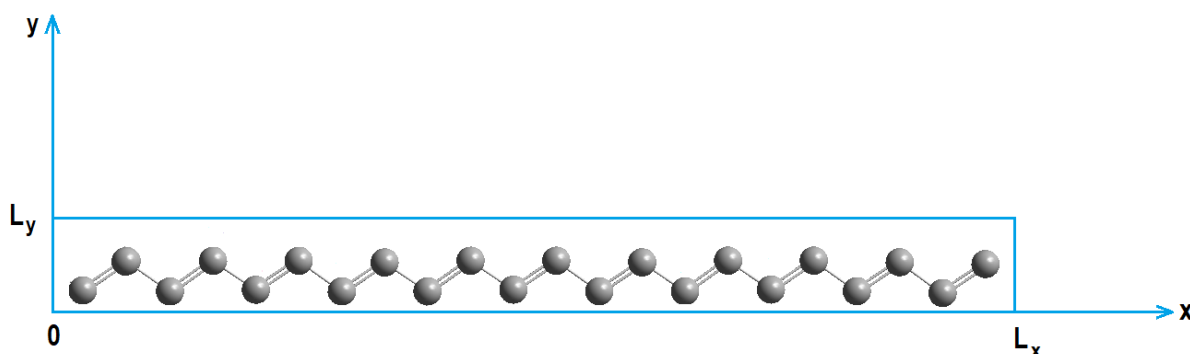
Figure 3. Schematic representation of the conjugated carbon atoms of β-carotene in a two-dimensional box.

Assume that the conjugated segment is made up of conjugated bonds that are all-*trans* to each other. The motion of the π-electrons is studied in the two-dimensional rectangular box with the dimensions $L_x = 26.0$ Å, $L_y = 3.0$ Å (Figure 3).

5.7. **Calculate** the energies (in J) of the highest occupied and the lowest unoccupied energy levels and the wavelength (in nm) at which the transition between these energy levels occurs.

5.8. What should be the L_x value (in Å) in order for the molecule to absorb light at the experimental λ_{max}=455 nm if L_y is kept constant at 3.0 Å. (Assume that the quantum numbers for homo and lumo are the same as in the question 5.7.)

Solution:

5.1. Which two of the sentences given below are correct? **Tick** only one answer which includes correct sentences in your answer sheet.

☐ **a)** i and ii	☐ **b)** i and iii	☒ **c)** i and iv	☐ **d)** i and v
☐ **e)** ii and iii	☐ **f)** ii and iv	☐ **g)** ii and v	☐ **h)** iii and iv
☐ **j)** iii and v	☐ **k)** iv and v		

13 points for the correct answer.

5.2. Calculate the energies (in J) of the lowest two levels.

Calculation:

$L = 1.40 \times 22 = 30.8 \text{ Å}$

$E_n = \frac{n^2 h^2}{8 m_e L^2} = n^2 \ (6.351 \times 10^{-21}) \text{ J} \quad E_1 = 6.351 \times 10^{-21} \text{ J} \quad E_2 = 2.540 \times 10^{-20} \text{ J}$

13 points. 3 points for correct box length, 5 points for each correct energy value.
No partial credit will be given.

5.3. Draw the wavefunctions of the lowest two energy levels with proper labelling the x-axis.

15 points. 3 points for labelling the x-axis and 6 points for the correct drawing of the wavefunctions.
No partial credit will be given.

5.4. <u>**Sketch**</u> the energy level diagram up to n = 4 showing the relative spacing.

8 points. The lowest 4 energy levels, the energy scale and the relative spacing between the energy levels must be shown.
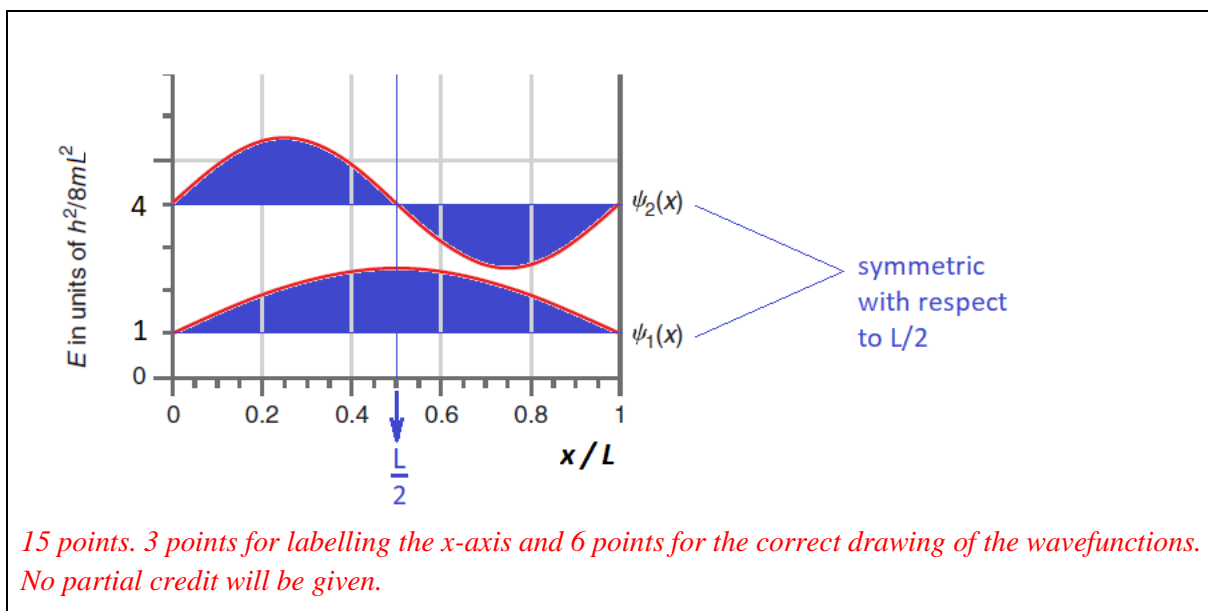
5.5. Calculate the total π-energy (in J) of the molecule?

Calculation:

$$E_{\pi(total)} = 2 \sum_{i=1}^{occupied\ levels} E_i$$

E_π (total) = 2 × (E$_1$+E$_2$+E$_3$+E$_4$+E$_5$+E$_6$+E$_7$+E$_8$+E$_9$+E$_{10}$+E$_{11}$) = 6.427 × 10^{-18} J

12 points for the correct answer. 4 points if the multiplication by 2 is forgotten.
No partial credit will be given.

48

5.6. <u>Calculate</u> the wavelength (in nm) at which the transition between the highest occupied and lowest unoccupied energy levels occurs.

Calculation:

The quantum numbers for the highest occupied and lowest unoccupied energy levels are 11 and 12, respectively.

$$\Delta E = E_{12} - E_{11} = E_n = \frac{12^2 h^2}{8 m_e L^2} - \frac{11^2 h^2}{8 m_e L^2} = \frac{23 h^2}{8 m_e L^2} = \frac{hc}{\lambda} \text{ then,}$$

$$\lambda = \frac{8 m_e c L^2}{23 h} = 1360 \text{ nm}$$

10 points for the correct answer.
If wavelength expression is written correctly but the result is calculated wrongly then 3 points will be deducted.
1 point will be deducted for incorrect unit.

5.7. <u>Calculate</u> the energies (in J) of the highest occupied and the lowest unoccupied energy levels and the wavelength (in nm) at which the transition between these energy levels occurs.

Calculation:

$$E_{n_x, n_y} = \left[\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} \right] \left\{ \frac{h^2}{8 m_e} \right\} = \left[\frac{n_x^2}{26^2} + \frac{n_y^2}{3^2} \right] 6.025 \times 10^{-18} \text{ J, where } L_x \text{ and } L_y \text{ should be in Å.}$$

The quantum numbers and the energies of the highest occupied and the lowest unoccupied energy levels are:

$n_x = 11, n_y = 1$ and $n_x = 12, n_y = 1$

$$E_{11,1} = \left[\frac{11^2}{26^2} + \frac{1^2}{3^2} \right] 6.025 \times 10^{-18} \text{ J} = 17.48 \times 10^{-19} \text{ J}$$

$$E_{12,1} = \left[\frac{12^2}{26^2} + \frac{1^2}{3^2} \right] 6.025 \times 10^{-18} \text{ J} = 19.53 \times 10^{-19} \text{ J}$$

The transition wavelength is:

$\Delta E = E_{12,1} - E_{11,1} = (19.53 - 17.48) \times 10^{-19} \text{ J} = 2.050 \times 10^{-19} \text{ J}$
$\Delta E = E_{photon} = (hc)/\lambda$ **and** $\lambda = (hc)/\Delta E = 9.69 \times 10^{-7} \text{ m}$, $\lambda = 969 \text{ nm}$

17 points for the correct answer.
12 points for correct energies
5 points for the correct wavelength
1 point will be deducted for incorrect unit.
No partial credit will be given.

5.8. What should be the L_x value (in Å) in order for the molecule to absorb light at the experimental λ_{max} if L_y is kept constant at 3.0 Å. (Assume that the quantum numbers for homo and lumo are the same as in the question 5.7.)

Calculation:

$$\Delta E = \left[\frac{12^2}{L_x^2} + \frac{1^2}{L_y^2} - \frac{11^2}{L_x^2} - \frac{1^2}{L_y^2}\right]\left\{\frac{h^2}{8m_e}\right\} = \left[\frac{23}{L_x^2}\right]6.025 \times 10^{-18} = \frac{1.386 \times 10^{-18}}{L_x^2} \quad (\text{L}_x \text{ is in Å})$$

$$\Delta E = E_{photon} = (hc)/\lambda \rightarrow \frac{1.386 \times 10^{-18}}{L_x^2} = \frac{6.626 \times 10^{-34} \times 2.998 \times 10^8}{455 \times 10^{-9}}$$

$$L_x = 1.782 \times 10^{-9}\ m \quad L_x = 17.82\ \text{Å}$$

12 points for the correct answer.
No partial credit will be given.
1 point will be deducted for incorrect unit.

50

	Question	6.1	6.2	6.3	6.4	6.5	6.6	6.7	6.8	**Total**
Problem 6	Points	5	12	6	3	6	6	5	3	**80**
12% of the total	Question	6.9	6.10	6.11	6.12	6.13				
	Points	8	6	6	8	6				

Problem 6. Thermodynamics through an Interstellar Journey

Part 1

In a hypothetical universe, an unknown amount of diborane participates in the following reaction:

$$B_2H_6(g) + 6\ H_2O(l) \rightarrow 2\ H_3BO_3(s) + 6\ H_2(g)$$
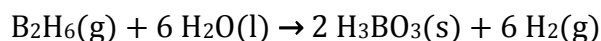
Assume that in this hypothetical universe, $H_3BO_3(s)$ obtained from this reaction was completely sublimed at 300 K. The necessary energy for sublimation was obtained through work released by **one cycle** of an ideal heat engine in which one mole of monoatomic perfect gas flows through the cycle described in the pressure (p) – volume (V) diagram below:

- A→B; isothermal reversible expansion receiving 250 J by heat transfer (q_H) at a temperature of 1000 K (T_H) from a hot source.
- B→D; reversible adiabatic expansion.
- D→C; isothermal reversible compression at a temperature of 300 K (T_C) releasing some amount of heat (q_C) to a cold sink.
- C→A; reversible adiabatic compression.
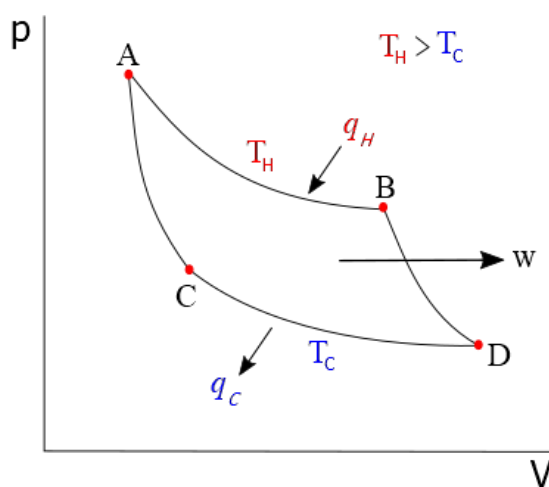
After heat transfers, the remaining energy is released as work (w). Also, q_H and q_C are related to T_C and T_H as follows:

$$\frac{|q_H|}{|q_C|} = \frac{T_H}{T_C}$$

The efficiency of the cycle can be found by work released by cycle (w) divided by heat absorbed by cycle (q_H).

You are provided with the change in enthalpies of the following reactions at 300 K.

(1) $B_2H_6(g) + 6\ Cl_2(g) \rightarrow 2\ BCl_3(g) + 6\ HCl(g)$ $\Delta_r H(1) = -1326\ \textbf{kJ mol}^{-1}$

(2) $BCl_3(g) + 3\ H_2O(l) \rightarrow H_3BO_3(g) + 3\ HCl(g)$ $\Delta_r H(2) = -112.5\ \textbf{kJ mol}^{-1}$

(3) $B_2H_6(g) + 6\ H_2O(l) \rightarrow 2\ H_3BO_3(s) + 6\ H_2(g)$ $\Delta_r H(3) = -493.4\ \textbf{kJ mol}^{-1}$

(4) $\frac{1}{2}H_2(g) + \frac{1}{2}\ Cl_2(g) \rightarrow HCl(g)$ $\Delta_r H(4) = -92.3\ \textbf{kJ mol}^{-1}$
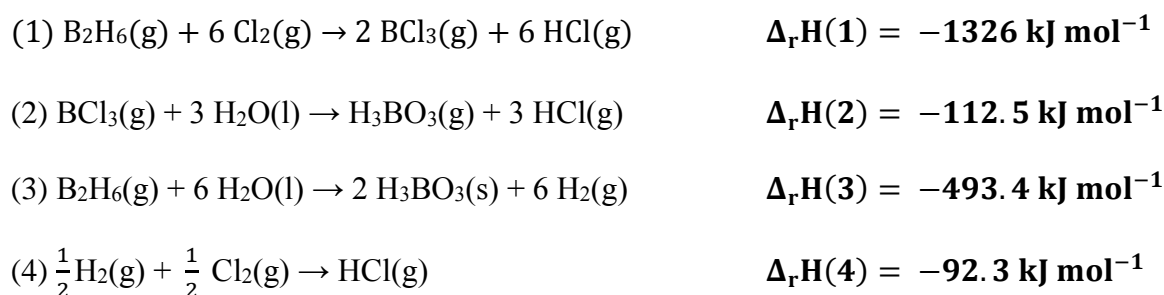
6.1. <u>Calculate</u> the molar enthalpy of sublimation (in kJ mol^{-1}) for H_3BO_3 at 300 K.

6.2. <u>Calculate</u> the $\Delta_r U$ (internal energy) in terms of kJ mol^{-1} at 300 K for the reactions (2) and (4) given above (assume ideal gas behavior for each gaseous species in each reaction).

6.3. <u>Calculate</u> the amount of overall work produced by a heat engine (|w|) in terms of J and the amount of overall heat released to the cold sink ($|q_C|$) in terms of J.

6.4. <u>Calculate</u> the efficiency of the heat engine described above.

6.5. <u>Calculate</u> the entropy change (ΔS) for A→B and D→C processes in the heat engine in terms of J K^{-1}.

6.6. <u>Calculate</u> the Gibbs energy change (ΔG) in terms of J for A→B and D→C processes in the heat engine.

6.7. <u>Calculate</u> the ratio of pressure at point A to the pressure at point B in the cycle (standard pressure: 1 bar).

6.8. <u>Calculate</u> the amount of $H_2(g)$ (in moles) produced according to the reaction given at the beginning of the task for one cycle of the engine.

Part 2

Interstellar journeys can be done by using diborane as rocket fuel. Combustion of diborane is shown below:

$$B_2H_6 \text{ (g)} + 3O_2 \text{ (g)} \rightarrow B_2O_3 \text{ (s)} + 3H_2O \text{ (g)}$$
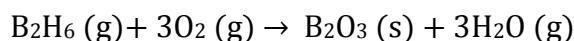
Combustion of diborane is experimented in a 100 L closed container at different temperatures and the equilibrium amounts were recorded.

	8930 K	**9005 K**
B_2H_6(g)	0.38 mol	0.49 mol
H_2O(g)	0.20 mol	0.20 mol

Partial pressure of O_2 (g) was stabilized to 1 bar and kept constant at all conditions. Assume that in this hypothetical universe; $\Delta_rS°$ and $\Delta_rH°$ are independent of temperature, the standard molar entropy (S°) of B_2O_3(s) does not change with pressure, all the gas species behave as an ideal gas, and all species remain in the same phase, without any further decomposition before or after reaction, at all temperatures then:

6.9. <u>Calculate</u> K_p (pressure based equilibrium constant) at 8930 K and 9005 K.

6.10. <u>Calculate</u> $\Delta_rG°$ of the reaction in terms of kJ mol^{-1} at 8930 K and 9005 K. (If you failed to find K_p, please use K_p (8930 K) =2, K_p (9005 K) = 0.5)

6.11. <u>Calculate</u> $\Delta_rG°$(in terms of kJ mol^{-1}), $\Delta_rH°$ (in terms of kJ mol^{-1}), and $\Delta_rS°$ (in terms of J mol^{-1}K^{-1})of the combustion reaction at 298 K. (If you failed to find K_p, please use K_p (8930 K) =2, K_p (9005 K) = 0.5)

6.12. <u>Tick</u> the correct answer in the table by determining whether combustion reactions are favored or not at given T below under standard pressure (1 bar).

	favored	Unfavored
298 K	☐	☐
8930 K	☐	☐
9005 K	☐	☐
9100 K	☐	☐

6.13. Calculate the $\Delta_f H$ (kJ mol^{-1}) and S°(kJ mol^{-1} K^{-1}) of H$_2$O(g) using the values given in the table below. ($\Delta_f H$ = enthalpy of formation, S° = standard entropy)

(If you fail to find $\Delta_r H$° and $\Delta_r S$° of the combustion, please use ΔH° = 1000 kJ mol^{-1}, ΔS°= 150 J K^{-1} mol^{-1})

	ΔH_f (298 K)	S° (298 K)
B$_2$H$_6$ (g)	36.40 kJ mol^{-1}	0.23 kJ mol^{-1} K^{-1}
O$_2$ (g)	0.00 kJ mol^{-1}	0.16 kJ mol^{-1} K^{-1}
B$_2$O$_3$ (s)	−1273 kJ mol^{-1}	0.05 kJ mol^{-1} K^{-1}

Solution:

6.1. <u>Calculate</u> the molar enthalpy of sublimation (in kJ mol^{-1}) for H_3BO_3 at 300 K.

Calculation:

Hess rule:

$$\Delta H(3) - 2 \times \Delta H(2) + 12 \times \Delta H(4) - \Delta H(1) = -2 \times \Delta H_{sub}(H_3BO_3)$$

$$\Delta H_{sub}(H_3BO_3) = 25\ kJ\ mol^{-1}$$

5 points.

2 points will be deducted if student forgets to divide by 2 in last step
3 points will be deducted if Hess rule is applied correctly, but the answer is incorrect due to miscalculation.
If the answer is incorrect due to any other reason, Zero point will be given
If any other unit than asked unit is used in the answer, 0.5 points will be deducted.

6.2. <u>Calculate</u> the Δ_rU (internal energy) in terms of kJ mol^{-1} at 300 K for the reactions (2) and (4) given above (assume ideal gas behavior for each gaseous species in each reaction).

Calculation:

$$\Delta U = \Delta H - \Delta(PV) = \Delta H - (\Delta n_{gas})RT$$
$$RT = 8.3145\ J\ mol^{-1}\ K^{-1} \times 300\ K = 2.494\ kJ\ mol^{-1}$$
$$\Delta U = \Delta H - (\Delta n_{gas}) \times 2.494\ kJ\ mol^{-1}$$
$$\Delta U(2) = -112.5\ kJ - (3\ mol) \times 2.494\ kJ\ mol^{-1} = -120.0\ kJ$$
$$\Delta U(4) = -92.3\ kJ - (0) \times 2.494\ kJ\ mol^{-1} = -92.3\ kJ$$

6x2=12 points.
For each calculation considering that the logic for solving this question is correctly established;
1 point will be deducted if the answer is not correct in due to miscalculation.
If the logic for solving this question is not established correctly, no points will be given.
If any other unit than asked unit is used in the answer, 0.5 points will be deducted.

6.3. <u>Calculate</u> the amount of work produced by a heat engine (w) in terms of J and the amount of heat released to the cold sink (q$_C$) in terms of J.

Calculation:

$$\frac{|q_H|}{|q_C|} = \frac{T_H}{T_C} \rightarrow \frac{250\,J}{q_C} = \frac{1000\,K}{300\,K} \rightarrow |q_C| = 75\,J$$
$$|w| = q_H - |q_C| = 250\,J - 75\,J = 175\,J$$

*For w= 3 points, for 3 q$_c$=3 points, in total **6 points**.*
If q$_c$ is incorrect due to miscalculation, 1 point will be deducted.
If w is incorrect due to miscalculation, 1 point will be deducted.
If w is incorrect due to incorrect q$_c$ calculated in this section, zero point will be deducted.
If w is incorrect due to incorrect q$_c$ calculated in this section and there are miscalculations, 1 point will be deducted.
If any other unit than asked unit is used in the answer, 0.5 points will be deducted.

6.4. <u>Calculate</u> the efficiency of the heat engine described above.

Calculation:

$$\boldsymbol{efficiency} = \frac{|w|}{|q_H|} = \frac{175\,J}{250\,J} = \boldsymbol{0.70}$$

3 points.
If efficiency is in correct due to miscalculation, 1 point will be deducted.
If efficiency is incorrect due to incorrect w obtained in 6.3, zero point will be deducted.
If efficiency is incorrect due to incorrect w obtained in 6.3 and there are miscalculations, 1 point will be deducted.
If any unit is used in the answer, 0.5 points will be deducted.

6.5. Calculate the entropy change (ΔS) for A→B and D→C processes in the heat engine in terms of J K^{-1}.

Calculation:

$$\Delta S = \frac{dq_{reversible}}{T}$$

For A→B

$$\boldsymbol{\Delta S_{A \to B}} = \frac{250\,J}{1000\,K} = \boldsymbol{0.25\,J\,K^{-1}}$$

For D→C

$$\boldsymbol{\Delta S_{D \to C}} = \frac{-75\,J}{300\,K} = \boldsymbol{-0.25\,J\,K^{-1}}$$

*3 points for A→B, 3 points for D→C, in total **6 points**.*
If $\boldsymbol{\Delta S_{A \to B}}$ is incorrect due to miscalculation, 1 points will be deducted.
Since q$_H$ is provided in the question, If $\boldsymbol{\Delta S_{A \to B}}$ is incorrect due to any other reason, no points will be given
If $\boldsymbol{\Delta S_{D \to C}}$ is incorrect due to miscalculation, 1 points will be deducted.
If $\boldsymbol{\Delta S_{D \to C}}$ is incorrect due to incorrect q$_c$ obtained in 6.3, Zero point will be deducted. However, if there are miscalculations, 1 points will be deducted.
If any other unit than asked unit is used in the answer, 0.5 points will be deducted.

6.6. Calculate the Gibbs energy change (ΔG) in terms of J for A→B and D→C processes in the heat engine.

Calculation:

$$\Delta G = \Delta H - T\Delta S, for\ isothermal\ processes\ \Delta H = 0, then\ \Delta G = -T\Delta S$$

$$\Delta \boldsymbol{G_{A \to B}} = -0.25\,J\,K^{-1} \times 1000\,K = \boldsymbol{-250\,J}$$

$$\Delta \boldsymbol{G_{D \to C}} = -(-0.25\,J\,K^{-1}) \times 300\,K = \boldsymbol{75\,J}$$

*3 points for A→B, 3 points for D→C, in total **6 points**.*
If $\Delta \boldsymbol{G_{A \to B}}$ is incorrect due to miscalculation, 1 points will be deducted.
If $\Delta \boldsymbol{G_{D \to C}}$ is incorrect due to miscalculation, 1 points will be deducted.
If $\Delta \boldsymbol{G_{A \to B}}$ is incorrect due to incorrect $\boldsymbol{\Delta S_{A \to B}}$ obtained in 6.5, zero point will be deducted. But if there are miscalculations, 1 points will be deducted.
If $\Delta \boldsymbol{G_{D \to C}}$ is incorrect due to incorrect $\boldsymbol{\Delta S_{D \to C}}$ obtained in 6.5, zero point will be deducted. But if there are miscalculations, 1 points will be deducted.
If ΔH is not considered to be zero, no points will be given.

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If any other unit than asked unit is used in the answer, 0.5 points will be deducted.

6.7. Calculate the ratio of pressure at point A to the pressure at point B in the cycle.

Calculation:

$$\Delta S = \frac{dq_{reversible}}{T} = nRln\frac{V_B}{V_A}$$

$$0.25 \, J \, K^{-1} = 1 \, mol \times 8.314 \, J \, mol^{-1}K^{-1}ln\frac{V_B}{V_A}$$

$$ln\frac{V_B}{V_A} = 0.03007 \;\rightarrow\; \frac{V_B}{V_A} = 1.03$$

$$\frac{V_B}{V_A} = \frac{P_A}{P_B} \;\rightarrow\; \boldsymbol{\frac{P_A}{P_B} = 1.03}$$

5 points.
If student can find up to $ln\frac{V_B}{V_A}$ with correct value and calculate no further, 3 points will be deducted
If student can find up to $ln\frac{V_B}{V_A}$ with incorrect value and calculate no further, 3.5 points will be deducted
If student can find up to $\frac{V_B}{V_A}$ with correct value and calculate no further, 2 points will be deducted
If student can find up to $\frac{V_B}{V_A}$ with incorrect value and calculate no further, 2.5 points will be deducted
If student gets incorrect $\frac{P_A}{P_B}$ due to miscalculation, 1.5 points will be deducted.
If student uses incorrect ΔS obtained from 6.5 or given in the question, no points will be deducted.
If any unit is used in the answer, 0.5 points will be deducted.

6.8. <u>Calculate</u> the amount of $H_2(g)$ (in moles) produced during the formation of boric acid.

Calculation:

$$\frac{0.175\ kJ}{25\ kJ\ mol^{-1}} = 7\ \times 10^{-3} moles\ of\ H_3BO_3\ is\ sublimated$$

$$(7 \times 10^{-3}) \times 3 = 21 \times 10^{-3}\ moles\ of\ H_2\ is\ generated$$

3 points.
If student gives incorrect answer due to miscalculation in any step, no points will be given.
If student gives incorrect answer due to incorrect w obtained in 6.3, no points will be deducted. If
there are miscalculations, the grading scheme given above will be applied.
If student gives incorrect answer due to incorrect sublimation enthalpy obtained in 6.1, no points
will be deducted. If there are miscalculations, the grading scheme given above will be applied.
If any other unit than asked unit is used in the answer, 0.5 points will be deducted.

6.9. <u>Calculate</u> K_p (pressure based equilibrium constant) at 8930 K and 9005.

Calculation:

$$PV = nRT \rightarrow P = \frac{nRT}{V} \rightarrow P = \frac{n \times 0.08205\ L\ atm\ mol^{-1}K^{-1} \times T}{100\ L}$$

At 8930 K,

$$For\ B_2H_6(g) \rightarrow P_{B_2H_6(g)} = \frac{0.38\ mol \times 0.08205\ L\ atm\ mol^{-1}K^{-1} \times 8930\ K}{100\ L}$$
$$= 2.784\ atm = 2.821\ bar$$
$$For\ H_2O(g) \rightarrow P_{H_2O(g)} = \frac{0.20\ mol \times 0.08205\ L\ atm\ mol^{-1}K^{-1} \times 8930\ K}{100\ L} = 1.465\ atm$$
$$= 1.484\ bar$$

At 9005 K,

$$For\ B_2H_6(g) \rightarrow P_{B_2H_6(g)} = \frac{0.49\ mol \times 0.08205\ L\ atm\ mol^{-1}K^{-1} \times 9005\ K}{100\ L}$$
$$= 3.618\ atm = 3.666\ bar$$

$$For\ H_2O(g) \rightarrow P_{H_2O(g)} = \frac{0.20\ mol \times 0.08205\ L\ atm\ mol^{-1}K^{-1} \times 9005\ K}{100\ L} = 1.478\ atm$$
$$= 1.498\ bar$$
$$\boldsymbol{K_p\ at\ 8930\ K} = \frac{(P_{H_2O(g)})^3}{(P_{O_2(g)})^3 \times P_{B_2H_6(g)}} = \frac{(1.484)^3}{(1)^3 \times 2.821} = \boldsymbol{1.159}$$

$$K_p \ at \ 9005 \ K = \frac{(P_{H_2O(g)})^3}{(P_{O_2(g)})^3 \times P_{B_2H_6(g)}} = \frac{(1.498)^3}{(1)^3 \times 3.666} = \mathbf{0.917}$$

2x4 points for K$_p$.
For each calculation of K$_p$,
If answer is incorrect due to miscalculation, 1 point will be deducted.
If answer is incorrect due to incorrect $P_{B_2H_6(g)}$ calculated in this part, no points will be deducted.
However, if there are miscalculation, 1 point will be deducted.
If answer is incorrect due to incorrect K$_p$ calculated in this part, no points will be deducted.
If answer is incorrect due to miscalculation and incorrect K$_p$, 1 point will be deducted.

6.10. **Calculate** $\Delta_r G°$ of the reaction in terms of kJ mol^{-1} at 8930 K and 9005 K (use three decimal places for your result).
(If you failed to find K$_p$, please use K$_p$ (8930 K) =2, K$_p$ (9005 K) = 0.5)

Calculation:

The equilibrium constant is determined by gaseous species, K$_p$ is going to be used to calculate $\Delta G°$:

$$\Delta G° = -RT ln K_p$$

$$\mathbf{\Delta G° \ at \ 8930 \ K} = -8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \times 8930 \ K \ ln1.159 = \mathbf{-10.956 \ kJ \ mol^{-1}}$$

$$\mathbf{\Delta G° \ at \ 9005 \ K} = -8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \times 9005 \ K \ ln0.917 = \mathbf{6.488 \ kJ \ mol^{-1}}$$

*3 points for each $\Delta G°$, in total **6 points**.*
For each $\Delta G°$;
If $\Delta G°$ is incorrect due to miscalculation, 1 points will be deducted.
If student uses incorrect value for K$_p$ obtained from 6.9 or provided in this question, no points will be deducted. If there are miscalculations, if there are miscalculations, 1 point will be deducted.
If any other unit than asked unit is used in the answer, 0.5 points will be deducted.

6.11. **Calculate** $\Delta_r G°$(in terms of kJ mol^{-1}), $\Delta_r H°$ (in terms of kJ mol^{-1}), and $\Delta_r S°$ (in terms of J mol^{-1}K^{-1})of the combustion reaction at 298 K.

(If you failed to find K$_p$, please use K$_p$ (8930 K) =2, K$_p$ (9005 K) = 0.5)

Calculation:

$\Delta G° = \Delta H° - T\Delta S°$

$\Delta G°(8930\ K) = -10956\ J\ mol^{-1} = \Delta H° - 8930\ K \times \Delta S°$

$\Delta G°(9005\ K) = 6488\ J\ mol^{-1} = \Delta H° - 9005\ K \times \Delta S°$

$\boldsymbol{\Delta S° = -249.1\ J\ mol^{-1}K^{-1}}$

$\boldsymbol{\Delta H° = -2237.1\ kJ\ mol^{-1}}$

$\boldsymbol{\Delta G°(298\ K) = -2237.1\ kJ\ mol^{-1} - 298\ K \times (-0.2491\ kJ\ mol^{-1}K^{-1})}$
$\boldsymbol{= -2162.9\ kJ\ mol^{-1}}$

*2 points for °, 2 points for $\boldsymbol{\Delta H°}$, 2 points for $\boldsymbol{\Delta G°(298\ K)}$, in total **6 points**.*
For ΔS° and ΔH°, if student gives incorrect answer due to miscalculation, 1 point will be deducted.
****
Students may calculate ΔS° after finding ΔH° by using;
$$lnK = -\frac{\Delta_r H°}{RT} + \frac{\Delta_r S°}{R}$$
If student gives incorrect answer due to miscalculation, 1 point will be deducted.
If student gives incorrect answer due incorrect ΔH° obtained by in this part, zero point will be deducted. If there are miscalculations, 1 point will be deducted.
****
For ΔG°, if student gives incorrect answer due to miscalculation, 1 point will be deducted.
For ΔG°, if student gives incorrect answer due to incorrect ΔS° obtained in this part, zero point will be deducted. If there are miscalculations, 1 point will be deducted.
For ΔG°, if student gives incorrect answer due to incorrect ΔH° obtained in this part, zero point will be deducted. If there are miscalculations, 1 point will be deducted.
For ΔG°, if student gives incorrect answer due to incorrect ΔS° and ΔH° obtained in this part, zero point will be deducted. If there are miscalculations, 1 point will be deducted.

If student uses any incorrect value for $\Delta G°$ and/or K$_p$ obtained from 6.9 and 6.10 or given in this question, no points will be deducted. If there are miscalculations, If there are miscalculations, 1 point will be deducted.

Students who solved this problem by using;

$$ln\frac{K_2}{K_1} = -\frac{\Delta_r H°}{R}(\frac{1}{T_2} - \frac{1}{T_1})$$

Correct answers obtained by using this equation will be graded over 6 points with *2 points for **ΔS°*** ,
*2 points for **ΔH°**, 2 points for **ΔG°**($\mathbf{298\ K}$)*

However;

For ΔH°, if student gives incorrect answer due to miscalculation, 1 point will be deducted.

For ΔS°, if student gives incorrect answer due to miscalculation, 1 point will be deducted.

For ΔS°, if student gives incorrect answer due incorrect ΔH° obtained by using equation above, zero point will be deducted. If there are miscalculations, 1 point will be deducted.

****

Students may calculate ΔS° after finding ΔH° by using;

$$lnK = -\frac{\Delta_r H°}{RT} + \frac{\Delta_r S°}{R}$$

If student gives incorrect answer due to miscalculation, 1 point will be deducted.

If student gives incorrect answer due incorrect ΔH° obtained by in this part, zero point will be deducted. If there are miscalculations, 1 point will be deducted.

****

For ΔG°, if student gives incorrect answer due to miscalculation, 1 point will be deducted.

For ΔG°, if student gives incorrect answer due to incorrect ΔH° obtained in this part, zero point will be deducted. If there are miscalculations, 1 point will be deducted.

For ΔG°, if student gives incorrect answer due to incorrect ΔS° obtained in this part, zero point will be deducted. If there are miscalculations, 1 point will be deducted.

For ΔG°, if student gives incorrect answer due to incorrect ΔS° and ΔH° obtained in this part, zero point will be deducted. If there are miscalculations, 1 point will be deducted.

If student uses any incorrect value for *ΔG°* and/or K$_p$ obtained from 6.9 and 6.10 or given in this question, no points will be deducted. If there are miscalculations, the grading scheme above will be applied

If any other unit than asked unit is used in the answer, 0.5 points will be deducted.

6.12. **Tick** the correct answer on the table by determining whether combustion reactions are favored or not at given T below under standard pressure (1 bar).
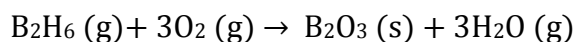
	Favored	Unfavored
298 K	☒	☐
8930 K	☒	☐
9005 K	☐	☒
9100 K	☐	☒
8 points. Each correct answer is 2 points.		

6.13. <u>**Calculate**</u> the Δ_fH (kJ mol^{-1}) and S°(kJ mol^{-1} K^{-1}) of H$_2$O(g) using the values given in the table below. (Δ_fH = enthalpy of formation, S° = standard entropy)

(If you fail to find Δ_rH° and Δ_rS° of the combustion, please use ΔH° = 1000 kJ mol^{-1}, ΔS°= 150 J K^{-1} mol^{-1})

Calculation:

$$B_2H_6\ (g)+ 3O_2\ (g) \rightarrow\ B_2O_3\ (s) + 3H_2O\ (g)$$

$$\Delta H^\circ = \left[\Delta H_f\left(B_2O_3(s)\right) + 3 \times \Delta H_f\left(H_2O(g)\right)\right] - \left[\Delta H_f\left(B_2H_6(g)\right) + 3 \times \Delta H_f\left(O_2(g)\right)\right]$$

$$\Delta S^\circ = \left[S^\circ\left(B_2O_3(s)\right) + 3 \times S^\circ\left(H_2O(g)\right)\right] - \left[S^\circ\left(B_2H_6(g)\right) + 3 \times S^\circ\left(O_2(g)\right)\right]$$

$$\Delta H_f\left(H_2O(g)\right) = -309.2\ kJ\ mol^{-1}$$

$$S^\circ\left(H_2O(g)\right) = 0.137\ \text{kJ mol}^{-1}\ \text{K}^{-1}$$

3 points for $\Delta H_f\left(H_2O(g)\right)$, *3 points for* $S^\circ\left(H_2O(g)\right)$, *in total* **6 points**.
If $\Delta H_f\left(H_2O(g)\right)$ is in correct due to miscalculation, 2 points will be deducted.
If $S^\circ\left(H_2O(g)\right)$ is in correct due to miscalculation, 2 points will be deducted.
No points will be deducted if wrong values are obtained for ΔH° and ΔS° from 6.11 or the values provided here. If there are miscalculations, 2 points will be deducted for each.

If any other unit than asked unit is used in the answer, 0.5 points will be deducted.

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| Problem 7	Question	7.1	7.2	7.3	7.4	7.5	7.6	7.7	7.8	7.9	Total
12% of the total	Points	4	8	6	8	8	14	19	12	6	85

Problem 7. Phthalocyanines
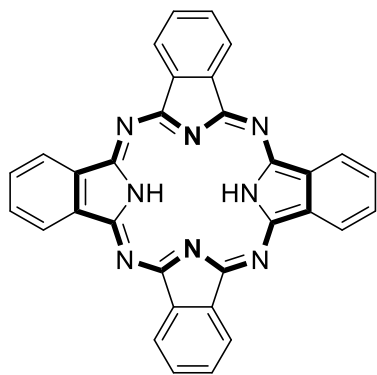

1

Emeritus Professor Özer Bekaroğlu

The term phthalocyanine (Pc) takes its origin from the Greek "naphtha", which means rock oil, and "cyanine", which means dark blue. Turkish scientist Özer Bekaroğlu can be regarded as the pioneer of Pc chemistry in Turkey.

Metal-free phthalocyanine (**1**, H_2Pc) is a large planar macrocyclic compound with the formula $(C_8H_4N_2)_4H_2$.
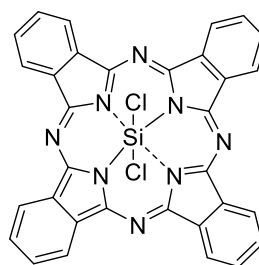
7.1. How many π-electrons are there in the bold region of the H_2Pc molecule in compound **1** shown above?
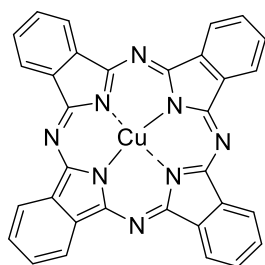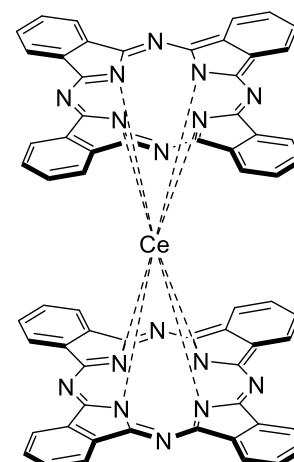

CuPc
2
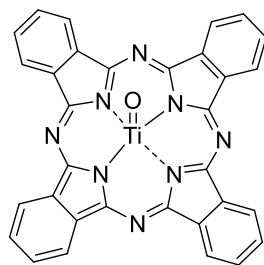
TiOPc
3

SiCl₂Pc
4

Ce(Pc)₂
5

Pcs containing one or two metal ions are called metallo-phthalocyanines (MPcs) and they exhibit different geometries as given above.

7.2. Complete the table in your answer sheet by determining the coordination number of central ions in **2–5**.

Central ion	Copper ion	Titanium ion	Silicon ion	Cerium ion
Coordination number				

7.3. Complete the table in your answer sheet by determining the oxidation number of each metal (Cu, Ti, and Ce) in **2**, **3**, and **5**.

Metal in compounds	2	3	5
Oxidation number			

7.4. Complete the table in your answer sheet by determining the geometry of compounds **2–5**.

Geometry	Compound
Octahedral	
Square prism	
Square pyramidal	
Square planar	

7.5. Complete the table in your answer sheet by determining the magnetic property of compounds **2–5**.

- Use the letter "**p**" for paramagnetic property and letter "**d**" for a diamagnetic property.

| Compound	Magnetic property
2	
3	
4	
5	

7.6. <u>Write</u> the ground-state electron configuration of the silicon (Si) ion in the compound **4** and **<u>find</u>** all the quantum numbers for the 2p electrons in its ground state.

Electron configuration:				
	n	*l*	*m₁*	*mₛ*
Quantum numbers for 2p electrons:				

Metal-free phthalocyanine (**1**, H$_2$Pc) is commonly formed through the cyclotetramerization of phthalonitriles. On the other hand, Pcs having different substituents are called asymmetric, which can be prepared by the statistical cyclization of two different phthalonitriles. This method has no selectivity and the product is a mixture of all possible isomers.

7.7. <u>Draw</u> the possible products that may occur in the statistical cyclization method by using **F** and **G**. If there are any stereoisomers label as *cis-* or *trans-*.

- **F** and **G** represent two different symmetrical phthalonitriles.
- One of the products is **F₄** as given below.
- Draw other products similar to the format of **F₄**.

F₄
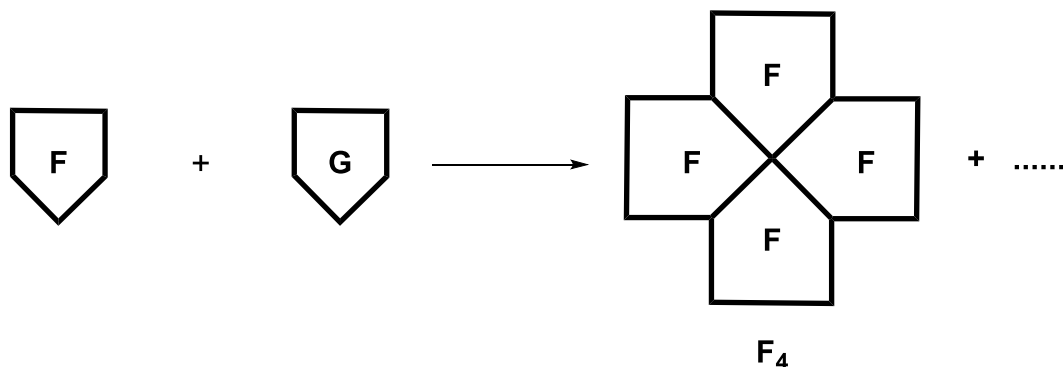
Pcs are used as photosensitizers in the photodynamic therapy (PDT) of cancer due to their strong absorption in the visible spectrum and high molar absorption coefficients. PDT consists of three essential components: **photosensitizer**, light, and oxygen. None of these is individually toxic, but together they initiate a photochemical reaction resulting in the generation of cytotoxic singlet oxygen (^{1}O$_2$) that can destroy cancer cells.

$$\text{(multiplicity) } ^1O_2$$

- The multiplicity of an energy level is defined as $2S+1$
- If the two spins are parallel ($\uparrow\uparrow$), $S = 1$, and if the two spins are antiparallel ($\uparrow\downarrow$), $S = 0$.

7.8. Draw the molecule orbital (MO) diagram of the lowest energy singlet state of dioxygen ($^1O_2$) and calculate bond order.
- There are no unpaired electrons in that state!

7.9. If the wavelength of the light needed to excite triplet oxygen into singlet oxygen is 1270 nm, **calculate** the energy (in kJ/mol) needed for this transition process.

Solution:

7.1. How many π-electrons are there in the bold region of the H_2Pc molecule in compound **1** shown above?

> The number of π-electrons in an H_2Pc: **18 π-electrons**
>
> *4 points for correct answer.*
> *0 points if the number of electrons is not correct.*

7.2. <u>Complete</u> the table in your answer sheet by determining the coordination number of central ions in **2–5**.

Central ion	Copper ion	Titanium ion	Silicon ion	Cerium ion
Coordination number	4	5	6	8

2 points for each correct answer (8 points in total).
0 points if the answer is not correct.

7.3. <u>Complete</u> the table in your answer sheet by determining the oxidation number of each metal (Cu, Ti, and Ce) in **2**, **3**, and **5**.

Metal in compounds	2	3	5
Oxidation number	+2	+4	+4

2 points for each correct answer (6 points in total).
0 points if the answer is not correct.

7.4. <u>Complete</u> the table in your answer sheet by determining the geometry of compounds **2–5**.

Geometry	Compound
Octahedral	4
Square prism	5
Square pyramidal	3
Square planar	2

2 points for each correct answer (8 points in total).
0 points if the answer is not correct.

**7.5. <u>Complete</u>** the table in your answer sheet by determining the magnetic property of compounds **2**–**5**.

Compound	Magnetic property
2	p
3	d
4	d
5	d
2 points for each correct answer (8 points in total). *0 points if the answer is not correct.*	

7.6. <u>Write</u> the ground-state electron configuration of the silicon (Si) ion in the compound **4** and **<u>find</u>** all the quantum numbers for the 3p electrons in its ground state.

Electron configuration: Si^{4+}: [He] $2s^2 2p^6$				
2 points for writing electron configuration. (0 points if the electron configuration is not correct.)				
	n	l	m_l	m_s
	2	1	+1	+1/2
	2	1	0	+1/2
	2	1	-1	+1/2
Quantum numbers for 2p electrons:	2	1	+1	-1/2
	2	1	0	-1/2
	2	1	-1	-1/2
	2 points for each correct quantum set (12 points in total). *0 points if one of the quantum number is not correct in the set.*			

7.7. <u>**Draw**</u> the possible products that may occur in the statistical cyclization method by using **F** and **G**. If there are any stereoisomers label as *cis-* or *trans-*.
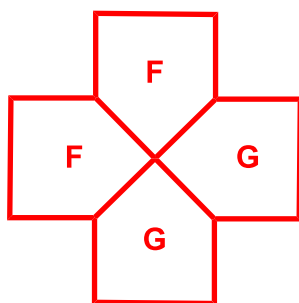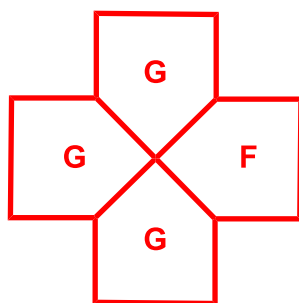
Products:
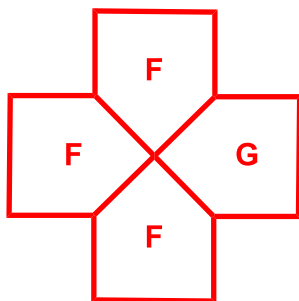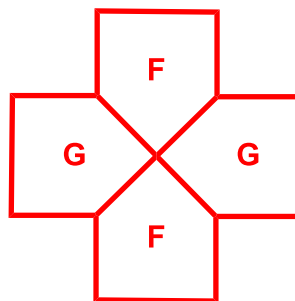
F_3G *trans*-F_2G_2
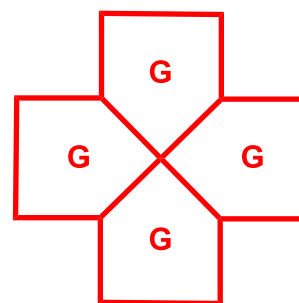
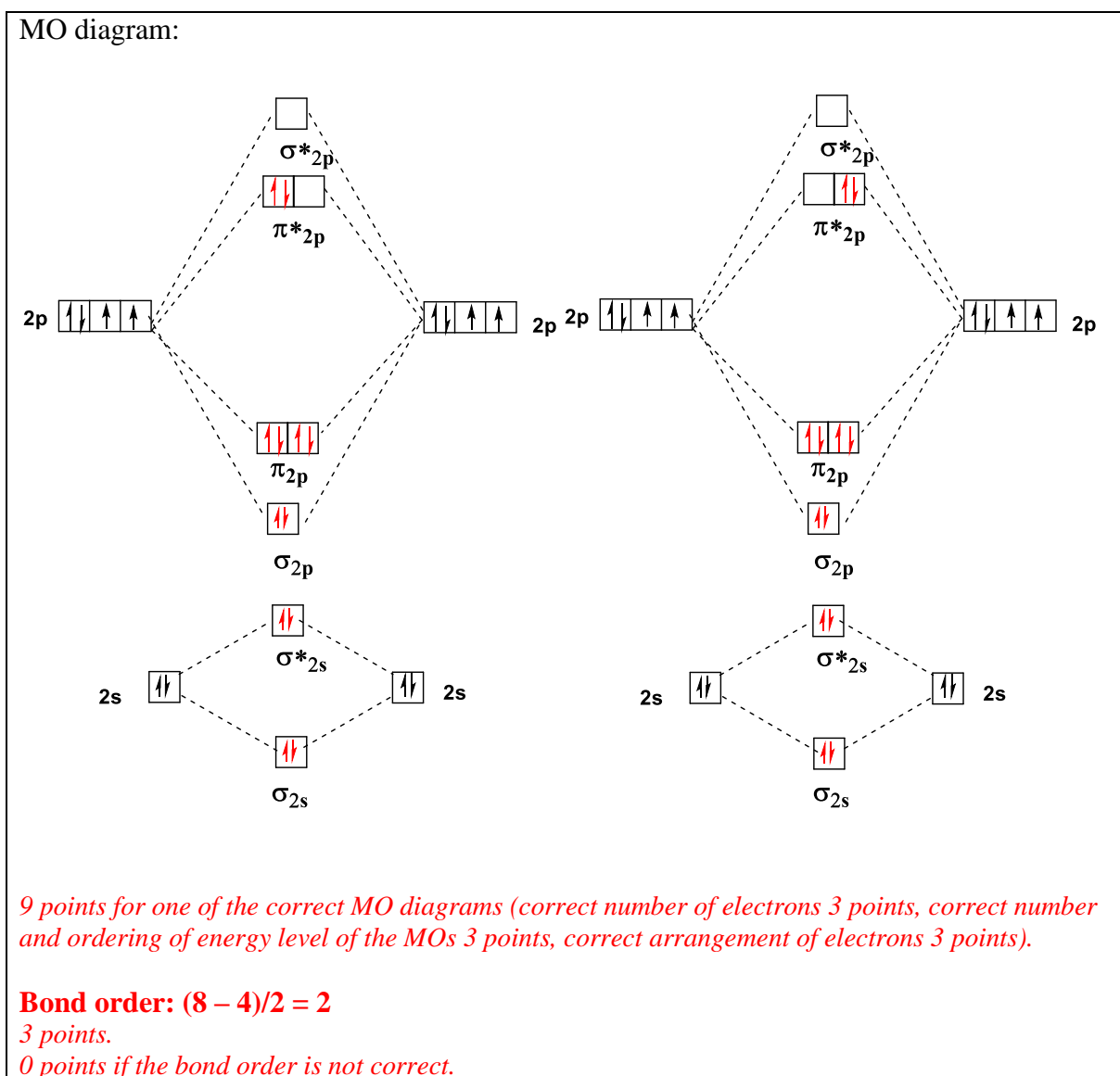*cis*-F_2G_2 G_3F G_4

3 points for each of the structures (15 points in total).
2 point for each of the streoisomers (4 points in total).
0 points if the products or isomers are not correct.

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7.8. <u>Draw</u> the molecule orbital (MO) diagram of the lowest energy singlet state of dioxygen ($^1O_2$) and calculate bond order.

MO diagram:

9 points for one of the correct MO diagrams (correct number of electrons 3 points, correct number and ordering of energy level of the MOs 3 points, correct arrangement of electrons 3 points).

Bond order: (8 – 4)/2 = 2
3 points.
0 points if the bond order is not correct.

7.9. If the wavelength of the light needed to excite triplet oxygen into singlet oxygen is 1270 nm, **calculate** the energy (in kJ/mole) needed for this transition process.

Calculation:

1 *nm* = 1 × 10^{-9} m and 1270 *nm* = 1.270 × 10^{-6} *m*
$$E = h \times c \div \lambda$$

E = (6.6261 × 10^{-34} *J s*) (2.9979 × 10^8 *ms^{-1}*) ÷ 1.270 × 10^{-6} *m* = 1.564 × 10^{-19} J and

1.564 × 10^{-22} kJ

4 points.

For 1 mol, multiply by Avogadro's constant = (1.564 × 10^{-22} kJ) (6.0221 × 10^{23} mol^{-1})

= 94.19 kJ/mol

2 points.
0 points if the calculation is not correct.

	Question	8.1	8.2	8.3	8.4	8.5	8.6	8.7	8.8	**Total**
	Points	3	3	4	4	4	4	6	3	
Problem 8	Question	8.9	8.10	8.11	8.12	8.13	8.14	8.15	8.16	
14% of the total	Points	2	3	2	4	4	4	2	2	**58**
	Question	8.17								
	Points	4								

Problem 8. Boron Compounds and Hydrogen Storage

Turkey has **73%** of the **world's boron reserves**.
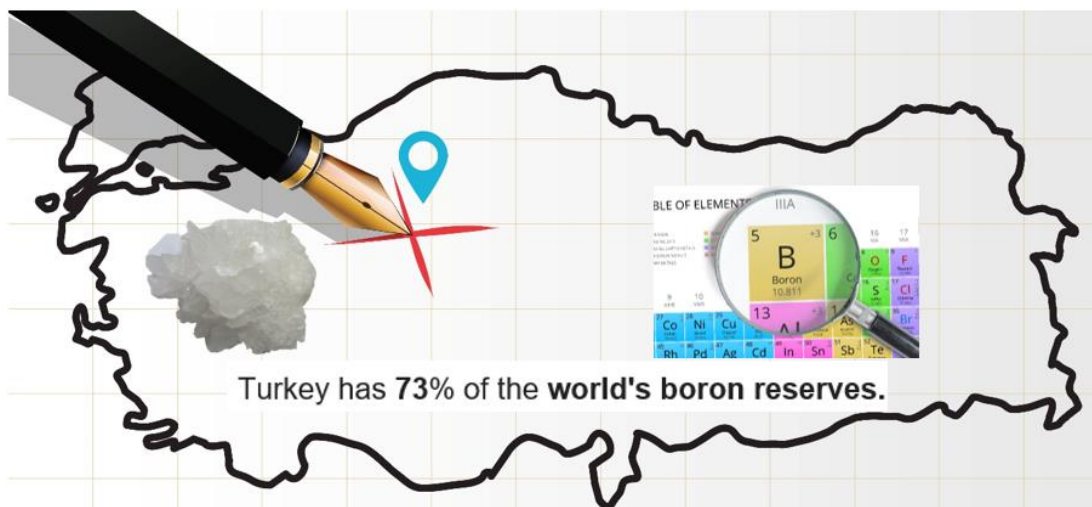
Sodium borohydride ($NaBH_4$) and ammonia borane (BNH_6) are the most studied chemical hydrogen storage materials. In this question, you will explore the chemistry of boron and the use of boron compounds as hydrogen storage materials.

Borax ($Na_2B_4O_7 \cdot nH_2O$) is a boron mineral that is produced by ETI Mining Company in Turkey. $NaBH_4$ can be synthesized by the reduction of anhydrous borax with metallic sodium under high-pressure hydrogen gas in the presence of silicon dioxide (silica) at 700 ºC, namely the Bayer process. In this process, all hydrogen is stored in NaBH₄. On the other hand, it has been shown that ammonia borane (BNH_6) can be synthesized by the reaction of $NaBH_4$ and ammonium sulfate in dry tetrahydrofuran (THF) at 40 °C (**Hint:** BNH₆ synthesis must be conducted in a well-ventilated fume-hood because flammable gas is generated as one of the by-products). While $NaBH_4$ is an ionic compound, ammonia borane is a Lewis acid–base adduct.

8.1. Write a balanced chemical equation for the synthesis of $NaBH_4$ from anhydrous borax.

8.2. Write a balanced chemical equation for the synthesis of ammonia borane from NaBH₄.

8.3. Draw the molecular geometry of the BH_4^- ion and BNH_6 molecule.

8.4. Calculate the hydrogen content of $NaBH_4$ and BNH_6 as a percentage by mass (wt%).

The hydrogen stored in both compounds can be released via hydrolysis reactions in the presence of a suitable catalyst at room temperature. Upon the hydrolysis reactions, 4 and 3 moles of H_2 gas are released from the hydrolysis of 1 mole of $NaBH_4$ and BNH_6, respectively, along with metaborate anion including B-O bonds.

8.5. <u>Write</u> the balanced chemical equations for the hydrolysis of $NaBH_4$ and BNH_6.

One of the simplest stable borates is diboron trioxide (B_2O_3). Higher borates such as $B_3O_6^{3-}$ having cyclic structures containing B-O-bonds can be formed. Since B_2O_3 is an acidic compound, it is easily reacted with water to produce boric acid (H_3BO_3). On the other hand, the high temperature and high-pressure reaction of B_2O_3 with ammonia yields two-dimensional boron nitride, which consists of planar graphite-like sheets of alternating B and N atoms.

8.6. <u>Write</u> the balanced chemical equations for the synthesis of boric acid and boron nitride.

8.7. <u>Draw</u> the molecular structures of the $B_3O_6^{3-}$ ion, boric acid, and a single two-dimensional boron nitride sheet. **Hint:** show at least 10 B atoms in the boron nitride structure.

Furthermore, B-H compounds, called boranes, are an important class of boron compounds. The simplest stable borane is diborane (B_2H_6) and many of the higher boranes can be prepared by the pyrolysis of diborane. Diborane can be synthesized via metathesis of a boron halide and a hydride source.

8.8. <u>Write</u> a balanced chemical equation for the synthesis of diborane from the reaction of BF_3 and $LiBH_4$. **Hint:** both products are boron compounds.

8.9. <u>Draw</u> the molecular geometry of the diborane molecule. **Hint:** there is no B-B bond in the structure.

BH_3 (borane) is an unstable and highly reactive molecule. Therefore, it is not possible to isolate it as BH_3 under ordinary conditions. However, it can be stabilized via its reaction with carbon monoxide to yield borane carbonyl (BH_3CO) compound, which is an adduct of borane. The preparation of BH_3CO plays an important role in exploring the chemistry of boranes as it indicates the likely existence of the borane molecule.

8.10. <u>Sketch</u> the Lewis dot structure of $BH_3 - CO$ molecule by showing the formal charges.

8.11. Which of the statements given in your answer sheet is observed in the $C - O$ bond of a CO molecule upon the bond formation between BH_3 and CO? **Tick** the correct box.

☐ It gets longer because there will be π-back donation from BH_3 to CO.

☐ It gets longer because CO donates π-bonding electrons to BH_3.

☐ No or slight change on it because CO donates its mainly non-bonding electrons to BH_3.

☐ It gets shorter because CO donates π* anti-bonding electrons to BH_3.

Borazine consists of single and double bonded cyclic $B - N$ units and hydrogen atoms attached to these atoms with the molecular formula $B_3N_3H_6$ and is isostructural to benzene. Borazine can be synthesized by using a two-step procedure including the synthesis of symmetrically trisubstituted chlorine derivatives of borazine ($B_3N_3H_3Cl_3$) from the reaction of ammonium chloride and boron trichloride, and then reduction of $B_3N_3H_3Cl_3$ with $LiBH_4$ in THF.

8.12. Write the balanced chemical equations for the two-step synthesis of borazine starting from ammonium chloride in THF (tetrahydrofuran). **Hint:** THF stabilizes one of the products by forming a Lewis acid-base adduct.

8.13. Draw the molecular structures of borazine and its symmetrically trisubstituted chlorine derivative.

Catalysts are substances that accelerate the rate of reactions by allowing them to proceed in a lower energy pathway. The catalytic activity of the catalysts is generally determined by the turnover frequency (TOF), which is calculated by dividing the molar amount of the product to the mole of active catalyst and the time (TOF = mole product/(mole catalyst x time)). A typical hydrolysis of BNH_6 was carried out in 10.0 mL of water by using 100.0 mM BNH_6 and 5.0 mg of CuPt/C catalyst (CuPt alloy nanoparticles supported on carbon black containing 8.2 wt% Pt atom). 67.25 mL of hydrogen gas was generated in 5 minutes.

8.14. Assuming the catalytic reaction is performed under standard conditions (1 atm and 273.15 K), **calculate** the TOF (min^{-1}) of the CuPt/C catalyst **in terms of only Pt atoms** in the hydrolysis of BNH_6 by considering the volume of the hydrogen gas generated.

As a result of detailed crystal analysis of a synthesized Cu_xPt_y alloy nanoparticles (the subscripts indicate molar percentages of the atoms in the alloy structure), it was determined that the face centered cubic (fcc) unit cell was formed by Pt atoms and the Pt atoms on the face of the fcc unit cell are supposed to be replaced with Cu atoms to form Cu_xPt_y displacement alloy nanoparticles. According to this information, answer the following questions.

8.15. <u>Determine</u> the composition of the alloy nanoparticles by finding x and y in the Cu_xPt_y.

8.16. <u>Sketch</u> the shape of the described crystal unit cell of Cu_xPt_y alloy nanoparticles by showing the position of all atoms on the unit cell.

8.17. Another alloy has a Cu_2Pt_1 composition. Assume that this alloy also has a fcc unit cell with an edge length of 380 pm, but the Cu and Pt atoms are randomly distributed in the atomic positions. **<u>Calculate</u>** the density of this alloy in g/cm^3.

Solution:

8.1. <u>Write</u> a balanced chemical equation for the synthesis of $NaBH_4$ from anhydrous borax.

$Na_2B_4O_7 + 16Na + 8H_2 + 7SiO_2 \rightarrow 4NaBH_4 + 7Na_2SiO_3$ *(3 points)*
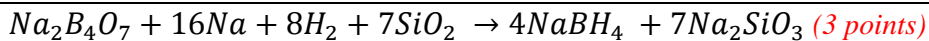
No partial point will be given if the stoichiometry is incorrect
No penalty will be given for writing another silicate product if the balanced chemical equation is correct.

8.2. <u>Write</u> a balanced chemical equation for the synthesis of ammonia borane (BNH_6) from $NaBH_4$.

$2NaBH_4 + (NH_4)_2SO_4 \rightarrow 2BNH_6 + 2H_2 + Na_2SO_4$ *(3 points)*

No partial point will be given if the stoichiometry is incorrect.
-1 point if molecular formula of the side product (Na₂SO₄) is written incorrectly.
-1 points if the hydrogen gas is not written in the product side

8.3. <u>Draw</u> the molecular geometry of the BH_4^- ion and BNH_6 molecule

(2 points)　　　　　　　　　　　　　　　*(2 points)*
-1 point if the molecular geometry is not shown
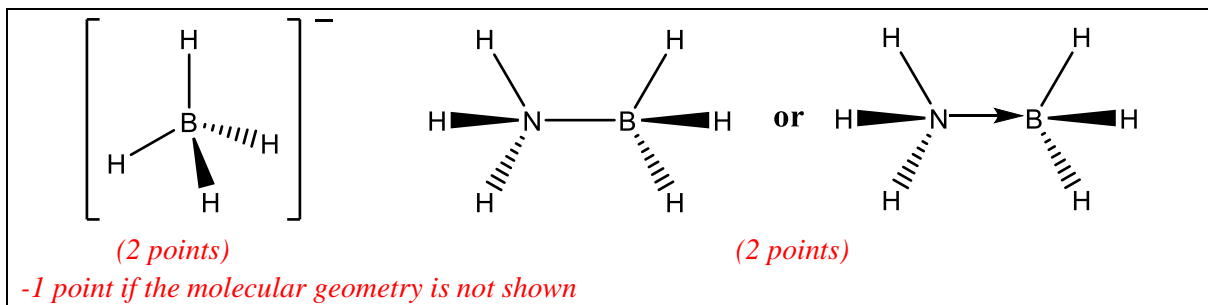
8.4. <u>Calculate</u> the hydrogen content of $NaBH_4$ and BNH_6 as a percentage by mass (wt%).

$wt\% \, H \, (NaBH_4) = \frac{4 \times (A_w(H))}{M_w(NaBH_4)} \times 100 = \frac{4.032}{37.83} = 10.65\%$ *(2 points)*

$wt\% \, H \, (BNH_6) = \frac{6 \times (A_w(H))}{M_w(BNH_6)} \times 100 = \frac{6.048}{30.87} = 19.59\%$ *(2 points)*

No partial point given if any mistake occurs.

**8.5.** <u>**Write**</u> the balanced chemical equations for the hydrolysis of $NaBH_4$ and BNH_6.

$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2$ *(2 points)*
$BNH_6 + 2H_2O \rightarrow NH_4BO_2 + 3H_2$ *(2 points)*
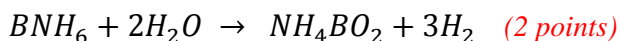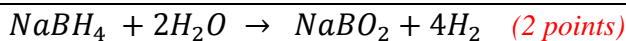
No partial points will be given if the total stoichiometry is incorrect
No penalty for writing NaBO₂ as Na⁺ + BO₂⁻ or NH₄BO₂ as NH₄⁺ + BO₂⁻
No penalty for writing other borates if the stoichiometry is correct
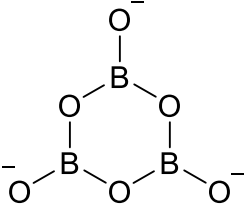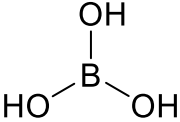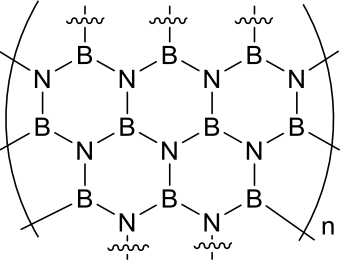
8.6. <u>**Write**</u> the balanced chemical equations for the synthesis of boric acid and boron nitride.

$B_2O_3 + 3H_2O \rightarrow 2H_3BO_3$ *(2 points)*
$B_2O_3 + 2NH_3 \xrightarrow{high\ T/high\ P} 2BN + 3H_2O$ *(2 points)*
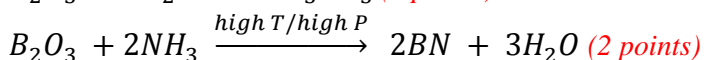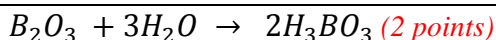
No partial points will be given if the total stoichiometry is incorrect.
No penalty if the high T/high P on the reaction arrow is missed.

8.7. <u>**Draw**</u> the molecular structures of the $B_3O_6^{3-}$ ion, boric acid, and a single two-dimensional boron nitride sheet (**Hint:** show at least 10 B atoms).

$B_3O_6^{3-}$	Boric acid	Boron nitride
(2 points) *No point if the cyclic structure is not shown* *-1 point if the charges on oxygen atoms are missed*	*(2 points)* *-1 point if the trigonal planar geometry is not shown*	*(2 points)* *-No point if less than 10 B atoms are represented in the structure* *-1 point if the continuing part is not shown*

8.8. <u>**Write**</u> a balanced chemical equation for the synthesis of diborane from the reaction of BF_3 and $LiBH_4$. (**Hint:** both products are boron compounds)

$3LiBH_4 + 4BF_3 \rightarrow 2B_2H_6 + 3LiBF_4$ *(3 points)*
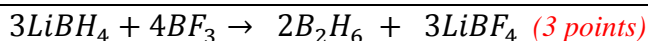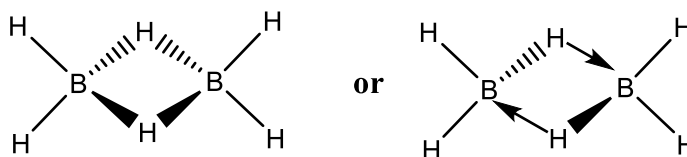
No partial point will be given if the stoichiometry is incorrect
-1 point if molecular formula of the side product (LiBF₄) is written incorrectly.

8.9. <u>Draw</u> the VSEPR molecular geometry of the diborane molecule (**Hint:** there is no B-B bond in the structure).
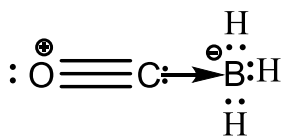

(2 points)

-1 point if the 3D structure is not shown
No point if a B-B bond is presented in the structure

8.10. <u>Sketch</u> the Lewis dot structure of BH_3CO molecule by showing the formal charges.

(3 points)

-1 point if the formal charges are not represented or represented incorrectly.
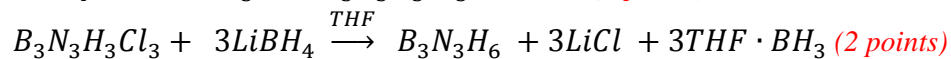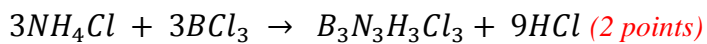*No penalty will be given if the arrow is not represented.*

8.11. Which of the following statements is observed in the $C - O$ bond of a CO molecule upon the bond formation between BH_3 and CO?

☐ It gets longer because there will be π-back donation from BH_3 to CO.
☐ It gets longer because CO donates π-bonding electrons to BH_3.
☒ No or slight change on it because CO donates its mainly non-bonding electrons to BH_3.
☐ It gets shorter because CO donates π* anti-bonding electrons to $BH_3.$

(2 points)
*No point if more than one box is clicked.*

79

8.12. <u>Write</u> the balanced chemical equations for the two-step synthesis of borazine starting from ammonium chloride in THF. (**Hint:** THF stabilizes one of the products).

$3NH_4Cl + 3BCl_3 \rightarrow B_3N_3H_3Cl_3 + 9HCl$ *(2 points)*

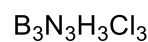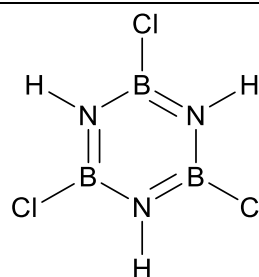$B_3N_3H_3Cl_3 + 3LiBH_4 \xrightarrow{THF} B_3N_3H_6 + 3LiCl + 3THF \cdot BH_3$ *(2 points)*

No partial point will be given if the total stoichiometry is wrong.
-1 point for each if molecular formula of the side products is written incorrectly.

8.13. <u>Draw</u> the molecular structures of borazine and its symmetrically trisubstituted chlorine derivative.
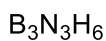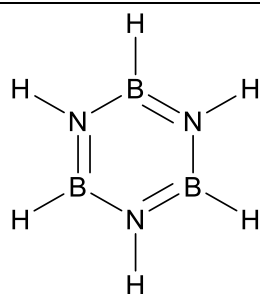
$B_3N_3H_6$

(2 points)

$B_3N_3H_3Cl_3$

(2 points)

No point will be given if the cyclic structure is not shown
No point will be given if the Cl atoms are bonded to N atoms in B₃N₃H₃Cl₃ molecule
-1 point for each molecule if the cyclic structure is shown but the double bonds are not
Mesomeric structures will also be accepted

8.14. Assuming the catalytic reaction is performed under standard conditions, **calculate** the TOF of the CuPt/C catalyst **in terms of only Pt atoms** in the hydrolysis of BNH_6 by considering the volume of the hydrogen gas generated.

$moles\ of\ H_2\ gas\ generated = \frac{67.25\ mL}{22.41\ mL} = 3.0\ mmol = 3\ \times 10^{-3}\ mol$ *(1 point)*

$moles\ of\ Pt = \left[(\frac{0.005 \times 8.2}{100})/195.1 \right] = 2.1 \times 10^{-6}\ mol$ *(1 point)*

$TOF = \frac{3 \times 10^{-3}\ mol\ H_2}{(2.1 \times 10^{-6}\ mol\ Pt) \times 5.0\ min} = 286\ min^{-1}$ *(2 points)*

(4 points in total)

No partial point given if any mistake occurs in the calculation of TOF.

8.15. Determine the composition of the alloy nanoparticles by finding x and y in the Cu_xPt_y

In a regular fcc unit cell,
$Corners = \frac{8 \times 1}{8} = 1\ Pt\ atom$
$Faces = \frac{6 \times 1}{2} = 3\ Pt\ atoms$
After the replacement surface Pt atoms with Cu atoms,
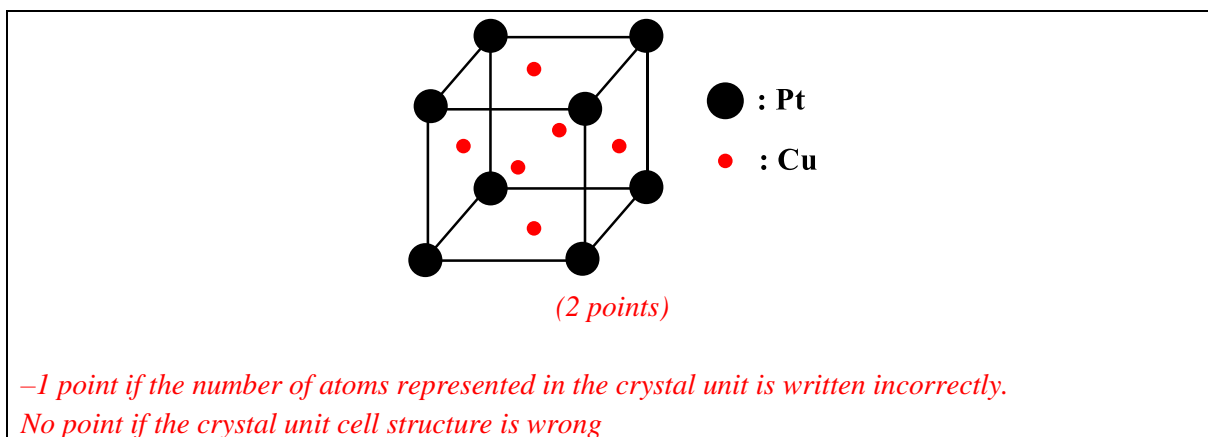
$Corners = \frac{8 \times 1}{8} = 1\ Pt\ atom$ *(1 point)*
$Faces = \frac{6 \times 1}{2} = 3\ Cu\ atoms$ *(1 point)*

Alloy composition $= Cu_3Pt$ *(2 points),* Cu$_{75}$Pt$_{25}$ is also accepted

(4 points in total)

No penalty will be given if the calculation of Pt atoms in a regular fcc unit cell or after replacements is not shown.

8.16. Sketch the shape of the described crystal unit cell of CuxPty alloy nanoparticles by showing the position of all atoms on the unit cell.

(2 points)

−1 point if the number of atoms represented in the crystal unit is written incorrectly.
No point if the crystal unit cell structure is wrong

8.17. Another alloy has a Cu_2Pt_1 composition. Assume that this alloy also has a fcc unit cell with an edge length of 380 pm, but the Cu and Pt atoms are randomly distributed in the atomic positions. **Calculate** the density of this alloy in g/cm^3.

Actual unit cell composition: $Cu_{2.66}Pt_{1.33}$ *(1 point)*

$V = A^3$
$a = 380\ pm = 3.80 \times 10^{-8} cm$
$V = (3.80 \times 10^{-8})^3 = 54.87 \times 10^{-24}\ cm^3$ *(1 point)*

$$d = \frac{m}{V} = \frac{[(2.66 \times (A_w(Cu)) + 1.33(A_w(Pt)]/N_A}{54.87 \times 10^{-24} cm^3}$$
$$= \frac{[(2.66 \times (63.54) + (195.1)x1.33]/6.02 \times 10^{23}}{54.87 \times 10^{-24}} = 12.97\ g/cm^3$$

(2 points)
(4 points in total)
1 point will be given if the density is calculated by not considering the actual alloy composition of $Cu_{2.66}Pt_{1.33}$ in the given fcc unit cell.

| Problem 9	Question	9.1	9.2	9.3	9.4	9.5	9.6	9.7	9.8	Total
12% of the total	Points	5	5	8	16	5	6	25	30	100

Problem 9. Quantification of Heavy Metal Ions

For the quantitative analysis of heavy metal ions in a factory's wastewater pool, the following steps have been applied by an analyzer at 298 K:

Step 1) 10-mL samples of each were obtained from five different regions in a wastewater pool, mixed in a 100-mL beaker, and then stirred for 5 minutes using a magnetic stirrer.

Step 2) 10-mL of sample solution was taken from the 100-mL beaker and 142 mg of Na_2SO_4 was added while stirring, followed by transfer to a three-electrode cell as seen in Figure 1a. In this electrochemical cell, Pt wire, Ag/AgCl (3 M KCl), and Pt foil served as the working, reference, and counter electrodes, respectively.

Step 3) These electrodes were connected to a potentiostat and a constant potential of –0.50 V vs. Ag/AgCl for 14 minutes was applied as seen in Figure 1b (horizontal line). It is assumed that 14 min. is sufficient to complete the expected electrochemical reactions.

(a)   **(b)**
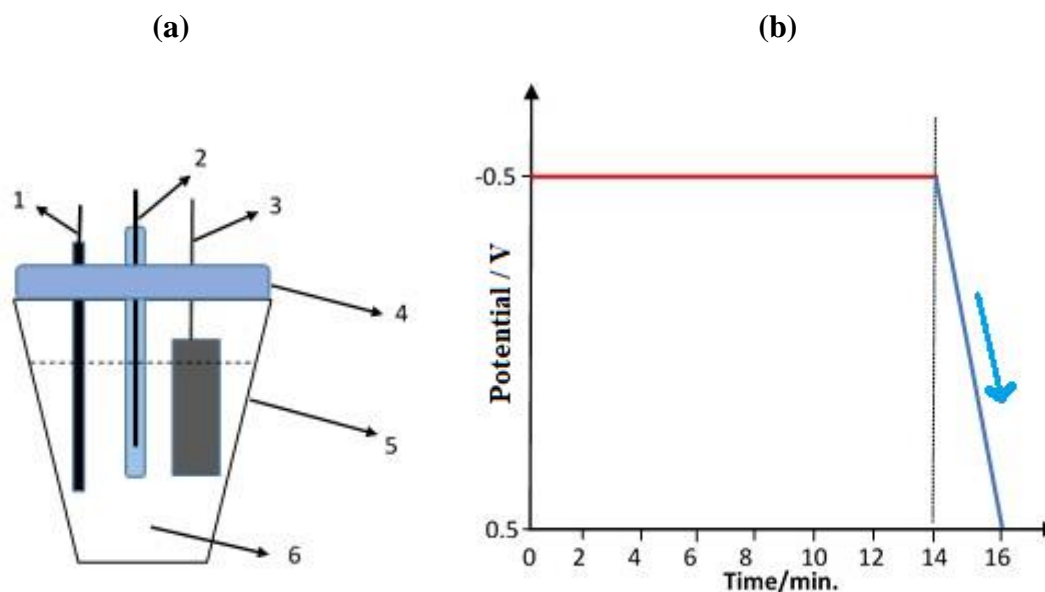
Figure 1. a) Electrochemical cell design; 1) Working electrode (Pt wire), 2) reference electrode (Ag/AgCl, 3M KCl), 3) counter electrode (Pt foil), 4) cell tap, 5) electrochemical cell, 6) 10-mL of sample solution. **b)** Potential change of working electrode as a function of time. y-axis: potential/V vs Ag/AgCl, x-axis: time/min.

Step 4) The electrodes were rinsed with distilled water, placed into another electrochemical cell including 10-mL of 0.1 M H_2SO_4 solution, and potential was scanned between –0.50 and +0.50 V as seen in Figure 1b (downward sloping line in 2 min.). Current vs. potential data for this step are presented in Figure 2a, which is like an excellent view of *Mount Ararat* (*Ağrı Dağı*), the highest mountain in Turkey (Figure 2b).
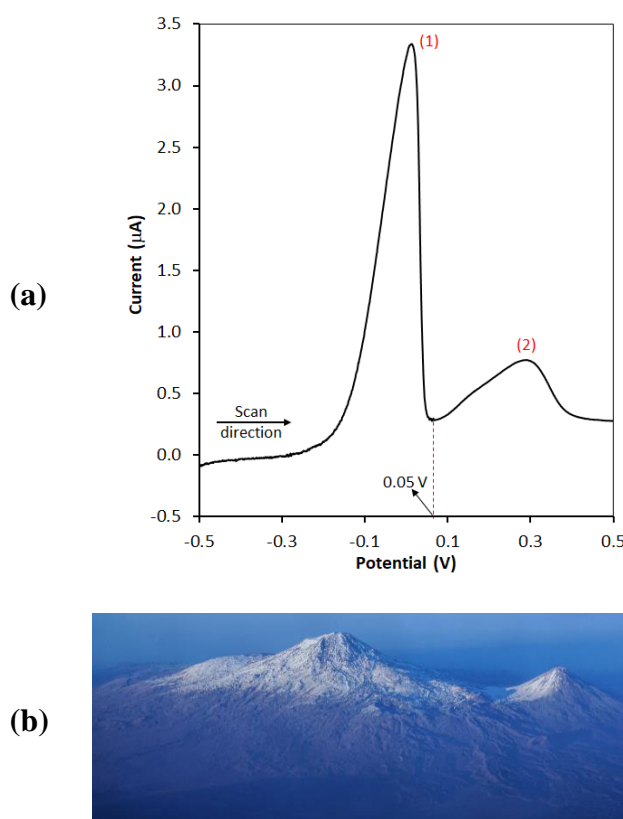

Figure 2. a) Potential scan of the working electrode as a function of current in 0.1 M H_2SO_4 solution after keeping it constant at a potential of –0.50 V in 10-mL of wastewater sample as seen in Figure 1b (horizontal line). y-axis: current/μA, x-axis: potential/V vs Ag/AgCl, **b)** A view of *Great and Little Ararat* peaks.

Step 5) Another 10-mL of the sample solution prepared in *step 1* was taken and the processes explained in *steps 2 and 3* were applied in that order. The electrodes were rinsed with distilled water and placed into 10-mL of 0.1 M H_2SO_4 solution. Then the potential of the working electrode was kept constant at +0.05 V for 14 minutes. It is assumed that 14 min. is sufficient to complete the expected electrochemical reactions.

Step 6) After *step 5* was performed, the solution in the electrochemical cell was placed in a suitable oven to evaporate at 150 °C until dry solid was obtained.

Step 7) 5-mL of ethylenediaminetetraacetic acid (EDTA, H₄Y) (Figure 3) solution was added to the solid obtained in *step 6* and it was shaken to dissolve. It is known that 1-mL of EDTA solution is equivalent to 3.85 mg/mL BaCO₃. Then, pH of the solution was adjusted to 10.0. Excess EDTA was titrated with standard 0.0010 M Ni(NO₃)₂ solution and it was observed that 95.60 mL of Ni(NO₃)₂ solution was consumed up to the endpoint.
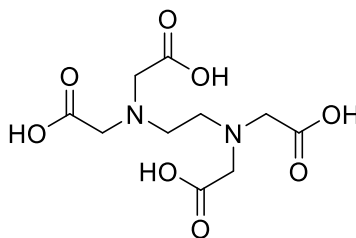
Figure 3. Chemical structure of EDTA (H₄Y).

- In water saturated with H₂S, equilibrium concentration of [H₂S] is 0.1 M.
- $K_{sp}(NiS) = 4.0 \times 10^{-20}$; $K_{sp}(CuS) = 1.0 \times 10^{-36}$
- $K_{a1}(H_2S) = 9.6 \times 10^{-8}$; $K_{a2}(H_2S) = 1.3 \times 10^{-14}$

-

| Reaction	E°/V (at 298 K)
$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$	−0.83
$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$	−0.24
$2H^+(aq) + 2e^- \rightarrow H_2(g)$	0.00
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	+0.34
$Ag^+(aq) + e^- \rightarrow Ag(s)$	+0.80
$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$	+1.23

9.1. Which of the following can be considered for peak 1 and peak 2 in Figure 2a, respectively? **Tick** the correct box on the answer sheet.

9.2. Which of the statements is expected, if the potential is applied as −1.2 V instead of −0.5 V at the first step (horizontal line) in Figure 1b? **Tick** the correct box on the answer sheet.

9.3. Calculate the scan rate of data presented in Figure 2a as mV/s at 298 K.

The potential of the following cell is measured as 0.437 V.

$Pt, H_2(0.92 \ bar)|HCl(1.50 \times 10^{-2} \ M), AgCl(sat)|Ag$
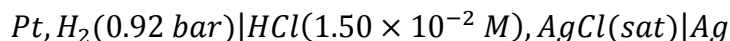
9.4. Calculate the standard electrode potential value (V) of half-cell of $AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$ at 298 K. *Note:* You must show all works.

9.5. Which of the statements is the main purpose of *step 5* in this analysis? **Tick** the correct box on the answer sheet.

9.6. Write net ionic equations for the complexation and the back titration reaction of *step 7* on the answer sheet

9.7. Calculate Ni^{2+} concentration as *mg/L* in the wastewater of the factory. *Note:* You must show all works.

9.8. Calculate the minimum pH value for starting the precipitation of Ni^{2+} ions in the solution obtained in *step 5* by passing H₂S gas into the solution until saturation. If you cannot solve question **9.7**, use 20 *mg/L Ni²⁺ sample* for this question. *Note:* You must show all works.

Solution:

9.1. Which of the following can be considered for peak 1 and peak 2 in Figure 2a, respectively? **Tick** the correct box on the answer sheet.

☐ Peak 1: electrochemical reduction of Ni / Peak 2: electrochemical reduction of Cu

☐ Peak 1: electrochemical reduction of Cu / Peak 2: electrochemical reduction of Ni

☐ Peak 1: electrochemical reduction of Ni / Peak 2: electrochemical oxidation of Cu

☒ Peak 1: electrochemical oxidation of Ni / Peak 2: electrochemical oxidation of Cu

☐ Peak 1: electrochemical oxidation of Cu / Peak 2: electrochemical oxidation of Ni

5 points for correct answer.

9.2. Which of the statement is expected, if the potential is applied as –1.2 V instead of -0.5 V at the first step (horizontal line) in Figure 1b? **Tick** the correct box on the answer sheet.

☐ NO evolution

☐ NO_2 evolution

☐ Nitrogen evolution   *5 points for correct answer.*

☐ Oxygen evolution

☒ Hydrogen evolution

9.3. Calculate the scan rate of data presented in Figure 2a as mV/s.

Calculation:

We can calculate the scan rate using the slope of Figure 1b (downward sloping line)
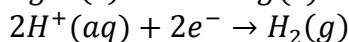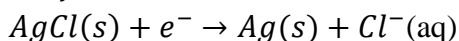

Scan rate = 1000 mV/120 s = 8.33 mV/s
8 points.

9.4. Calculate the standard electrode potential value of half-cell of $AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$. _Note:_ You must show all works.

Calculation:

$E_{cell} = E_{right} - E_{left}$ *(3 point)*

$Half - reactions$;
$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$
$2H^+(aq) + 2e^- \rightarrow H_2(g)$
$E_{cell} = \left(E^o_{AgCl/Ag} - 0.0592\log[Cl^-]\right) - \left(E^o_{H^+/H_2} - \frac{0.0592}{2}\log\frac{P_{H_2}}{[H^+]^2}\right)$ *(7 points)*

$0.437 = \left(E^o_{AgCl/Ag} - 0.0592\log 1.5\times 10^{-2}\right) - \left(0.00 - \frac{0.0592}{2}\log\frac{0.92}{(1.5\times 10^{-2})^2}\right)$ *(4 points)*

$E^o_{AgCl/Ag} = 0.22$ V *(2 point)*

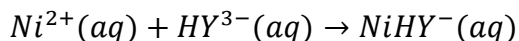*–2 points for each calculation error.*
–2 points for each wrong unit.

9.5. Which of the statements is the main purpose of *step 5* in this analysis? **Tick** the correct box on the answer sheet.

☐ Modification of Pt wire with Ni–Cu alloy film

☐ Modification of Pt wire with Ni film

☐ Electrochemical stripping of both Cu and Ni from Cu–Ni-modified Pt wire to the solution

☐ Electrochemical stripping of Cu from Cu–Ni-modified Pt wire to the solution

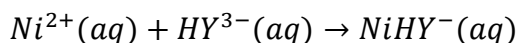☒ Electrochemical stripping of Ni from Cu–Ni-modified Pt wire to the solution

5 points for correct answer.

9.6. <u>Write</u> net ionic equations for the complexation and the back titration reaction of *step 7* in your answer sheet.

Complexation: $Ni^{2+}(aq) + Y^{4-}(aq) \rightarrow NiY^{2-}(aq)$ or

$$Ni^{2+}(aq) + HY^{3-}(aq) \rightarrow NiHY^{-}(aq)$$

Back titration: $Ni^{2+}(aq) + Y^{4-}(aq) \rightarrow NiY^{2-}(aq)$ or

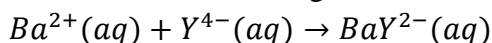$$Ni^{2+}(aq) + HY^{3-}(aq) \rightarrow NiHY^{-}(aq)$$

3 points for each correct answer.

9.7. <u>Calculate</u> Ni^{2+} concentration as *mg/L* in the wastewater of the factory. *<u>Note</u>:* You must show all works.
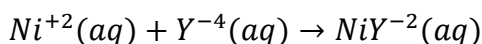

Calculation:

5 pieces of 10-mL samples were collected and the total sample volume is 50-mL. 10-mL of the part was taken from this 50-mL sample. *(2 point)*

EDTA titration; 3.85 mg BaCO₃/mL EDTA
$Ba^{2+}(aq) + Y^{4-}(aq) \rightarrow BaY^{2-}(aq)$

$$[EDTA] = \frac{\frac{3.85\, mg\, BaCO_3}{197\, mg\, BaCO_3} \times \frac{1\, mmol\, EDTA}{1\, mmol\, BaCO_3}}{\frac{1\, mmol\, BaCO_3}{1\, mL\, EDTA}} = 0.01954\, M\, EDTA \text{ (8 points)}$$

$Ni^{+2}(aq) + Y^{-4}(aq) \rightarrow NiY^{-2}(aq)$

$$mmol_{Ni^{+2}} = \left[\left(\frac{0.01954\, mmol\, EDTA}{1\, mL\, EDTA} \times 5.00\, mL\, EDTA\right) - \left(\frac{0.0010\, mmol\, Ni^{2+}}{1\, mL\, Ni^{2+}} \times \right.\right.$$
$$\left.\left. 95.60\, mL\, Ni^{2+} \times \frac{1\, mmol\, EDTA}{1\, mmol\, Ni^{2+}}\right)\right] \times \frac{1\, mmol\, Ni^{2+}}{1\, mmol\, EDTA} = 0.0021\, mmol\, Ni^{2+} \text{ (12 points)}$$

$$C_{Ni^{2+}} = \frac{\left(0.0021\, mmol\, Ni^{2+} \times \frac{58.7\, mg\, Ni^{2+}}{1\, mmol\, Ni^{2+}}\right) \times \frac{50\, mL}{10\, mL}}{0.05\, L\, sample} = 12.33\, mg/L \text{ (3 points)}$$

–3 points for each calculation error.
–3 points for each wrong unit.
*–3 points for each wrong conversion factor.*

9.8. Calculate the minimum pH value for starting the precipitation of Ni^{2+} ions in the solution obtained in *step 5* by passing H_2S gas into the solution until saturation. If you cannot solve question **9.7**, use 20 *mg/L Ni^{2+} sample* for this question. *Note:* You must show all works.
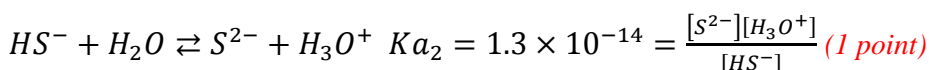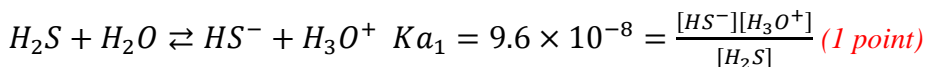

Calculation:

$[Ni^{2+}] = \frac{0.0021\ mmol\ Ni^{2+}}{10\ mL\ sample} = 2.1 \times 10^{-4} M$ or $[Ni^{2+}] = \frac{\frac{0.01233\ g\ Ni^{2+}}{58.7\ g/mol}}{1\ L\ sample} = 2.1 \times 10^{-4} M$
(6 points)
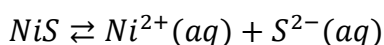
$NiS \rightleftarrows Ni^{2+}(aq) + S^{2-}(aq)$
$4.0 \times 10^{-20} = 2.1 \times 10^{-4} \times [S^{2-}]$
$[S^{2-}] = 1.905 \times 10^{-16}\ M$ *(6 points)*

$H_2S + H_2O \rightleftarrows HS^- + H_3O^+ \quad Ka_1 = 9.6 \times 10^{-8} = \frac{[HS^-][H_3O^+]}{[H_2S]}$ *(1 point)*

$HS^- + H_2O \rightleftarrows S^{2-} + H_3O^+ \quad Ka_2 = 1.3 \times 10^{-14} = \frac{[S^{2-}][H_3O^+]}{[HS^-]}$ *(1 point)*

$0.1 = [H_2S] + [HS^-] + [S^{2-}]$ *(1 points)*

$[H_2S] \gg [HS^-] + [S^{-2}]$ and $[H_2S] = 0.1\ M$ *(1 points)*

$Ka_1 \times Ka_2 = 1.25 \times 10^{-21} = \frac{[S^{2-}][H_3O^+]^2}{[H_2S]}$ *(7 points)*

$1.25 \times 10^{-21} = \frac{1.905 \times 10^{-16}[H_3O^+]^2}{0.1}$ *(4 points)*

$[H_3O^+] = 8.1 \times 10^{-4}\ M$
$pH = 3.09$ *(3 points)*

If Ni^{2+} concentration is taken 20 mg/L, the result is pH = 2.99

−3 points for each calculation error.
−3 points for each wrong unit.
−3 points for each wrong conversion factor.

The End