IChO

General Instructions

- Write only in pen. Your calculator should be non-programmable.

- This theoretical exam contains **28 pages of questions** and **39 pages of answers**, not including general instructions.

- 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 scrap 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 bathroom, etc), raise your hand and wait until an invigilator arrives.

Good luck / Don't screw up

Problems & **Grading Information**

Problem No	Title	Total Points	% of Total Score
1	Two Beauties of Turkey: the Van Cat and the Ankara Cat (Q: 3 pages, A: 2 pages)	24	8
2	A Tale of a Reactive Intermediate (Q: 3 pages A: 4 pages)	77	10
3	(±)-Coerulescine (Q: 3 pages, A: 3 pages)	51	8
4	Symmetry Does Matter! (Q: 3 pages, A: 4 pages)	66	10
5	Konya, Carrot, Beta-Carotene, Vitamin-A, Immune System, Vision (Q: 3 pages, A: 6 pages)	100	14
6	Thermodynamics through an Interstellar Journey (Q: 3 pages, A: 6 pages)	80	12
7	Phthalocyanines (Q: 3 pages, A: 5 pages)	85	12
8	Boron Compounds and Hydrogen Storage (Q: 3 pages A: 5 pages)	58	14
9	Quantification of Heavy Metal Ions (Q: 4 pages, A: 4 pages)	100	12
	TOTAL		**100**

Theory IChO 2020

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Physical Constants and Equations

Avogadro's number	$N_A = 6.0221 \times 10^{23}\,\text{mol}^{-1}$
Boltzmann constant	$k_B = 1.3807 \times 10^{23}\,\text{JK}^{-1}$
Universal gas constant	$R = 8.3145\,\text{JK}^{-1}\text{mol}^{-1} = 0.08205\,\text{atm LK}^{-1}\text{mol}^{-1}$
Speed of light	$c = 2.9979 \times 10^8\,\text{ms}^{-1}$
Planck's constant	$h = 6.6261 \times 10^{-34}\,\text{Js}$
Faraday's constant	$F = 9.6485 \times 10^4\,\text{C mol}^{-1}$
Mass of electron	$m_e = 9.1093 \times 10^{-31}\,\text{kg}$
Standard pressure	$p = 1\,\text{bar} = 10^5\,\text{Pa}$
Atmospheric pressure	$p_{\text{atm}} = 1.01325 \times 10^5\,\text{Pa} = 760\,\text{mmHg} = 760\,\text{torr}$
Zero of the Celsius scale	$273.15\,\text{K}$
1 picometer (pm)	$10^{-12}\,\text{m}; 1\,\text{Å} = 10^{-10}\,\text{m}$
1 nanometer (nm)	$10^{-9}\,\text{m}$
	$1\,\text{eV} = 1.6021 \times 10^{-19}\,\text{J}$
	$1\,\text{cal} = 4.184\,\text{J}$
	$1\,\text{amu} = 1.6605 \times 10^{-27}\,\text{kg}$
Charge of an electron	$1.6021 \times 10^{-19}\,\text{C}$
Ideal gas equation	$pV = nRT$

G0-5

Physical Constants and Equations

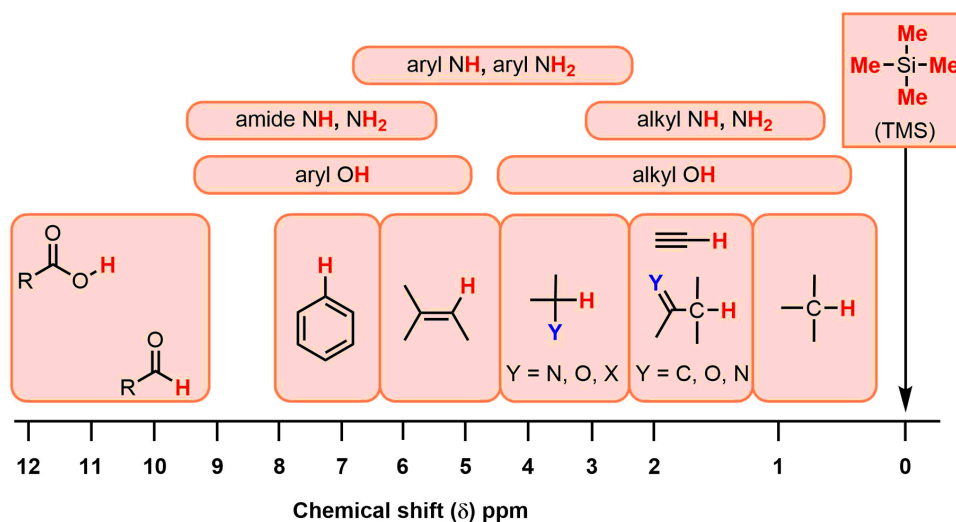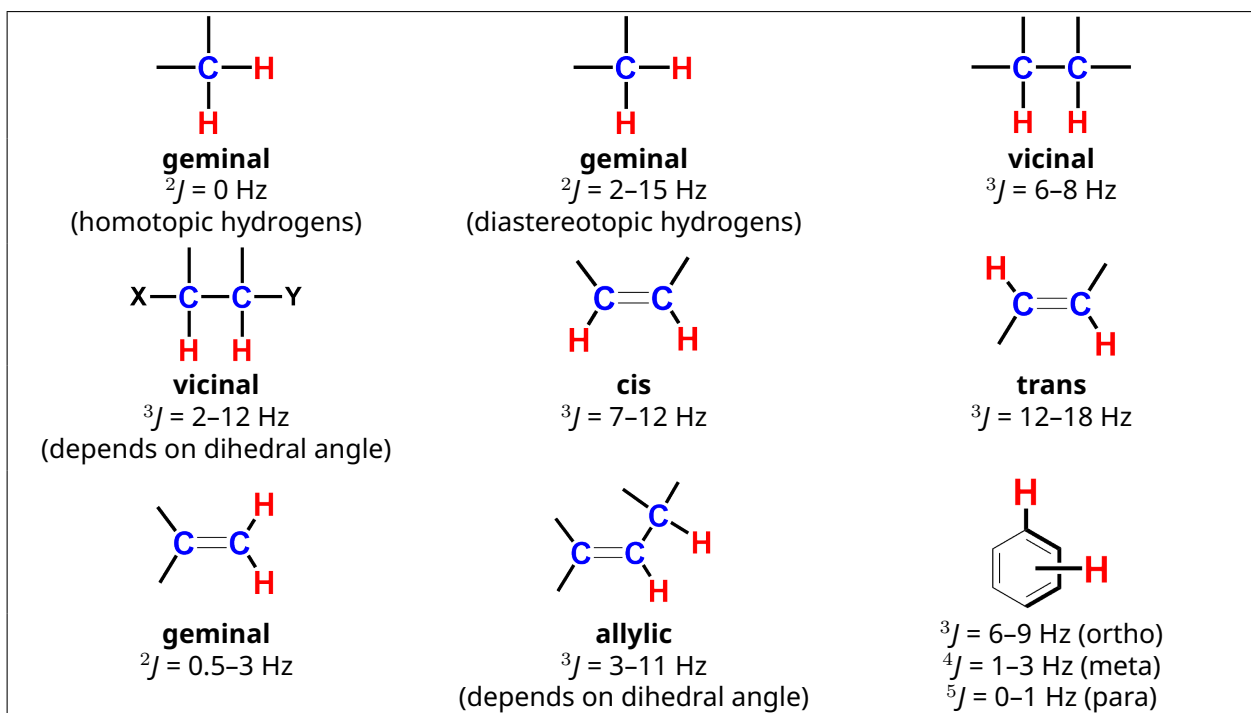| Enthalpy	$H = U + pV$
Gibbs free energy	$G = H - TS$
	$\Delta_r G = \Delta G^0 + RTlnQ$
	$\Delta_r G^0 = -RT \ln K = -nFE^0_{cell}$
Entropy change	$\Delta S = \dfrac{q_{\text{rev}}}{T}$, where q_{rev} is the heat for the reversible process
Entropy change	$\Delta S = nR \ln \dfrac{V_2}{V_1}$ (for isothermal expansion of an ideal gas)
Nernst equation	$E = E^0 + \dfrac{RT}{nF} \ln \dfrac{C_{\text{oxidation}}}{C_{\text{reduction}}}$
Energy of a photon	$E = \frac{hc}{\lambda}$
Integrated rate laws	
Zeroth-order	$[A] = [A]_0 - kt$
First-order	$\ln [A] = \ln [A]_0 - kt$
Second order	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$
Arrhenius equation	$k = Ae^{-E_a/RT}$
Equation of linear calibration curve	$y = mx + n$
Beer–Lambert equation	$A = \varepsilon lc$

Periodic Table of Elements

1																	18
1 H 1.008	2											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 -

The box key: atomic number / Symbol / atomic weight

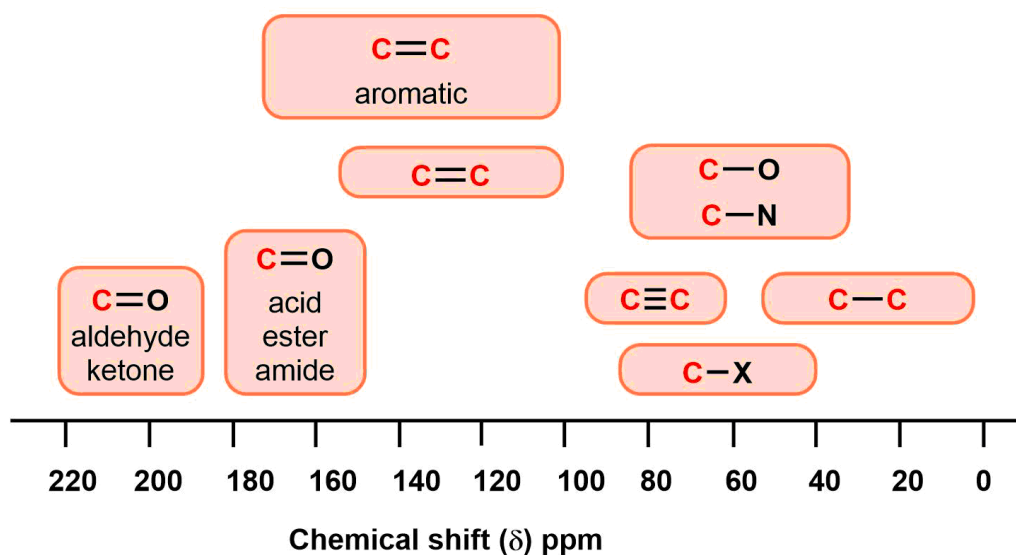| 57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm -	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
89 Ac -	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np -	94 Pu -	95 Am -	96 Cm -	97 Bk -	98 Cf -	99 Es -	100 Fm -	101 Md -	102 No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

2019 IYPT — International Year of the Periodic Table of Chemical Elements

IUPAC 100

Chemical shift (δ) ppm

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)

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

IR Absorption Frequency Table

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	

IR Absorption Frequency Table

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
cyclic	stretch	3-membered - 1850	strong
	stretch	4-membered - 1780	strong
	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

Two Beauties of Turkey: the Van Cat and the Ankara Cat
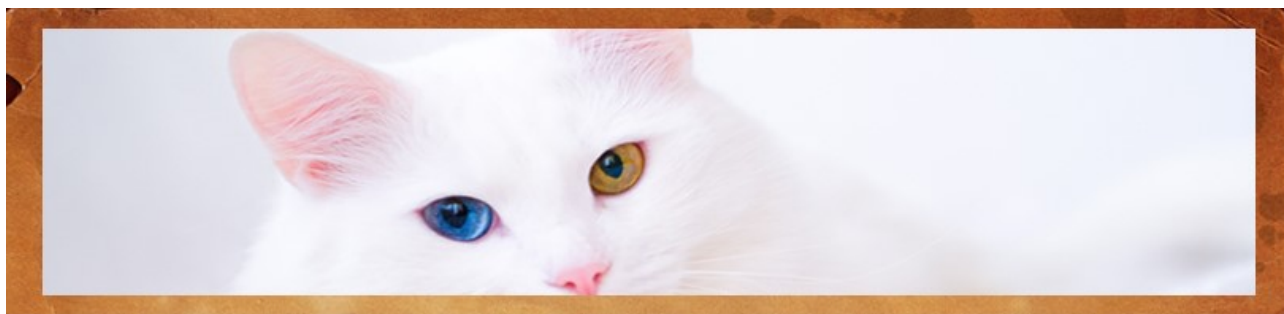
The most beautiful of cats, the Van cat is a purebreed living only in Lake Van basin. Another cat breed is the Ankara or Angora cat. They have two different eye colours.
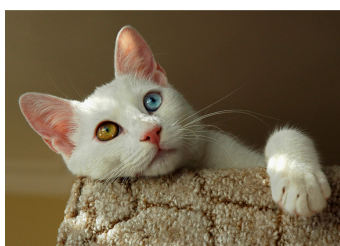
Van cat	Ankara cat	*Nepeta cataria* (catnip)

Both people and cats can be stressed. Just as people can be made happy by melatonin, cats can be made happy thanks to a natural product. Nepetalactone is 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
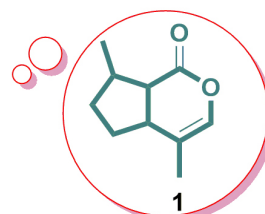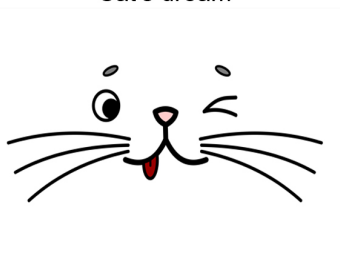
1
Nepetalactone

Total synthesis of nepetalactone:
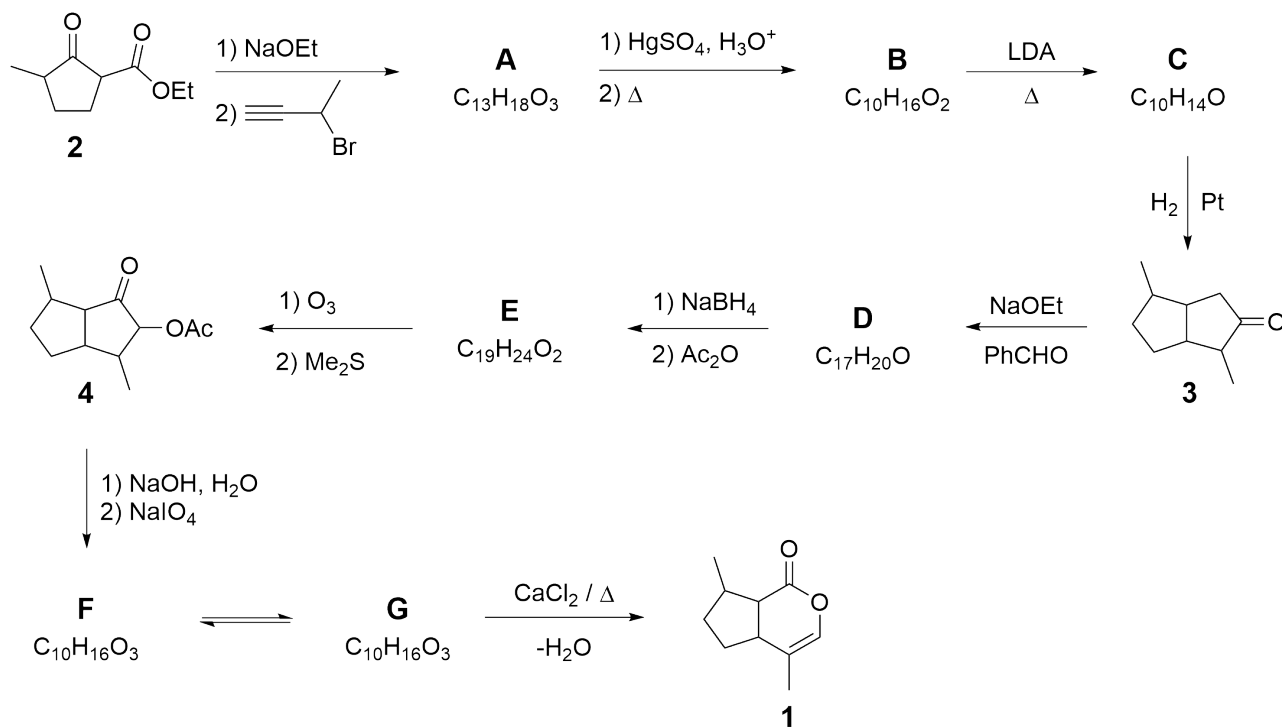
1.1	The above scheme describes the total synthesis of nepetalactone. **Draw** structures of **A–G**, without stereochemical detail.	14.0pt

Hints:

- Compound **A** has a 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 $\sim$ 9.8 ppm in the ^{1}H-NMR spectrum.

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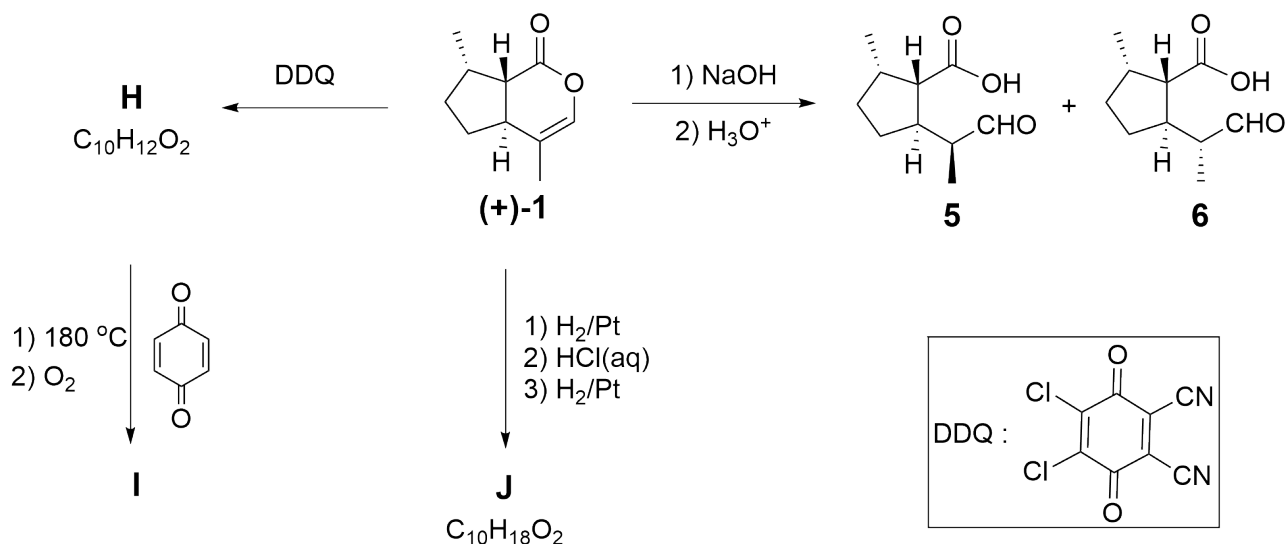
The above scheme includes a few reactions of one particular enantiopure isomer of nepetalactone, **1**. Three of the reaction products (**5**, **6**, and **J**) are used as insect repellents.

1.2	Which of the following describe(s) the relationship between **5** and **6**? **Tick** the box(es) next to the correct answer(s) on your answer sheet.	4.0pt

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

1.3	Draw the structures of **H**, **I**, and **J** indicating stereochemistry.	6.0pt

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.

Two Beauties of Turkey: the Van Cat and the Ankara Cat

1.1 (14.0 pt)

A	B
C	D
E	F
G	

1.2 (4.0 pt)

☐ Enantiomers
☐ Diastereomers
☐ Identical
☐ Stereoisomers

**1.3** (6.0 pt)

| H	I
J	

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 labelled 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**.
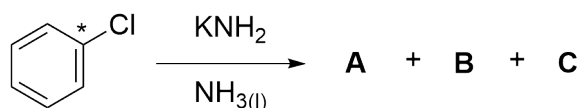
2.1	**Draw** the structures of **A**, **B** and **D**, and **provide** the formula of **C**. **Indicate** the position(s) of ^{14}C-labelled carbon(s) with an asterisk (*) whenever applicable. 7.0pt

Analysis of the ^{14}C-labelled product(s) was achieved via degradation experiments (the ^{14}C-labelled carbons are not shown on the structures). Radioactivities of the intermediates and final products were examined.
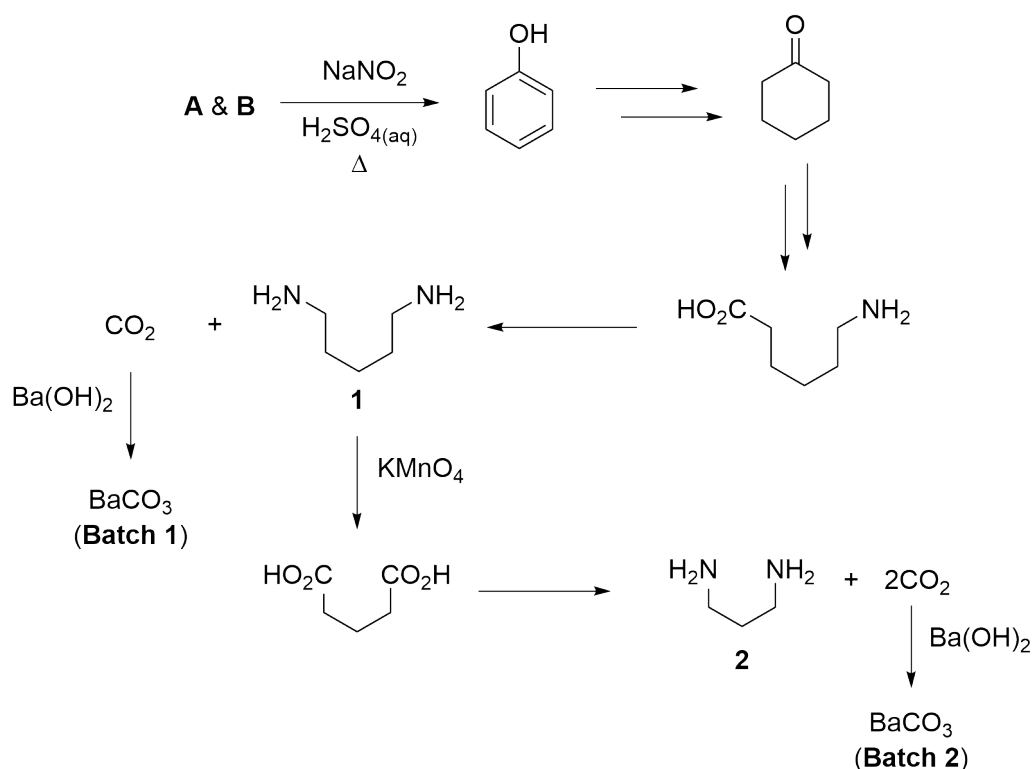
2.2 <u>Tick</u> the appropriate boxes on the answer sheet for the intermediates and prod-   9.0pt
ucts that you expect to exhibit radioactivity.

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**.

3   **4**
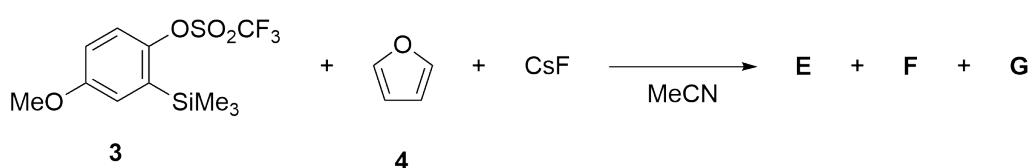
- Combustion analysis of **E** revealed the following atom content: 75.8% carbon, 5.8% hydrogen, and 18.4% oxygen.

- **E** does not have a proton that is exchangeable with D_2O in ^{1}H-NMR spectroscopy.

- **F** is an ionic compound.

2.3 <u>Determine</u> the structures of **E**, **F**, and **G** (without stereochemical detail).   8.0pt

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In the absence of a nucleophile or a trapping agent, arynes can undergo [2+2]-type cyclodimerisation or [2+2+2]-type cyclotrimerisation 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 dimerisation and trimerisation 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**.   16pt

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 ^{1}H-NMR and ^{13}C-NMR data for **L**, recorded in $CDCl_3$, are as follows:

- ^{1}H-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.

5   **6**
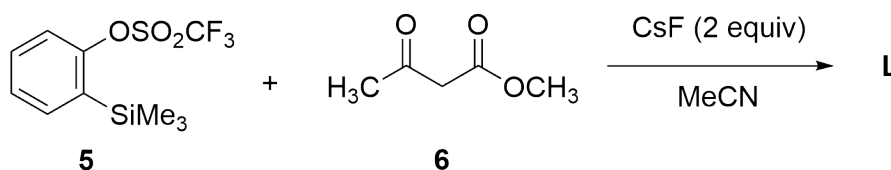
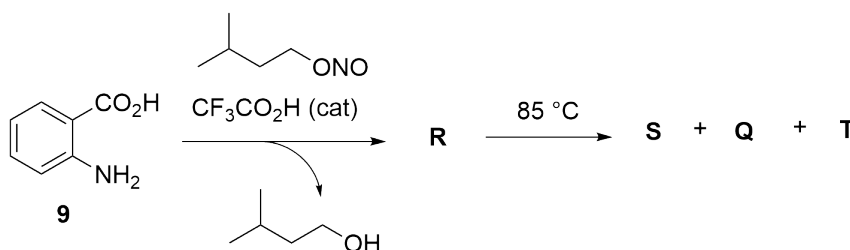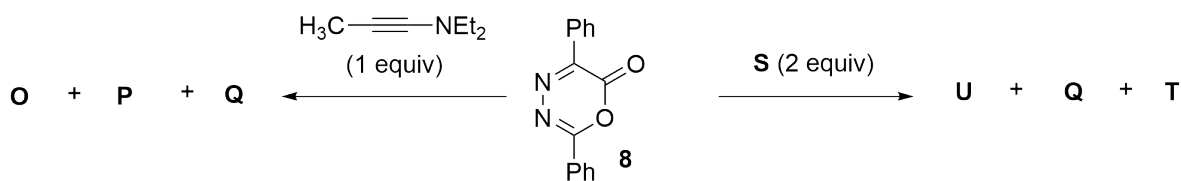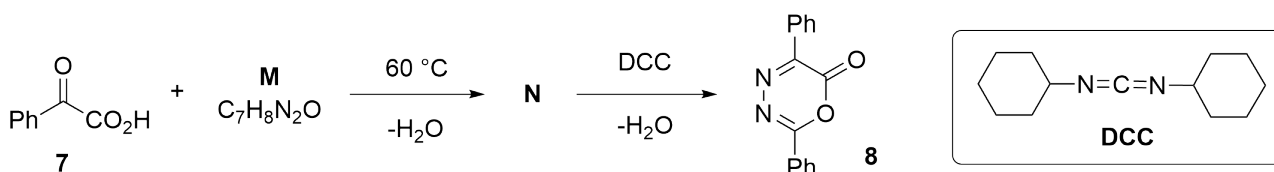| 2.5	**Determine** the structure of **L**.	5.0pt

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.	4.0pt

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**.	28.0pt

A Tale of a Reactive Intermediate

2.1 (7.0 pt)

A	B
C	D

2.2 (9.0 pt)

Considering only **A**:	Considering only **B**:
☐ Compound **1**	☐ Compound **1**
☐ $BaCO_3$ (Batch **1**)	☐ $BaCO_3$ (Batch **1**)
☐ Compound **2**	☐ Compound **2**
☐ $BaCO_3$ (Batch **2**)	☐ $BaCO_3$ (Batch **2**)

2.3 (8.0 pt)

E	F
G	

2.4 (16.0 pt)

H	I
J	**K**

2.5 (5.0 pt)

L

2.6 (4.0 pt)

☐ 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 of **6**.

☐ F^- acts as a nucleophile and attacks the ester group of **6**.
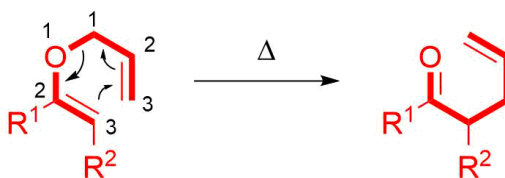
2.7 (28.0 pt)

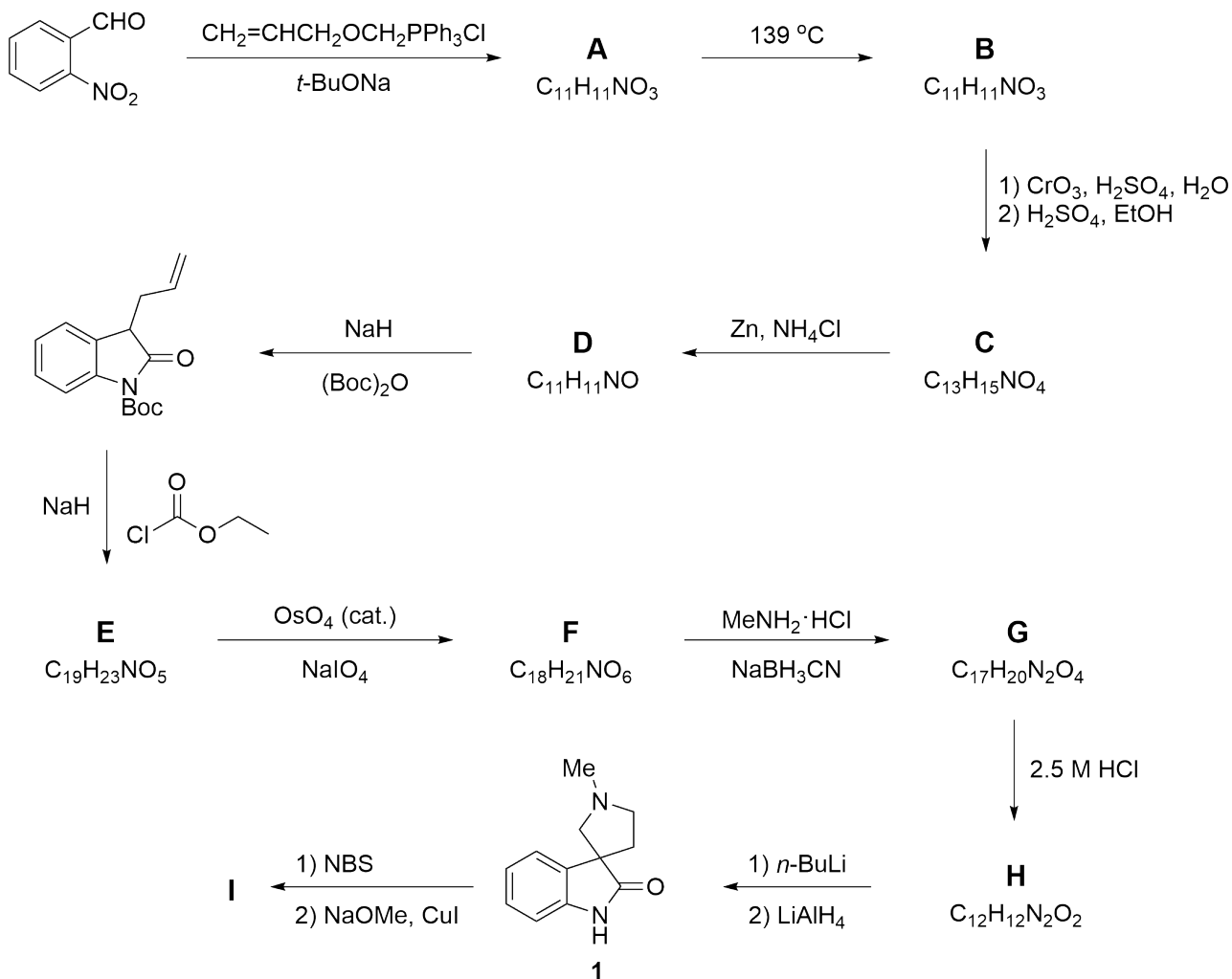| M	N
O and P	**Q**
R	**S**
T	**U**

(±)-Coerulescine

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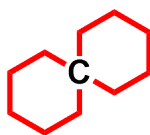
The Claisen rearrangement, which is a [3,3]-sigmatropic rearrangement, is a powerful carbon–carbon bond-forming reaction in which an allyl vinyl ether is converted thermally to an unsaturated carbonyl compound as shown in the scheme below. When compound **A** is heated, it undergoes a Claisen rearrangement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

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

$$\text{o-nitrobenzaldehyde (CHO, NO}_2\text{)} \xrightarrow[t\text{-BuONa}]{CH_2=CHCH_2OCH_2PPh_3Cl} \mathbf{A} \quad C_{11}H_{11}NO_3 \xrightarrow{139\ ^\circ C} \mathbf{B} \quad C_{11}H_{11}NO_3$$

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

$$\mathbf{D} \quad C_{11}H_{11}NO \xleftarrow[\ ]{Zn,\ NH_4Cl} \mathbf{C} \quad C_{13}H_{15}NO_4$$

allyl-oxindole-Boc $\xleftarrow[(Boc)_2O]{NaH}$ **D**

NaH, ethyl chloroformate (Cl—C(=O)—O—Et)

$$\mathbf{E} \quad C_{19}H_{23}NO_5 \xrightarrow[NaIO_4]{OsO_4\ (cat.)} \mathbf{F} \quad C_{18}H_{21}NO_6 \xrightarrow[NaBH_3CN]{MeNH_2\cdot HCl} \mathbf{G} \quad C_{17}H_{20}N_2O_4$$

2.5 M HCl

$$\mathbf{I} \xleftarrow[2)\ NaOMe,\ CuI]{1)\ NBS} \mathbf{1} \xleftarrow[2)\ LiAlH_4]{1)\ n\text{-BuLi}} \mathbf{H} \quad C_{12}H_{12}N_2O_2$$

1 (spiro compound with Me–N pyrrolidine and oxindole)

Boc : *tert*-butyl carbonate

NBS : *N*-bromosuccinimide

3.1	**Draw** the structures of **A** and **B**. • **A** is an inseparable mixture of *cis/trans* isomers. • **B** has an IR absorption at 1726 cm^{-1}.	8.0pt

3.2	**Draw** structures of **C**, **D**, **E**, and **F**. • **D**–**F** have bicyclic structures.	16.0pt

3.3	**Choose** the correct order of steps for the transformation of **F** to **G**.	4.0pt

3.4	**Draw** structures of **G** and **H** (both spiro compounds).	8.0pt

3.5	**Draw** the structure of the intermediate produced by treatment with *n*-BuLi in the step **H** → **coerulescine (1)**.	5.0pt

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.	5.0pt

3.7	When the allyl ether of 2-naphthol is heated a sigmatropic rearrangement is initiated. **Write** the structure of the major product isolated from this reaction.	5.0pt

IChO
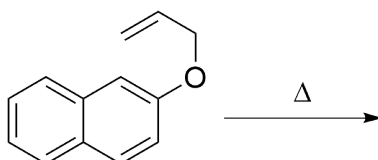
(±)-Coerulescine

3.1 (8.0 pt)

A	B

3.2 (16.0 pt)

C	D
E	**F**

3.3 (4.0 pt)

☐   Imine formation, then reduction, then amidation

☐   Amidation, then imine formation, then reduction

☐   Reduction, then amidation, then imine formation
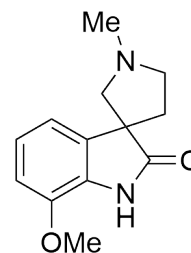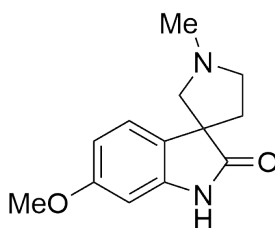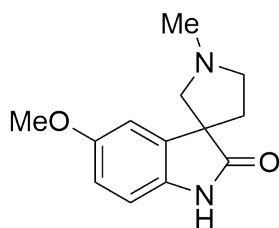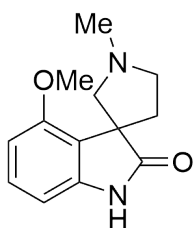
3.4 (8.0 pt)

G	H

3.5 (5.0 pt)

3.6 (5.0 pt)

☐ ☐ ☐ ☐

3.7 (5.0 pt)
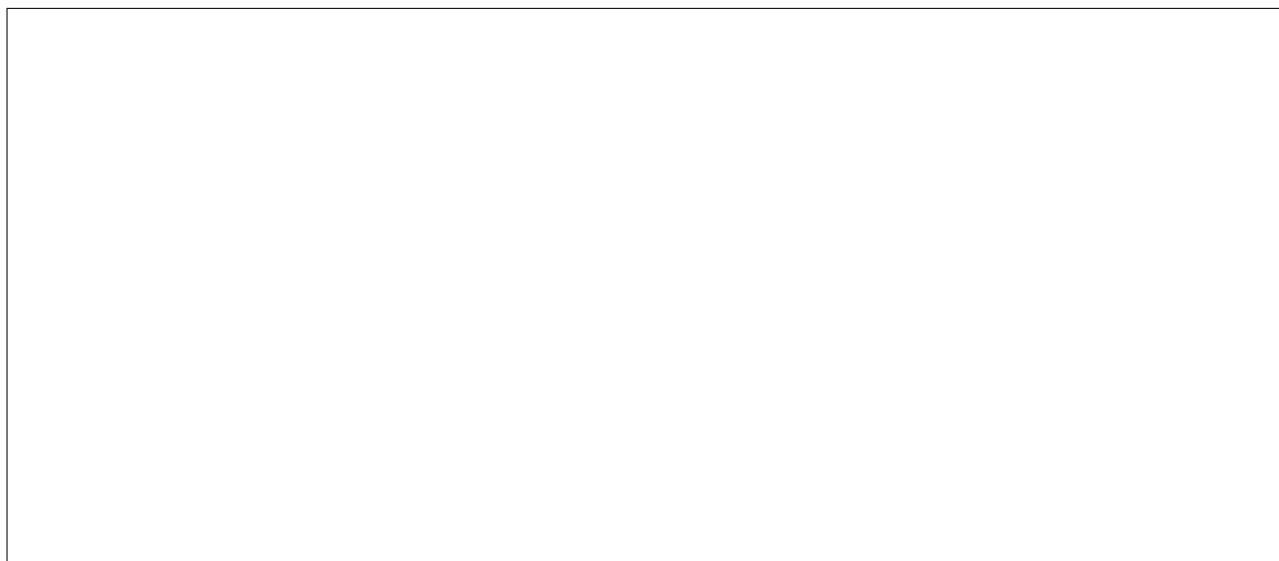
Symmetry Does Matter!

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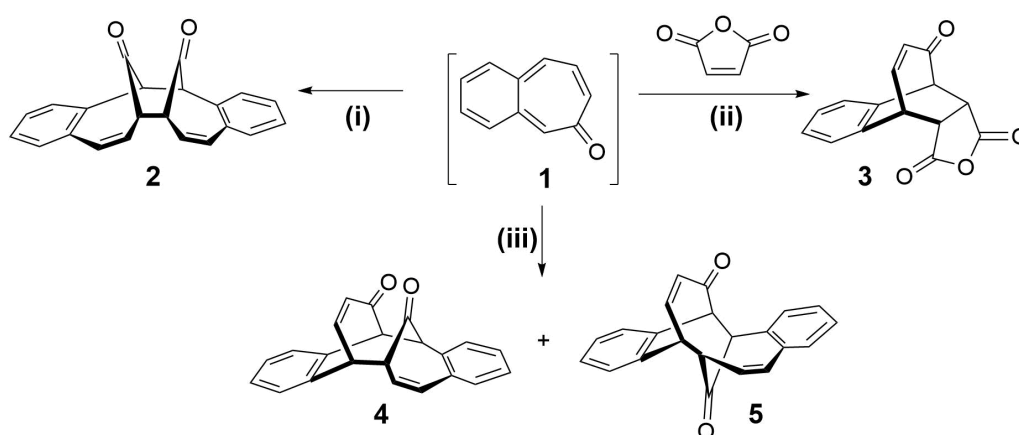
Woodward–Hoffmann rules				
	Electrocyclic reactions		**Cycloadditions**	
Number of electrons	Thermal (Δ)	Photochemical ($h\nu$)	Thermal (Δ)	Photochemical ($h\nu$)
4n (n = 1, 2, ..)	Conrotatory (con)	Disrotatory	Disfavoured	Favoured
4n+2 (n = 1, 2, ..)	Disrotatory (dis)	Conrotatory	Favoured	Disfavoured

---

4.1 **Fill** in the table for reactions (**i**)–(**iii**) or products **2**–**5**: 12.0pt

---

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 six-electron system in the benzene ring.


4.2 **Draw** the structures of the stable benzotropone isomers **A** (with 6 signals in its ^{13}C-NMR) and **B** (with 11 signals in its ^{13}C-NMR). 6.0pt
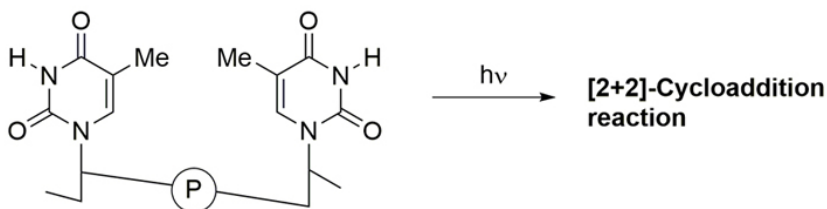

4.3 When the following tetraene is reacted under photochemical conditions, symmetry-allowed product(s) of three different ring sizes can form according to the Woodward–Hoffmann rules. **Tick** the correct answer in each row.

6.0pt

Prof. Dr. Aziz Sancar

[2+2]-Cycloaddition reaction
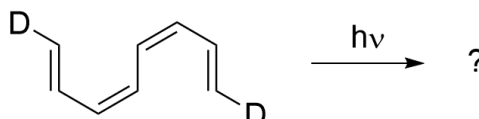
The Nobel Prize in Chemistry 2015 was awarded jointly to the Turkish scientist Aziz Sancar, Swedish scientist Tomas Lindahl, and American scientist Paul Modrich for their "mechanistic studies of DNA repair". Pyrimidine bases found in DNA may undergo a photochemical **[2+2]-cycloaddition reaction** in the presence of UV light (see above figure), causing damage to DNA, which may ultimately lead to skin cancer. Prof. Sancar focussed on the DNA repair mechanism for this type of damage.

Thymine (T) is one of the nucleobases that can undergo such a photochemical reaction. Assume that a solution of free thymine was subjected to UV irradiation.

T
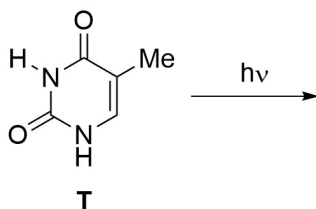
4.4 Considering stereochemistry, **draw** the structures of **all possible products** of this reaction between two free thymine (T) molecules. **Circle** the compound(s) which is/are chiral. Drawing only one enantiomer of an enantiomeric pair is sufficient. Note that only C=C bonds participate in this reaction.

16.0pt

A broad range of halogenated derivatives of norbornadiene (**N**) are known in the literature. Tribromo-norbornadiene ($C_7H_5Br_3$) has six achiral (meso) isomers. Three of these isomers (**6**, **7**, and **8**) are given below.

N   **6**   **7**   **8**
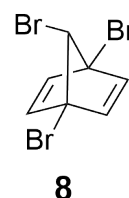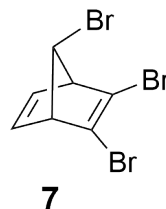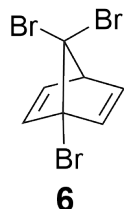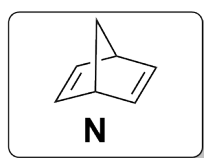
4.5 How many signals do you expect from the ^{13}C-NMR spectra of isomers **6**, **7**, and **8**? **Fill in** the following boxes.	9.0pt

4.6 **Draw** structures of the remaining achiral (meso) tribromo-norbornadiene ($C_7H_5Br_3$) isomers (**C**, **D**, and **E**) in addition to **6–8** using the given frameworks.	9.0pt

The NMR spectrum of ether **9** is not simple. The two methoxy 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, considering all resonance structures and symmetry, is shown as **11**.

9   **10**   **11**
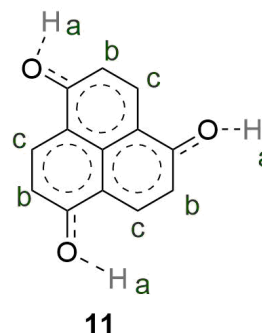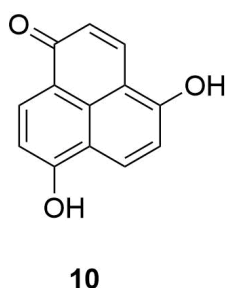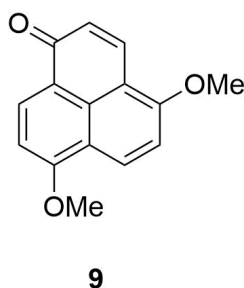
4.7 How many signals do you expect from the ^{13}C- and ^{1}H-NMR spectra of **12** and **13**?	8.0pt

12   **13**

$Ms = Me-S(=O)(=O)-$
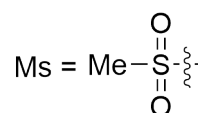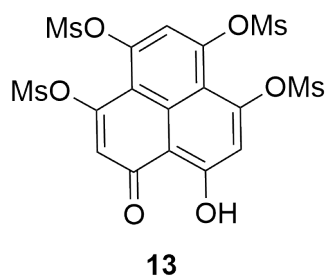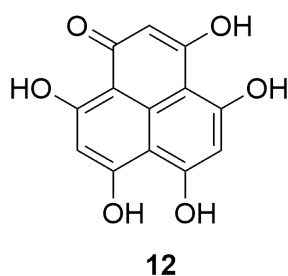
Symmetry Does Matter!

4.1 (12.0 pt)

Reaction	Product	[? + ?] cycloaddition	Δ or $h\nu$
i	2		
ii	3		
iii	4		
	5		

4.2 (6.0 pt)

A	B

4.3 (6.0 pt)

4.4 (16.0 pt)

4.5 (9.0 pt)

6	7	8

4.6 (9.0 pt)

C	D	E

4.7 (8.0 pt)

12

.... signals in ^{13}C-NMR

.... signals in ^{1}H-NMR

13

Ms = MeSO$_2$

.... signals in ^{13}C-NMR

.... signals in ^{1}H-NMR

Konya, Carrot, Beta-Carotene, Vitamin-A, Immune System, Vision

Mevlana (Rumi) was a mystic and Sufi poet who lived 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.

Carrots are an important source of β-carotene, which gives the vegetable its colour. 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 vision, the immune system, and growth and development.

β-Carotene has an extended polyene chain of 22 carbon atoms. It has 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. There are 22 π-electrons in the molecule (Figure 1).

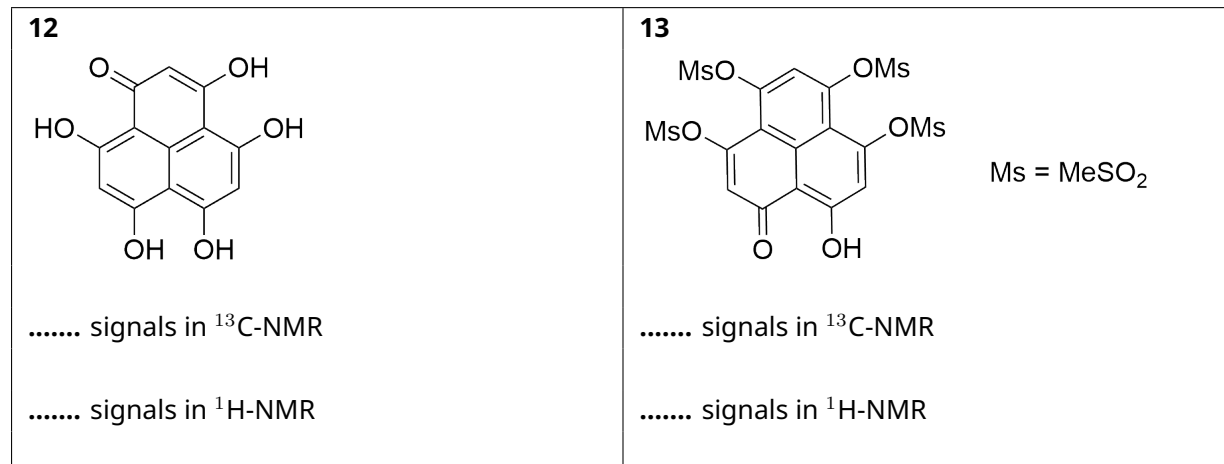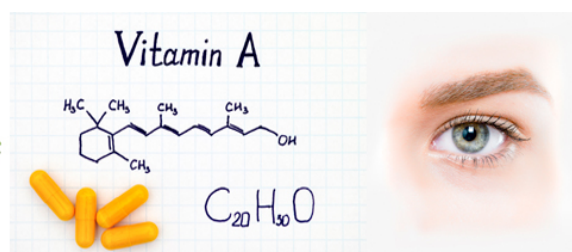**Figure 1.** Ball and stick representation of the structure of β-carotene. The grey and white spheres represent carbon and hydrogen atoms, respectively. The numbered carbon atoms belong to the linear conjugated π-segment of the molecule.
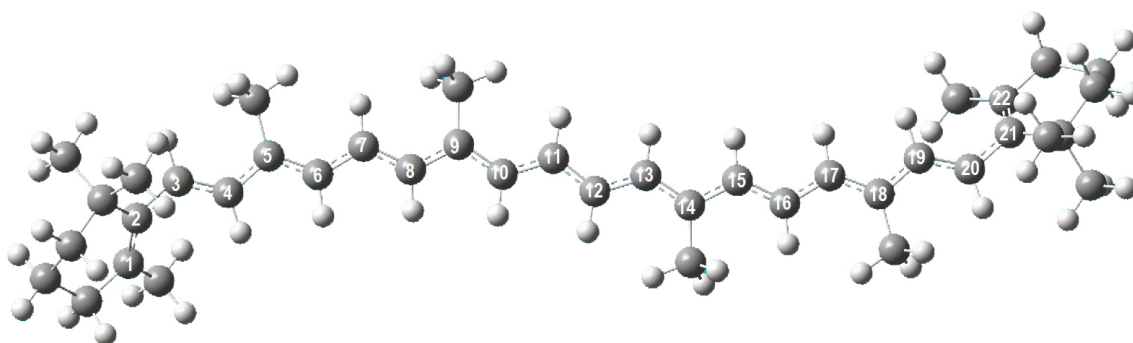
To a crude approximation, the electrons in the C $2p_z$ orbitals, which are perpendicular to the molecular plane, are assumed to move along the entire molecule, without interacting with each other. They are like independent particles confined in a molecule moving along the x-axis in one dimension. These characteristics of π-electrons allow them to be modelled as **particles in a one-dimensional box**.

The wavefunctions and energies of the quantised levels for an electron moving in a one-dimensional box with infinite potential walls are given below:

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

where n is the quantum number, $n = 1, 2, 3, 4, \ldots \infty$, and L is the box length.

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

In two dimensions, within the framework of the 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 are:

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

where n_x and 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.	13.0pt

The β-carotene molecule is orange in colour because:

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

ii) HOMO→LUMO transition occurs by absorption of an 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 does not absorb red/yellow light.

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.

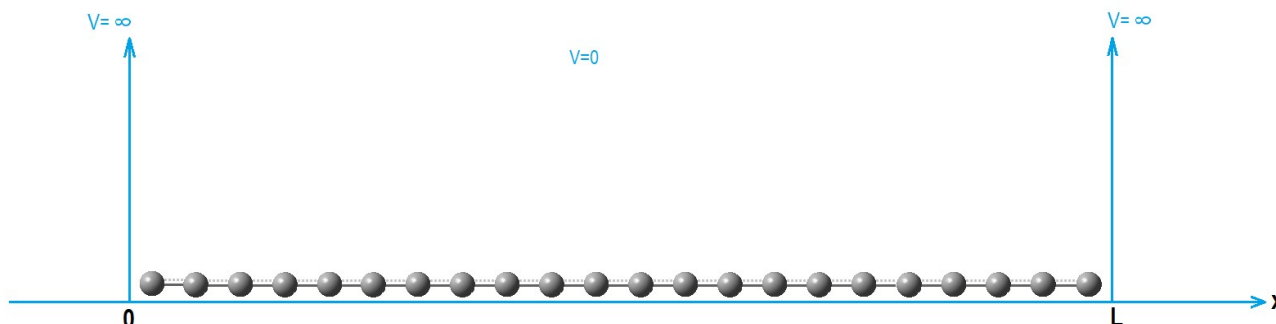**Use this information to answer questions 5.2–5.6.**

Figure 2. Schematic representation of the conjugated line segment made up of the carbon atoms of β-carotene in a one-dimensional box of length L.

5.2	**Calculate** the energies (in J) of the two lowest energy levels.	13.0pt

5.3	**Draw** the wavefunctions of the two lowest energy levels. Properly label the x-axis.	15.0pt

5.4	**Sketch** the energy level diagram up to $n = 4$ showing the relative spacing.	8.0pt

5.5	What is the total π-energy (in J) of the molecule?	12.0pt

5.6	**Calculate** the wavelength (in nm) at which the transition between the highest occupied and lowest unoccupied energy levels occurs.	10.0pt

Use the particle in a two-dimensional box model to answer questions 5.7–5.8.
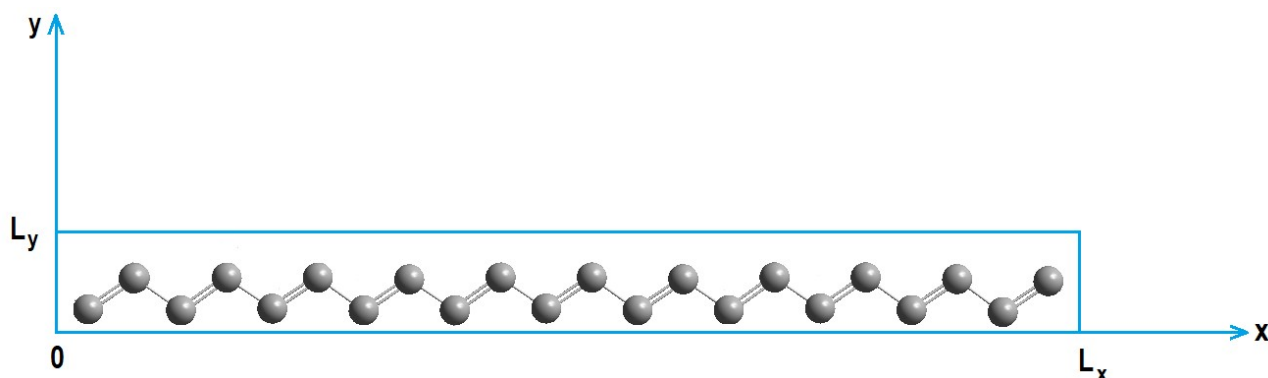

Figure 3. A schematic representation of the conjugated carbon atoms of β-carotene in a two-dimensional box.

Assume that the conjugated segment is all *trans* and the π-electrons are in a 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.	17.0pt

5.8	What should the L_x value be (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 the HOMO and LUMO are the same as in the question 5.7.)	12.0pt

Konya, Carrot, Beta-Carotene, Vitamin-A, Immune System, Vision

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5.1 (13.0 pt)

☐ **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

5.2 (13.0 pt)

Calculation:

A5-2
British English (United Kingdom)

5.3 (15.0 pt)

5.4 (8.0 pt)

5.5 (12.0 pt)

5.6 (10.0 pt)

calculation:

5.7 (17.0 pt)
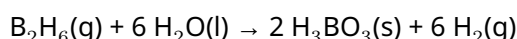
calculation:

5.8 (12.0 pt)

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 ideal 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.
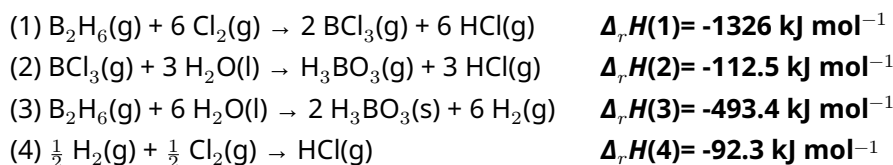- C→A; reversible adiabatic compression.
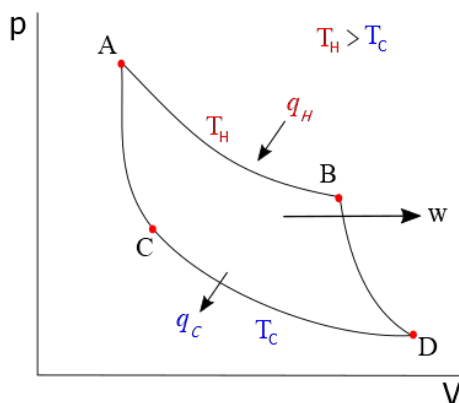
After heat transfers, the remaining energy is released as work (w). Also, q_H and q_C are related to T_C and T_H as follows:

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

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

You are provided with the enthalpy changes of the following reactions at 300 K.

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

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

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

(4) $\frac{1}{2}\ H_2(g) + \frac{1}{2}\ Cl_2(g) \rightarrow HCl(g)$ $\Delta_rH(4)$= **-92.3 kJ mol^{-1}**

6.1	**Calculate** the molar enthalpy of sublimation (in kJ mol^{-1}) for H_3BO_3 at 300 K.	5.0pt

6.2	**Calculate** the internal energy (Δ_rU, in kJ mol^{-1}) at 300 K for reactions (2) and (4) given above (assume ideal gas behavior for each gaseous species in each reaction).	12.0pt

6.3	**Calculate** the overall work produced by a heat engine ($|w|$, in J) and the overall heat released to the cold sink ($|q_C|$, in J).	6.0pt

6.4	**Calculate** the efficiency of the heat engine described above.	3.0pt

6.5	**Calculate** the entropy change (ΔS, in J K^{-1}) for A→B and D→C processes in the heat engine.	6.0pt

6.6	**Calculate** the Gibbs energy change (ΔG, in J) for A→B and D→C processes in the heat engine.	6.0pt

6.7	**Calculate** the ratio of the pressure at point A to the pressure at point B in the cycle (standard pressure: 1 bar).	5.0pt

6.8	**Calculate** 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.	3.0pt

Part 2

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

$$B_2H_6\ (g) + 3O_2\ (g) \rightarrow B_2O_3\ (s) + 3H_2O\ (g)$$
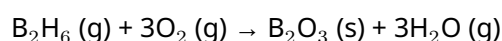
Diborane was combusted in a 100 L closed container at different temperatures, and the amounts of diborane and water were recorded at equilibrium.

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

The partial pressure of O_2 (g) was adjusted to 1 bar and kept constant at all conditions. Assume that in this hypothetical universe:

- $\Delta_r S°$ and $\Delta_r H°$ 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 ideal gases.

- All species remain in the same phase, without any further decomposition before or after reaction, at all temperatures.

6.9	**Calculate** K_p (pressure based equilibrium constant) at 8930 K and 9005 K.	8.0pt

6.10	**Calculate** $\Delta_r G°$ of the reaction in kJ mol^{-1} at 8930 K and 9005 K. (If you failed to find K_p, use K_p (8930 K) = 2, K_p (9005 K) = 0.5)	6.0pt

6.11	**Calculate** $\Delta_r G°$ (in kJ mol^{-1}), $\Delta_r H°$ (in kJ mol^{-1}), and $\Delta_r S°$ (in J mol^{-1}K^{-1}) of the combustion reaction at 298 K. (If you failed to find K_p, use K_p (8930 K) =2, K_p (9005 K) = 0.5)	6.0pt

6.12	Determine whether combustion reactions are favoured or not at the indicated temperatures at standard pressure (1 bar). **Tick** the correct answer for each temperature in the table.	8.0pt

6.13	**Calculate** the $\Delta_f H$ (kJ mol^{-1}) and S°(kJ mol^{-1} K^{-1}) of $H_2O(g)$ 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 $\Delta H°$ = 1000 kJ mol-1, $\Delta S°$= 150 J K^{-1} mol^{-1})	6.0pt

	$\Delta_f H$ (298 K)	S° (298 K)
B_2H_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_2O_3 (s)	–1273 kJ mol^{-1}	0.05 kJ mol^{-1} K^{-1}

Thermodynamics through an Interstellar Journey

6.1 (5.0 pt)

Show your calculation:

6.2 (12.0 pt)

Show your calculation:

6.3 (6.0 pt)

Show your calculation:

6.4 (3.0 pt)

Show your calculation:

6.5 (6.0 pt)

Show your calculation:

6.6 (6.0 pt)

Show your calculation:

6.7 (5.0 pt)

Show your calculation:

6.8 (3.0 pt)

Show your calculation:

6.9 (8.0 pt)

Show your calculation:

6.10 (6.0 pt)

Show your calculation:

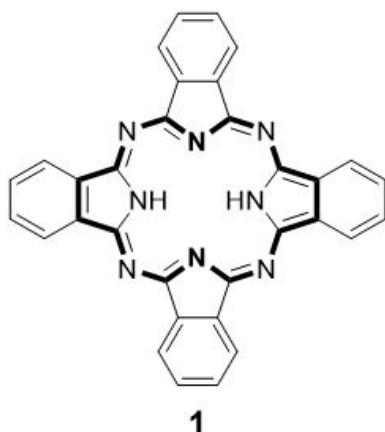**6.11** (6.0 pt)

Show your calculation:

6.12 (8.0 pt)

	Favoured	Unfavoured
298 K	☐	☐
8930 K	☐	☐
9005 K	☐	☐
9100 K	☐	☐

6.13 (6.0 pt)

Show your calculation:

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?	4.0pt

CuPc
2

TiOPc
3

SiCl₂Pc
4

Ce(Pc)₂
5
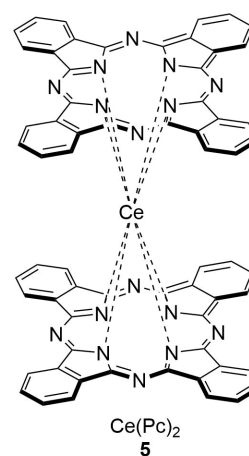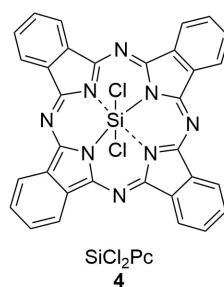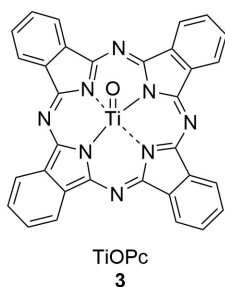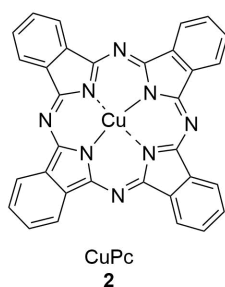
Pcs containing one or two metal ions are called metallo-phthalocyanines (MPcs) and exhibit different geometries as shown above.

| 7.2 | Determine the coordination number of the central ions in **2**–**5**. **Complete** the table in your answer sheet. | 8.0pt |

| 7.3 | Determine the oxidation number of each metal (Cu, Ti, and Ce) in **2**, **3**, and **5**. **Complete** the table in your answer sheet. | 6.0pt |

| 7.4 | Determine the geometry of compounds **2**–**5**. **Complete** the table in your answer sheet. | 8.0pt |

| 7.5 | Determine whether compounds **2**–**5** are paramagnetic or diamagnetic.
• Use the letter "**p**" for paramagnetic and letter "**d**" for diamagnetic. **Complete** the table in your answer sheet. | 8.0pt |

| 7.6 | **Write** the ground-state electron configuration of the silicon (Si) ion in compound **4**, and **write** all the quantum numbers for all the 2p electrons in its ground state. | 14.0pt |

Metal-free phthalocyanine (**1**, H_2Pc) can be formed through the cyclotetramerisation of phthalonitriles.

Asymmetric Pcs (where the substituents are not all the same) can be prepared by the statistical cyclisation of two different phthalonitriles. This method has no selectivity and the product is a mixture of all possible isomers.

| 7.7 | **Draw** the possible products that may occur in the statistical cyclisation method by using **F** and **G**. If there are any stereoisomers label these as *cis*- or *trans*-. | 19.0pt |

• **F** and **G** represent two different symmetrical phthalonitriles.
• One of the products is F_4 as given below.
• Draw the other products in the same format as F_4.

F_4
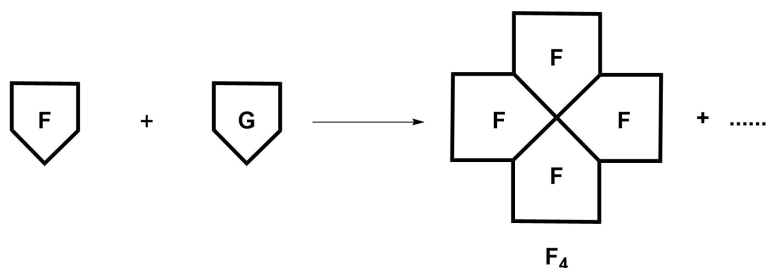
Pcs are used as photosensitisers in the photodynamic therapy (PDT) of cancer due to their strong absorption in the visible spectrum and high molar absorption coefficients. PDT consists of three essential components: **photosensitiser**, light, and oxygen. Together they initiate a photochemical reaction resulting in the generation of cytotoxic singlet oxygen ($^1O_2$) that can destroy cancer cells.

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

- The multiplicity of an energy level is defined as $2S+1$

- If the two spins are parallel (↑↑), $S = 1$, and if the two spins are antiparallel (↑↓), $S = 0$.

7.8	**<u>Draw</u>** the molecule orbital (MO) diagram of the lowest energy singlet state of dioxygen ($^1O_2$) and calculate the bond order. • There are no unpaired electrons in this state!	12.0pt

7.9	If the wavelength of the light needed to excite triplet oxygen into singlet oxygen is 1270 nm, **<u>calculate</u>** the energy (in kJ mol^{-1}) needed for this transition process.	6.0pt

Phthalocyanines

7.1 (4.0 pt)

The number of π-electrons in the bold region of the H_2Pc molecule:

7.2 (8.0 pt)

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

7.3 (6.0 pt)

Compound	2	3	5
Oxidation number of metal			

7.4 (8.0 pt)

Geometry	Compound
Octahedral	
Square prism	
Square pyramidal	
Square planar	

7.5 (8.0 pt)

Compound	Magnetic property
2	
3	
4	
5	

7.6 (14.0 pt)

Electron configuration:				
	n	l	m_1	m_s
Quantum numbers for 2p electrons:				

7.7 (19.0 pt)

Products:

7.8 (12.0 pt)

MO diagram:

Bond order:

7.9 (6.0 pt)

Show you calculation:

Energy = …………………… kJ/mol

Boron Compounds and Hydrogen Storage

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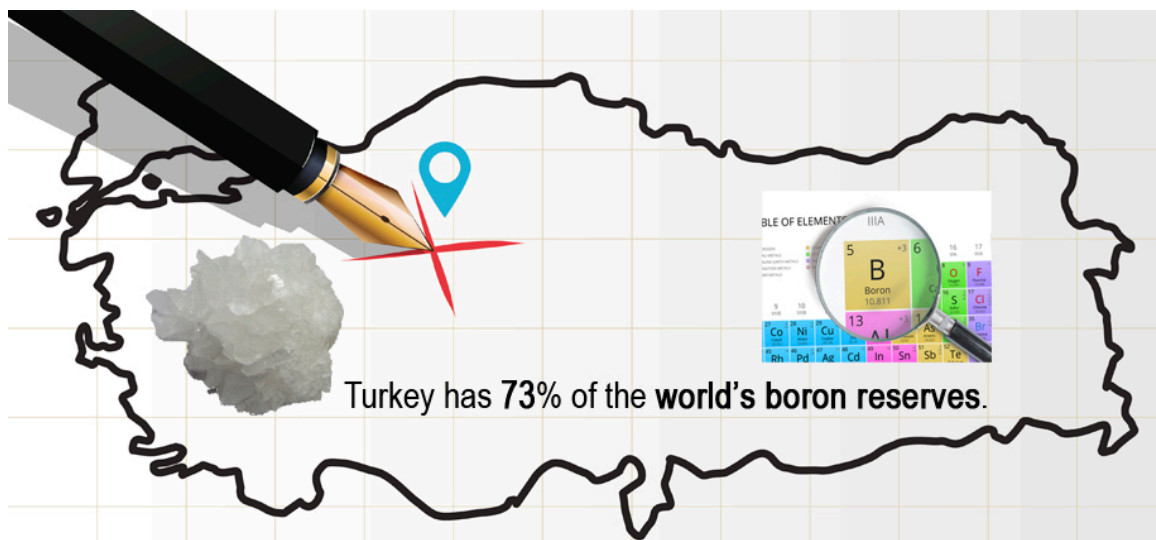
Sodium borohydride ($NaBH_4$) and ammonia borane (BNH_6) are the most studied chemical hydrogen storage materials. In this question, you will explore the chemistry of boron and the use of boron compounds as hydrogen storage materials.

Borax ($Na_2B_4O_7 \cdot nH_2O$) is a boron mineral that is produced by the ETI Mining Company in Turkey. $NaBH_4$ can be synthesised by the reduction of anhydrous borax with metallic sodium and silicon dioxide (silica) under high-pressure hydrogen gas at 700 °C, namely the Bayer process. In this process, all hydrogen is stored in $NaBH_4$. Alternatively, ammonia borane (BNH_6) can be synthesized by the reaction of $NaBH_4$ and ammonium sulfate in dry tetrahydrofuran (THF) at 40 °C. While $NaBH_4$ is an ionic compound, ammonia borane is a Lewis acid–base adduct.

Hint: BNH_6 synthesis must be conducted in a fume cupboard because a flammable gas is generated as one of the by-products.

8.1	<u>**Write**</u> a balanced chemical equation for the synthesis of $NaBH_4$ from anhydrous borax.	3.0pt
8.2	<u>**Write**</u> a balanced chemical equation for the synthesis of ammonia borane from $NaBH_4$.	3.0pt
8.3	<u>**Draw**</u> the molecular geometries of the BH_4^- ion and BNH_6 molecule.	4.0pt
8.4	<u>**Calculate**</u> the hydrogen content of $NaBH_4$ and BNH_6 as a percentage by mass (wt%).	4.0pt

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

8.5	**Write** the balanced chemical equations for the hydrolysis of $NaBH_4$ and BNH_6.	4.0pt

One of the simplest stable borates is diboron trioxide (B_2O_3). Higher borates, such as cyclic $B_3O_6^{3-}$ structures containing B-O bonds, can be formed. Since B_2O_3 is an acidic compound, it readily reacts with water to produce boric acid (H_3BO_3).

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	**Write** the balanced chemical equations for the synthesis of boric acid and boron nitride.	4.0pt

8.7	**Draw** the molecular structures of the $B_3O_6^{3-}$ ion, boric acid, and a single two-dimensional boron nitride sheet. **Show** at least 10 B atoms in the boron nitride structure.	6.0pt

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 synthesised via metathesis of a boron halide and a hydride source.

8.8	**Write** a balanced chemical equation for the synthesis of diborane from the reaction of BF_3 and $LiBH_4$. **Hint:** both products are boron compounds.	3.0pt

8.9	**Draw** the molecular geometry of the diborane molecule. **Hint:** there is no B-B bond in the molecule.	2.0pt

BH_3 (borane) is an unstable and highly reactive molecule. It is not possible to isolate it as BH_3 under ordinary conditions. However, it can be stabilised via its reaction with carbon monoxide to yield borane carbonyl (BH_3CO), 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	**Draw** the Lewis dot structure of BH_3CO molecule showing the formal charges.	3.0pt

8.11	Which statement given on the answer sheet is true of the $C-O$ bond of a CO molecule upon the bond formation between BH_3 and CO? **Tick** the correct box.	2.0pt

Borazine (with the molecular formula $B_3N_3H_6$) is isostructural to benzene. It consists of single and double bonded $B-N$ units in a cycle with hydrogen atoms attached.

Borazine can be synthesised using a two-step procedure. Initially ammonium chloride reacts with boron trichloride to prepare the symmetrically trisubstituted chlorine derivative of borazine ($B_3N_3H_3Cl_3$), which is then reduced by $LiBH_4$ in THF (tetrahydrofuran).

8.12	**Write** the chemical equations for the two-step synthesis of borazine. **Hint:** THF stabilises one of the products by forming a Lewis acid-base adduct.	4.0pt

8.13	**Draw** the molecular structures of borazine and its symmetrically trisubstituted chlorine derivative.	4.0pt

Catalysts are substances that increase the rate of reactions by allowing them to proceed via a lower energy pathway. The activity of a catalyst is determined by the turnover frequency, TOF:

TOF = moles of product/(moles of 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 min.

8.14	**Calculate** the TOF of the CuPt/C catalyst **in terms of only Pt atoms** (in min^{-1}) for the hydrolysis of BNH_6, by considering the volume of the hydrogen gas generated. Assume the catalytic reaction is performed under standard conditions (1 atm and 273.15 K).	4.0pt

Crystal analysis of Cu_xPt_y displacement alloy nanoparticles determined that the face centred cubic (fcc) unit cell was formed of Pt atoms. The Pt atoms on the faces were replaced with Cu atoms. The subscripts indicate molar ratios of the atoms in the alloy structure.

8.15	**Determine** the composition of the alloy nanoparticles by finding x and y in the Cu_xPt_y alloy composition.	2.0pt

8.16	**Sketch** the unit cell of Cu_xPt_y alloy nanoparticles, showing the position of atoms in the unit cell.	2.0pt

8.17	Another alloy has a Cu_2Pt_1 composition. Assume that this alloy also has an 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.	4.0pt

Boron Compounds and Hydrogen Storage

8.1 (3.0 pt)

8.2 (3.0 pt)

8.3 (4.0 pt)

8.4 (4.0 pt)

8.5 (4.0 pt)

8.6 (4.0 pt)

8.7 (6.0 pt)

$B_3O_6^{3-}$	Boric acid	Boron nitride

8.8 (3.0 pt)

8.9 (2.0 pt)

8.10 (3.0 pt)

8.11 (2.0 pt)

☐   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 because CO donates its mainly non-bonding electrons to BH_3.

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

8.12 (4.0 pt)

8.13 (4.0 pt)

8.14 (4.0 pt)

8.15 (2.0 pt)

8.16 (2.0 pt)

8.17 (4.0 pt)

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 analyser at 298 K:

Step 1) Five different 10 mL samples, each from a different part of the wastewater pool, were combined in a 100 mL beaker, and then stirred for 5 min.

Step 2) 10 mL of this combined solution was taken and 142 mg of Na_2SO_4 was added while stirring. This was then transferred to a three-electrode cell as seen in Figure 1a. In this electrochemical cell, Pt wire, Ag/AgCl (in 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 was applied for 14 min as shown in Figure 1b (horizontal line). It is assumed that 14 min is sufficient to complete the expected electrochemical reactions.
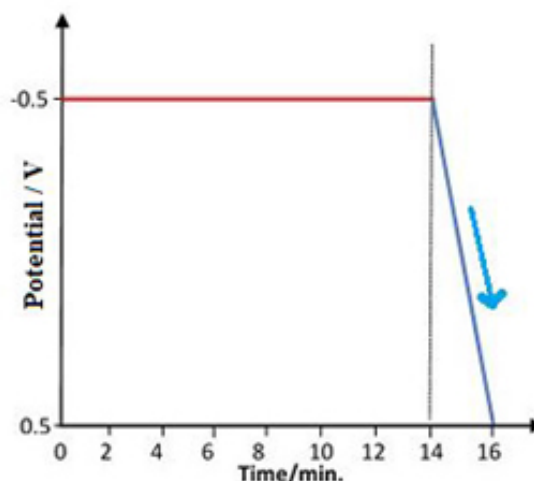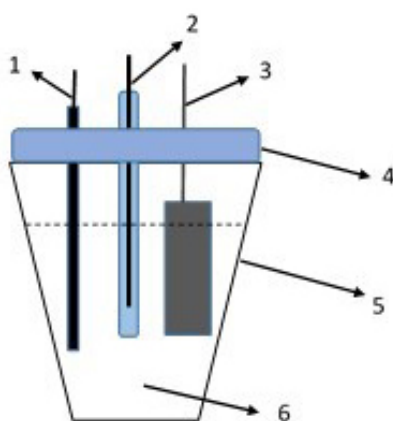

Figure 1. a) Electrochemical cell design; 1) Working electrode (Pt wire), 2) reference electrode (Ag/AgCl in 3 M KCl), 3) counter electrode (Pt foil), 4) cell tap, 5) electrochemical cell, 6) 10 mL of sample solution. **b)** Potential of working electrode as a function of time.

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 the potential was scanned between –0.50 and +0.50 V as seen in Figure 1b (downward sloping line for 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).
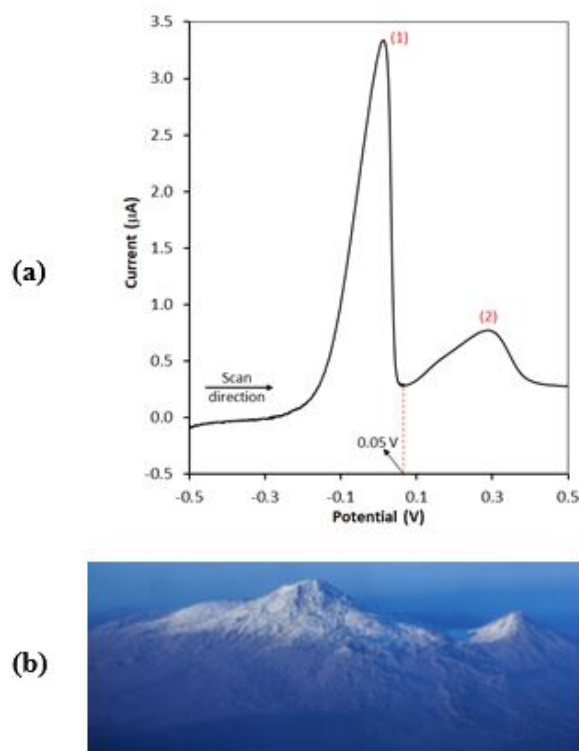
Figure 2. a) Potential scan of the working electrode as a function of current in 0.1 M H_2SO_4 solution after keeping it constant at a potential of –0.50 V in 10 mL of wastewater sample as seen in Figure 1b (horizontal line). y-axis: current/μA, x-axis: potential/V vs Ag/AgCl, b) A view of Great and 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 min. 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) 1 mL of a solution of ethylenediaminetetraacetic acid (EDTA, H_4Y) (Figure 3) had its equivalence point with 3.85 mg/mL $BaCO_3$.

5 mL of this EDTA solution was added to the solid obtained in step 6 and it was shaken to dissolve. Then, the pH of the solution was adjusted to 10.0. Excess EDTA was titrated with standard 0.0010 M $Ni(NO_3)_2$ solution, and it was observed that 95.60 mL of $Ni(NO_3)_2$ solution was consumed up to the endpoint.
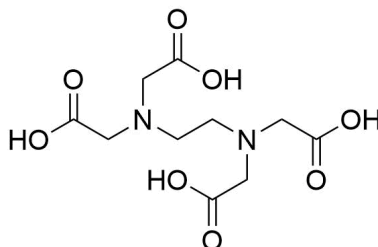
Figure 3. Chemical structure of EDTA (H_4Y).

- In water saturated with H_2S, the equilibrium concentration of $[H_2S]$ 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

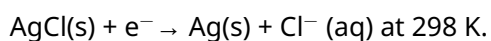| 9.1	Which of the following is a correct description for what is happening at peak 1 and peak 2 in Figure 2a? **Tick** the correct box on the answer sheet.	5.0pt

9.2	If, at the first step (horizontal line) in Figure 1b, the potential is applied as –1.2 V instead of –0.5 V, which gas is evolved? **Tick** the correct box on the answer sheet.	5.0pt

9.3	**Calculate** the scan rate of data presented in Figure 2a in mV/s at 298 K.	8.0pt

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

$$Pt, H_2 \text{ (0.92 bar)}|HCl(1.50\times10^{-2}M), AgCl(sat)|Ag$$
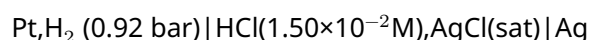
9.4	**Calculate** the standard electrode potential (in V) of the half-cell: $AgCl(s) + e^- \rightarrow Ag(s) + Cl^-$ (aq) at 298 K. *Note*: You must show all working.	16.0pt

9.5	Which of the statements describes the main purpose of *step* 5? **Tick** the correct box on the answer sheet.	5.0pt

9.6	**Write** net ionic equations for the complexation and the back titration reaction of *step* 7.	6.0pt

9.7	**Calculate** the Ni^{2+} concentration in mg/L in the wastewater of the factory. *Note:* You must show all working.	25.0pt

9.8	If you pass H_2S gas into the solution obtained in *step 5* until saturation, **calculate** the minimum pH value for precipitation of Ni^{2+} ions to occur. If you cannot solve question **9.7**, use a 20 mg/L Ni^{2+} sample for this question. *Note:* You must show all working.	30.0pt

Quantification of Heavy Metal Ions

9.1 (5.0 pt)

☐ 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

9.2 (5.0 pt)

☐ NO evolution
☐ NO_2 evolution
☐ Nitrogen evolution
☐ Oxygen evolution
☐ Hydrogen evolution

9.3 (8.0 pt)

Show your calculation:

Scan rate = ……………………………………………… mV/s

9.4 (16.0 pt)

Show your calculation:

Standard electrode potential =........................ V

9.5 (5.0 pt)

☐ 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

9.6 (6.0 pt)

Complexation:

Back titration:

9.7 (25.0 pt)

Show your calculation:

Ni^{2+} concentration: ……………………………… mg/L:

9.8 (30.0 pt)

Show your calculation:

Minimum pH value: ....