



General Instructions



- Only write with pen. Your calculator should be non-programmable.
- This theoretical exam booklet contains **63 pages**, not including the general instructions.
- This examination has **9 problems**.
- You will have **5 hours** to solve the exam.
- **Begin** only when the **START** announcement is called.
- All solutions must be written in pen in the appropriate boxes in the designated areas on the **answer sheets provided**. Use the back of the examination question paper sheets if you need paper to do roughwork. 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 final **STOP** announcement is called to indicate the end of the examination.
- You **must stop** working when the **STOP** announcement is called. Failure to stop writing will lead to the nullification of your exam.
- The official English version of this examination is also available on request if required. The official version should only be used for clarification purposes if necessary.
- You are not allowed to leave your workplace without permission. If you need any assistance (broken calculator, need to visit the bathroom, etc.), raise your hand and wait until an invigilator arrives.

GOOD LUCK!



Problems & Grading Information

Problem No	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



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Physical Constants and Equations

Avogadro's number	$N_A = 6.0221 \times 10^{23} \text{ mol}^{-1}$
Boltzmann constant	$k_B = 1.3807 \times 10^{23} \text{ J K}^{-1}$
Universal gas constant	$R = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} = 0.08205 \text{ atm L K}^{-1} \text{ mol}^{-1}$
Speed of light	$c = 2.9979 \times 10^8 \text{ m s}^{-1}$
Planck's constant	$h = 6.6261 \times 10^{-34} \text{ J s}$
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	$P_{atm} = 1.01325 \times 10^5 \text{ Pa} = 760 \text{ mmHg} = 760 \text{ torr}$
Zero of the Celsius scale	273.15 K
1 picometre (pm)	$10^{-12} \text{ m}; 1 \text{ Å} = 10^{-10} \text{ m}$
1 nanometre (nm)	10^{-9} 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	$PV = nRT$



Physical Constants and Equations

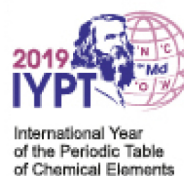
Enthalpy	$H = U + PV$
Gibbs free energy	$G = H - TS$
	$\Delta_r G = \Delta G^0 + RT \ln Q$
	$\Delta_r G^0 = -RT \ln K = -nFE_{cell}^0$
Entropy change	$\Delta S = \frac{q_{rev}}{T}$, where q_{rev} is heat for the reversible process
Entropy change	$\Delta S = nR \ln \frac{v_2}{v_1}$ (for isothermal expansion of an ideal gas)
Nernst equation	$E = E^0 + \frac{RT}{nF} \ln \frac{C_{oxidation}}{C_{reduction}}$
Energy of a photon	$E = \frac{hc}{\lambda}$
Integrated rate law	
Zero-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	$y = mx + n$
Lambert-Beer equation	$A = \varepsilon lc$



Periodic Table of Elements

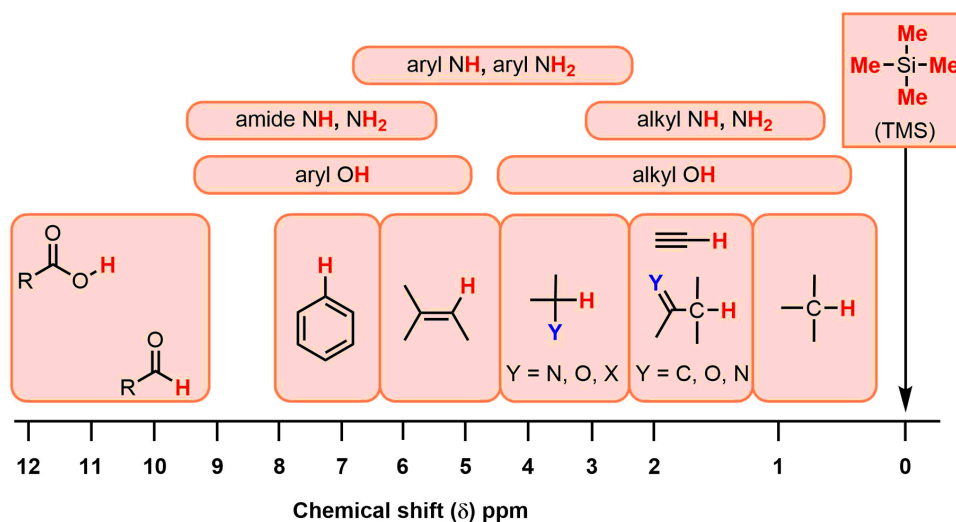
1																	18																		
<div>1 H 1.008</div>		2		<div><div>atomic number</div><div>Symbol</div><div>atomic weight</div></div>														13		14		15		16		17		<div>2 He 4.003</div>							
<div>3 Li 6.94</div>		<div>4 Be 9.01</div>																<div>5 B 10.81</div>		<div>6 C 12.01</div>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

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 -

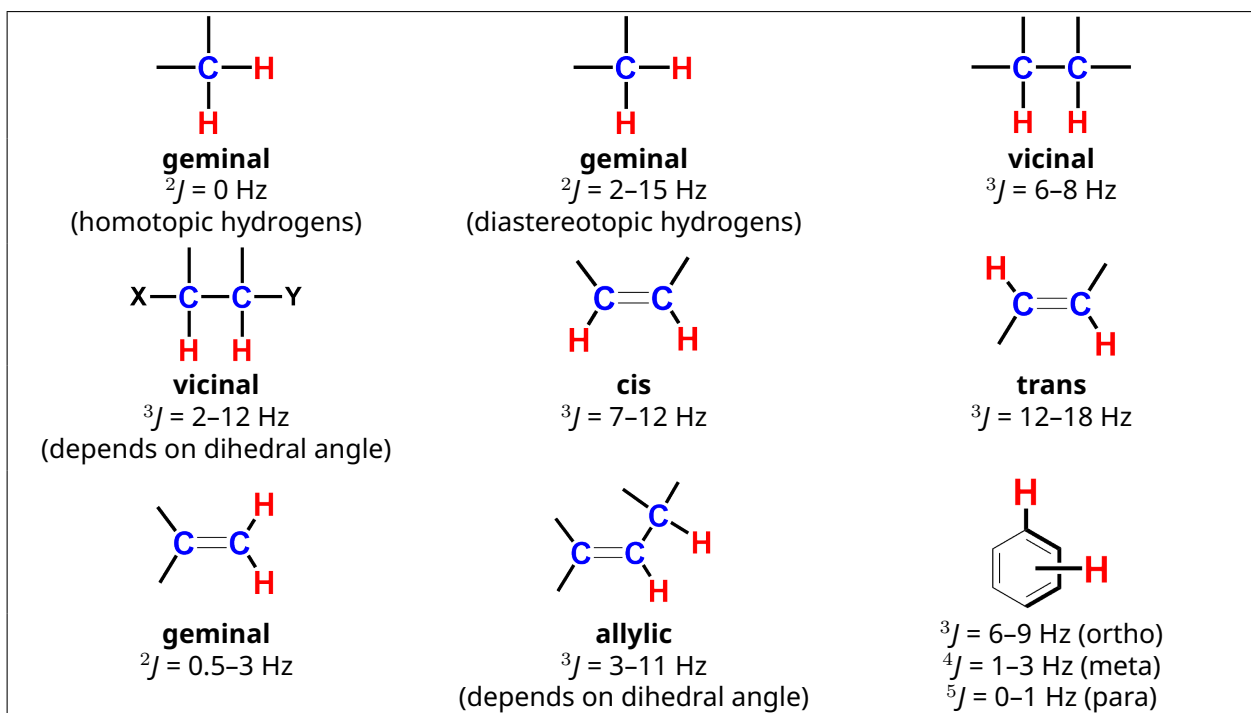


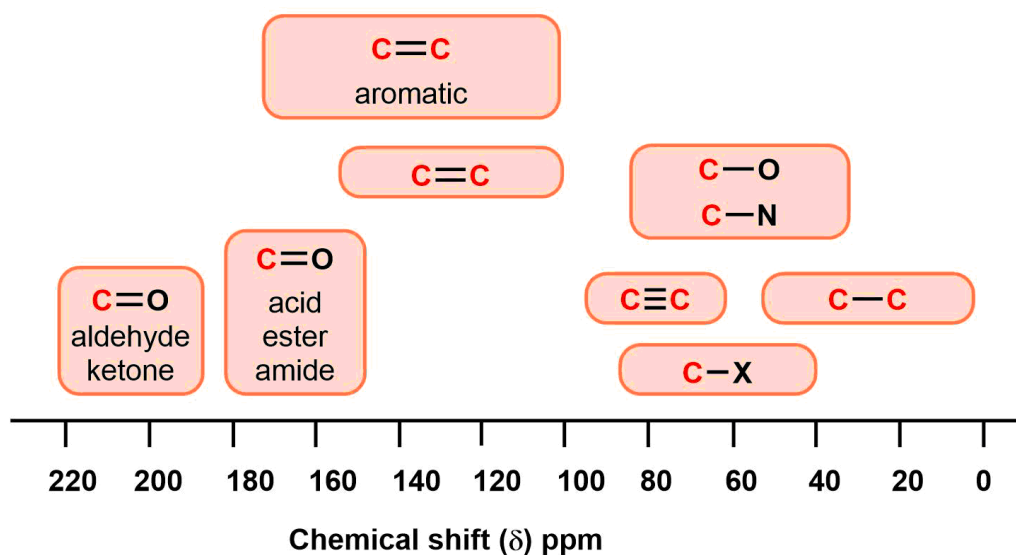
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Typical Coupling Constants







IR Absorption Frequency Table

Functional Group	Type of Vibration	Absorption Region (cm^{-1})	Frequency	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
$\text{C}\equiv\text{C}$	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	

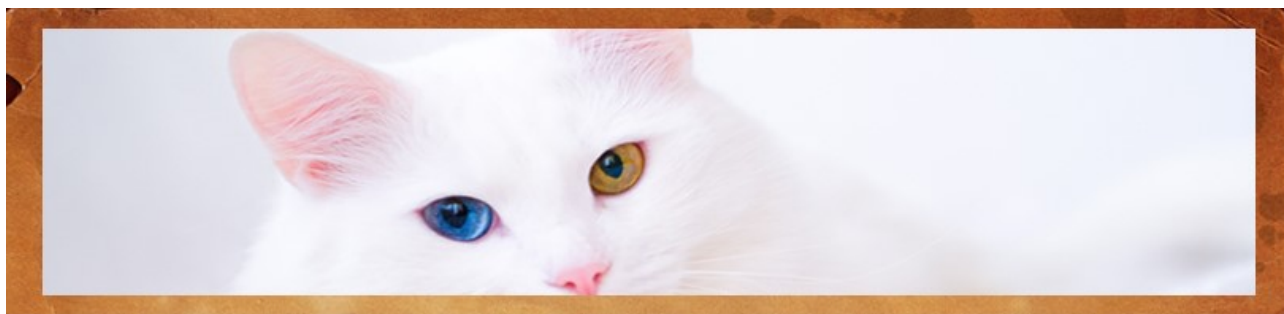


IR Absorption Frequency Table

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 \equiv 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

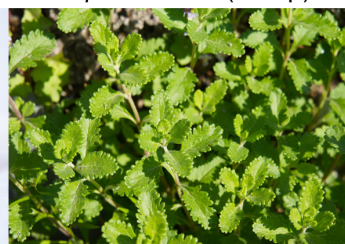


The most beautiful of cats, the Van cat is a pure breed living only in the Lake Van basin. Another endemic cat breed is the Ankara cat. They are called Angora cats. Their most important feature is their two different eye colors.

Van cat

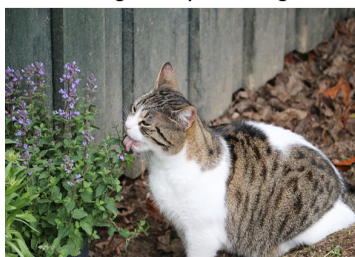


Ankara cat

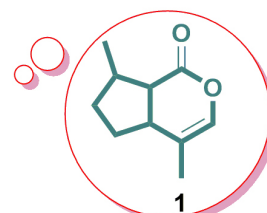
*Nepeta cataria* (catnip)

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 monoterpene compound derived from isoprene with two fused rings: a cyclopentane and a lactone.

Cat eating catnip in the garden



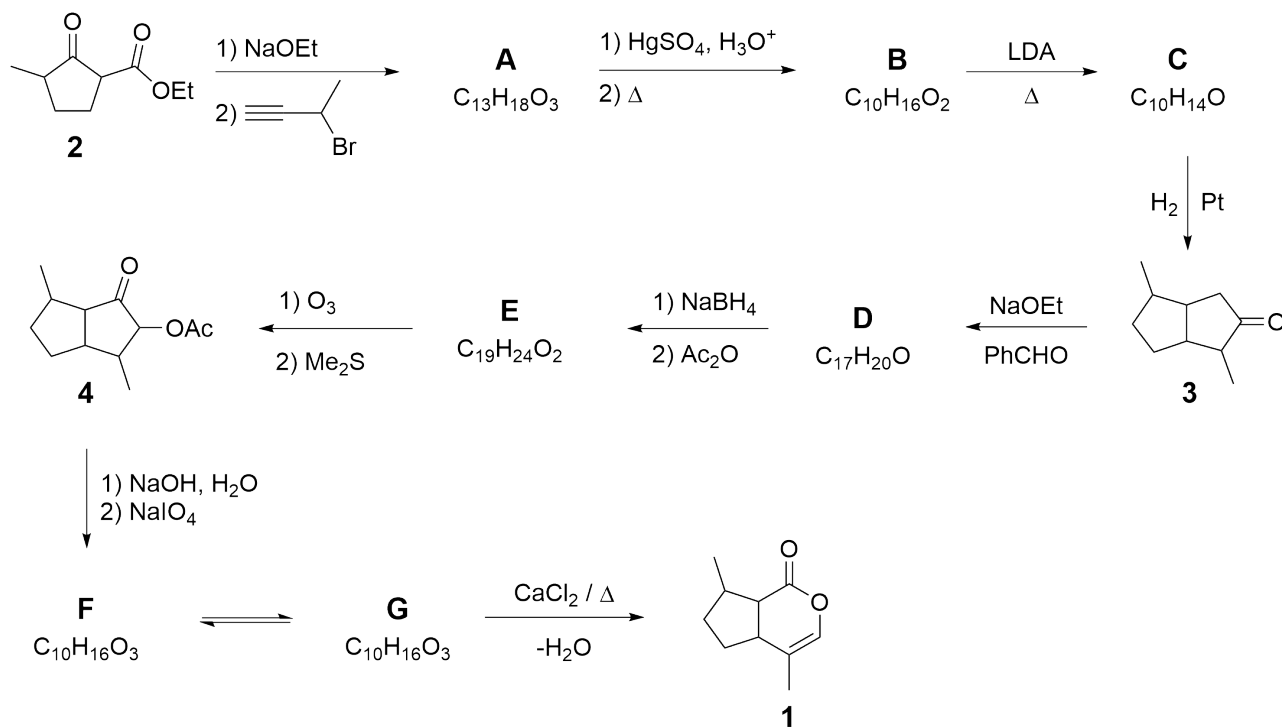
Cat's dream



Nepetalactone



Total synthesis of nepetalactone:



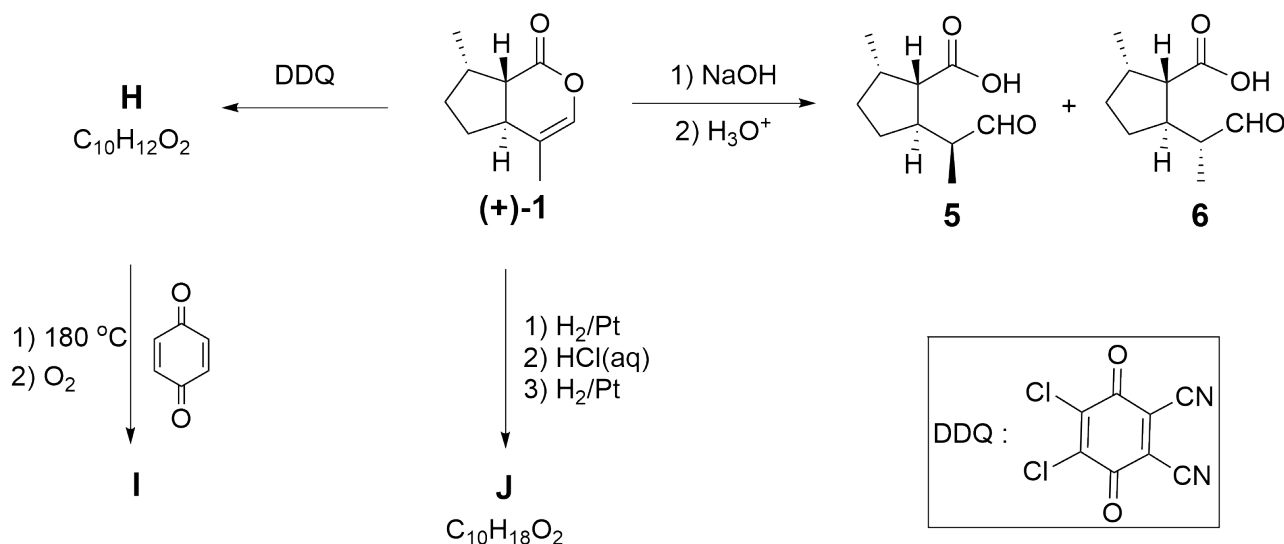
1.1 The scheme above describes the total synthesis of nepetalactone. **Draw** structures of **A–G**, without stereochemical details. 14.0pt

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 $\sim 9.8\text{ ppm}$ in the 1H -NMR spectrum.



Reactions of nepetalactone:



The scheme above 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 the highly conjugated compound **H**. The 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. 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	



A1-2

English (Ireland) (Ireland)

1.2 (4.0 pt)

- ☐ Enantiomers
- ☐ Diastereomers
- ☐ Identical
- ☐ Stereoisomers

1.3 (6.0 pt)

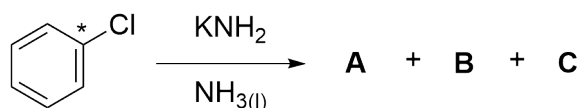
H	I
J	



A Tale of a Reactive Intermediate

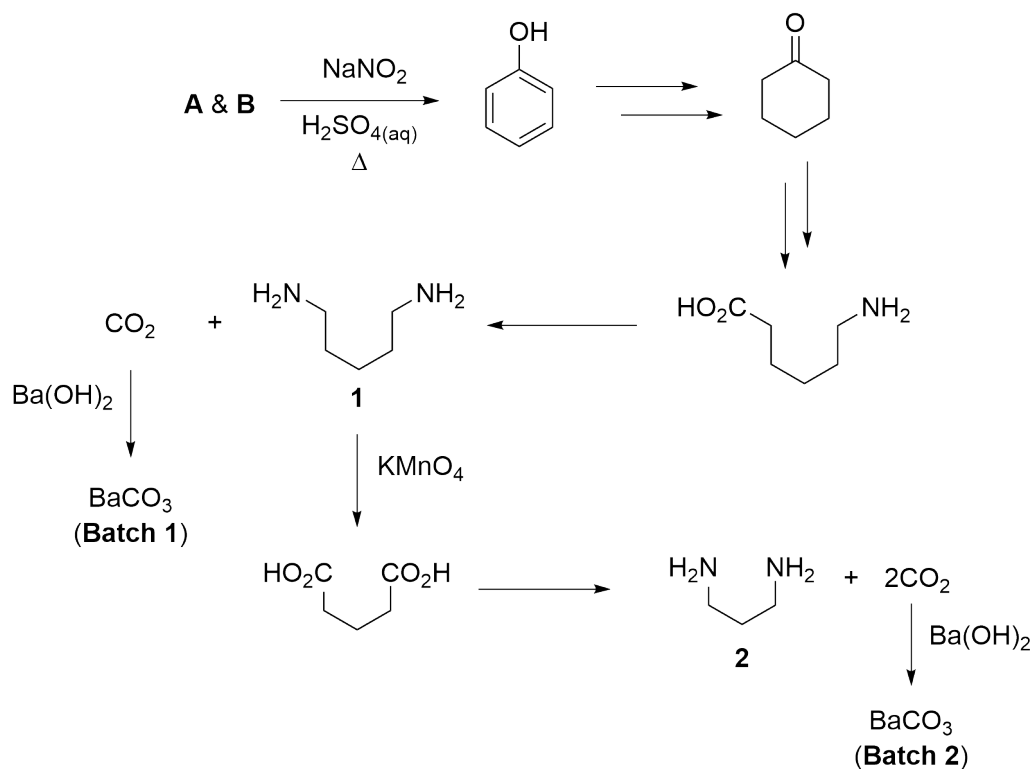
Arynes constitute a special class of reactive intermediates. The first experimental evidence for the structure of an aryne (benzyne) was demonstrated in 1953 via the elegant labeling experiments by John D. Roberts and coworkers.

In one such experiment, chlorobenzene, whose carbon at position 1 was 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**.



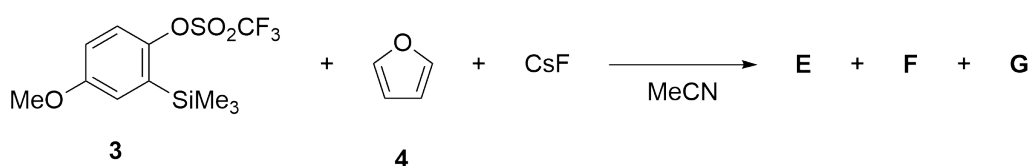
2.1 **Draw** the structures of **A**, **B** and **D**, and **provide** the formula of **C**. **Indicate** the position(s) of ^{14}C -labelled carbon(s) with an asterisk (*) whenever applicable. 7.0pt

Analysis of the ^{14}C -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.	9.0pt
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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 D₂O in ¹H-NMR spectroscopy.
- **F** is an ionic compound.

2.3 **Determine** the structures of **E**, **F**, and **G** (without stereochemical details). 8.0pt

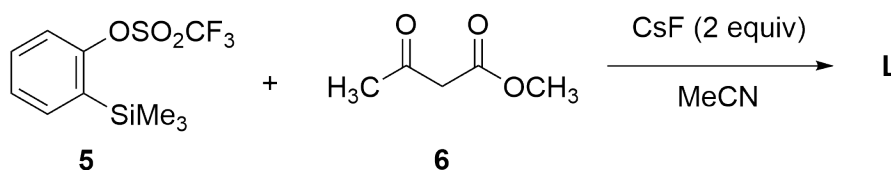
In the absence of a nucleophile or a trapping agent, arynes can undergo [2+2]-type cyclodimerization or [2+2+2]-type cyclotrimerization reactions under suitable conditions. The aryne derivative that is obtained when **3** is treated with one equivalent of CsF in MeCN can give, in principle, four different 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 Determine 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 ^1H -NMR and ^{13}C -NMR data for **L**, recorded 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.
- ¹³C-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 Determine the structure of **L**.

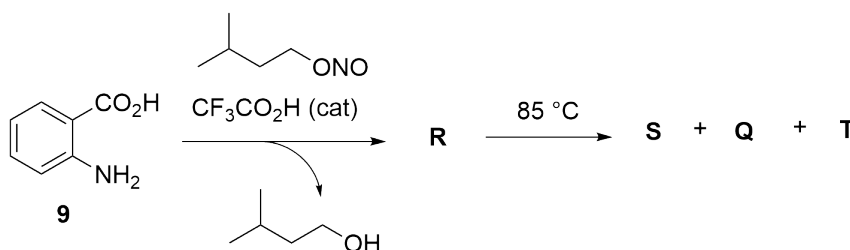
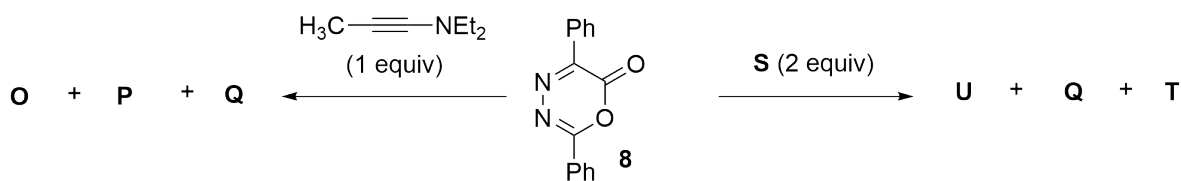
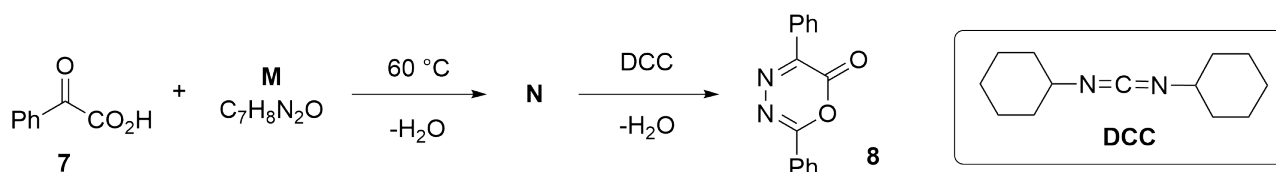
5.0pt

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? 4.0pt

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

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**:

- ☐ Compound **1**
- ☐ BaCO₃ (Batch **1**)
- ☐ Compound **2**
- ☐ BaCO₃ (Batch **2**)

Considering only **B**:

- ☐ Compound **1**
- ☐ BaCO₃ (Batch **1**)
- ☐ Compound **2**
- ☐ BaCO₃ (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 $-\text{SiMe}_3$ group of **5**.
- ☐ F^- acts as a base to deprotonate **6**.
- ☐ F^- acts as a nucleophile and attacks the ester group of **6**.



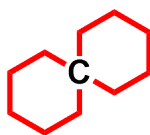
2.7 (28.0 pt)

M	N
O and P	Q
R	S
T	U



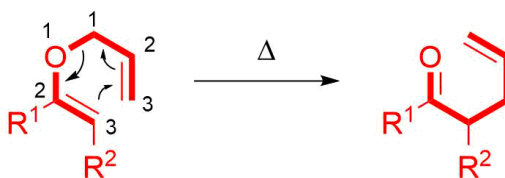
(±)-Coerulescine

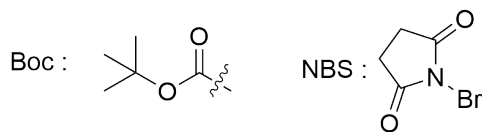
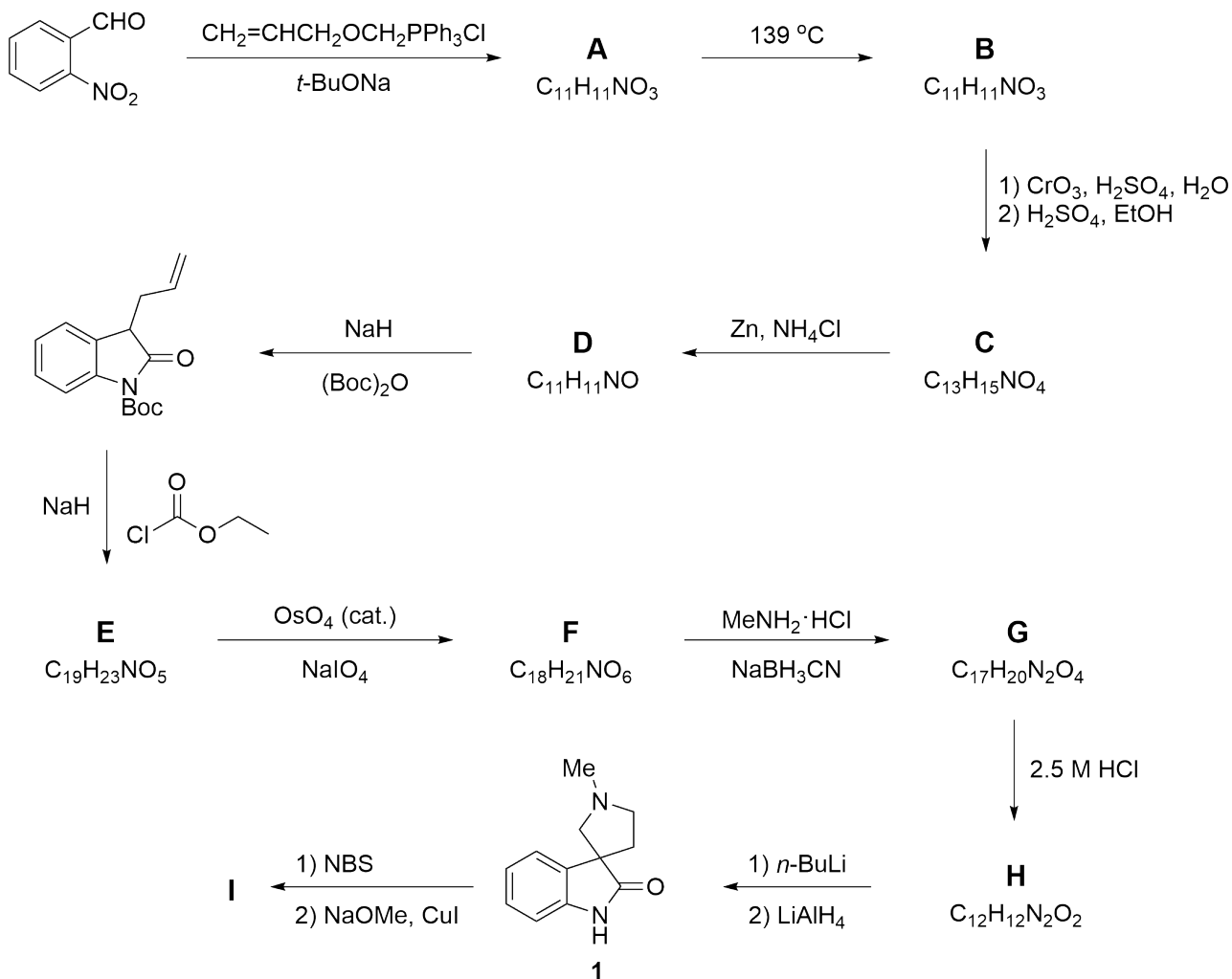
A spiro compound is typically an organic compound containing rings linked together by one common atom (spiroatom), such as the carbon atom shown in bold in the figure below. The spiro[pyrrolidin-3,3'-oxindole] ring system is a structural framework incorporated in several cytostatic alkaloids and unnatural compounds. Coerulescine (**1**) and horsfiline are the simplest prototype members of this subfamily that 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 details.







- 3.1 **Draw** the structures of **A** and **B**. 8.0pt
- **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**. 16.0pt
- **D–F** have bicyclic structures.

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

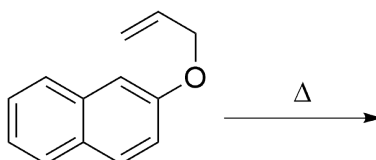
- 3.4 **Draw** structures for **G** and **H** (both of which are spiro compounds). 8.0pt

- 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 a 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 $^1\text{H-NMR}$ data: δ 7.05 (d, $J = 1.4\text{ Hz}$, 1H), 6.78 (d, $J = 8.0\text{ Hz}$, 1H), 6.72 (dd, $J = 8.0, 1.4\text{ Hz}$, 1H) ppm. 5.0pt

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





(±)-Coerulescine

3.1 (8.0 pt)

A

B

3.2 (16.0 pt)

C

D

E

F



3.3 (4.0 pt)

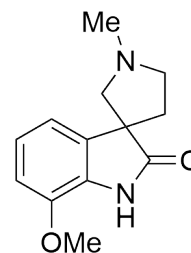
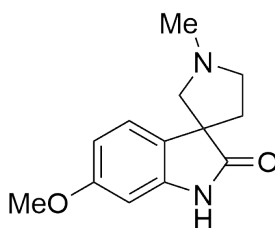
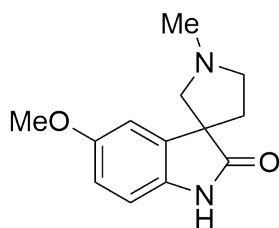
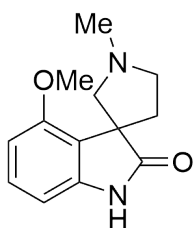
- ☐ Imine formation, then reduction, then amidation
- ☐ Amidation, then imine formation, then reduction
- ☐ Reduction, then amidation, then imine formation

3.4 (8.0 pt)

G

H

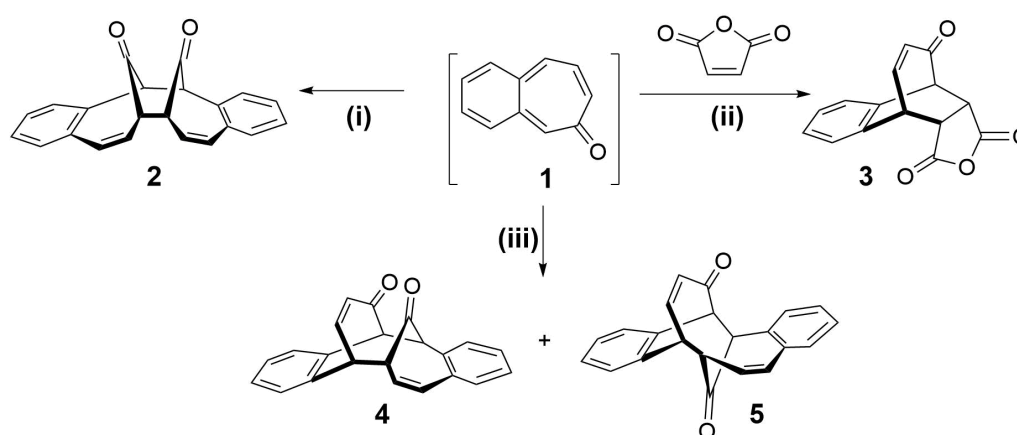
3.5 (5.0 pt)

**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 ($h\nu$)
$4n$ ($n = 1, 2, \dots$)	Conrotatory (con)	Disrotatory	Disfavoured	Favoured
$4n+2$ ($n = 1, 2, \dots$)	Disrotatory (dis)	Conrotatory	Favored	Disfavored

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

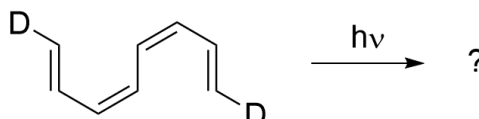
12.0pt

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 sextet electron system in the benzene ring.

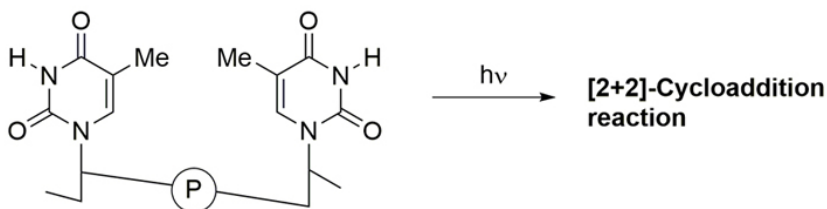
4.2 Draw the structures of the stable benzotropone isomers **A** (with 6 signals in its ^{13}C -NMR) and **B** (with 11 signals in its ^{13}C -NMR). 6.0pt



- 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

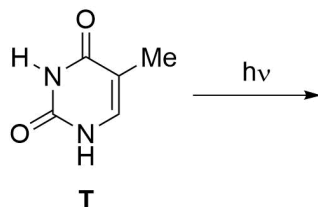


Prof. Dr. Aziz Sancar



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 figure above) 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.



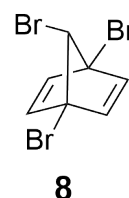
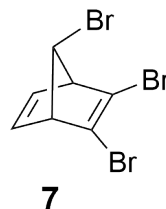
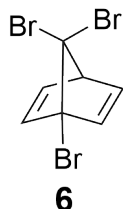
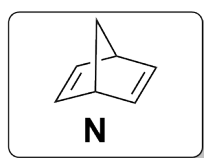
- 4.4** Considering stereochemistry, **draw** the structures of **all possible products** of this reaction between two free thymine (**T**) molecules. **Circle** the compound(s) which is/are chiral. Drawing only one enantiomer of an enantiomeric pair is sufficient. Please note that only C=C bonds participate in this reaction. 16.0pt

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



Q4-3

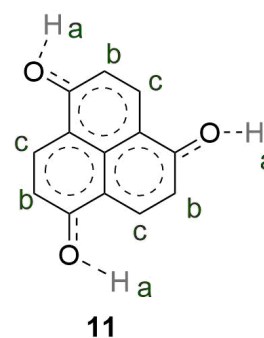
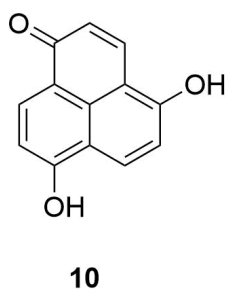
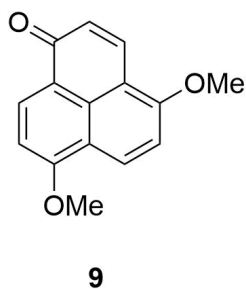
English (Ireland) (Ireland)



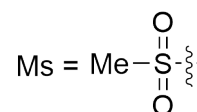
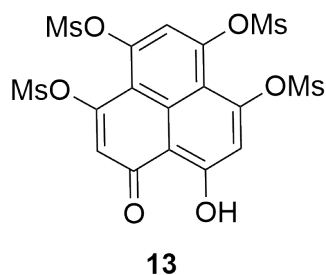
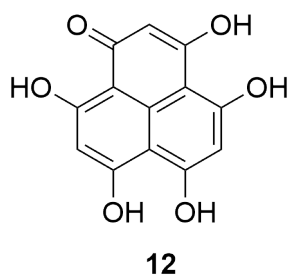
4.5 How many signals do you expect from the ^{13}C -NMR spectra of isomers **6**, **7**, and **8**? **Fill in** the boxes on the answer sheet. 9.0pt

4.6 **Draw** structures of the remaining achiral (meso) tribromo-norbornadiene ($\text{C}_7\text{H}_5\text{Br}_3$) isomers (**C**, **D**, and **E**) in addition to **6–8**, using the frameworks provided on the answer sheet. 9.0pt

The NMR spectrum of ether **9** is complex. 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**.



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



**A4-1**

English (Ireland) (Ireland)

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**

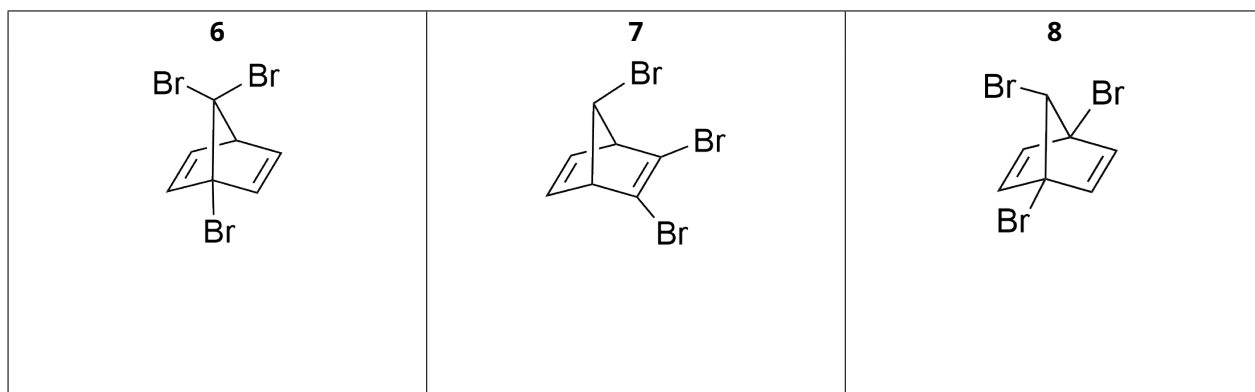
**4.3** (6.0 pt)

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<input type="checkbox"/>		<input type="checkbox"/>	
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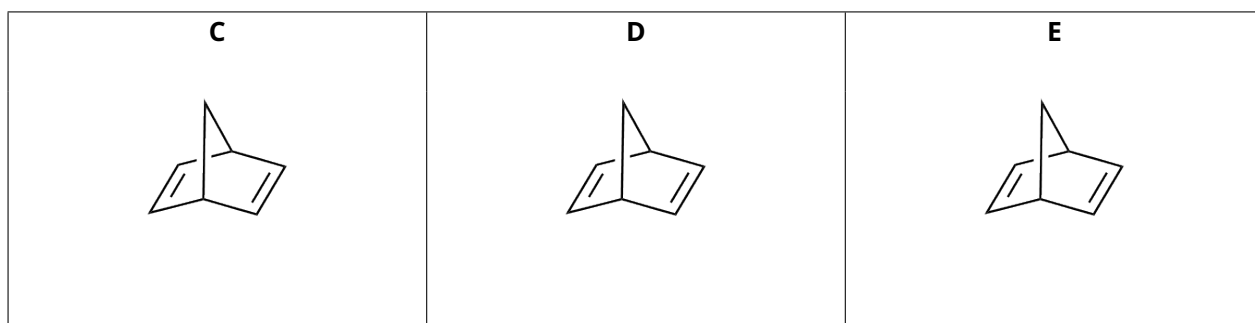
4.4 (16.0 pt)



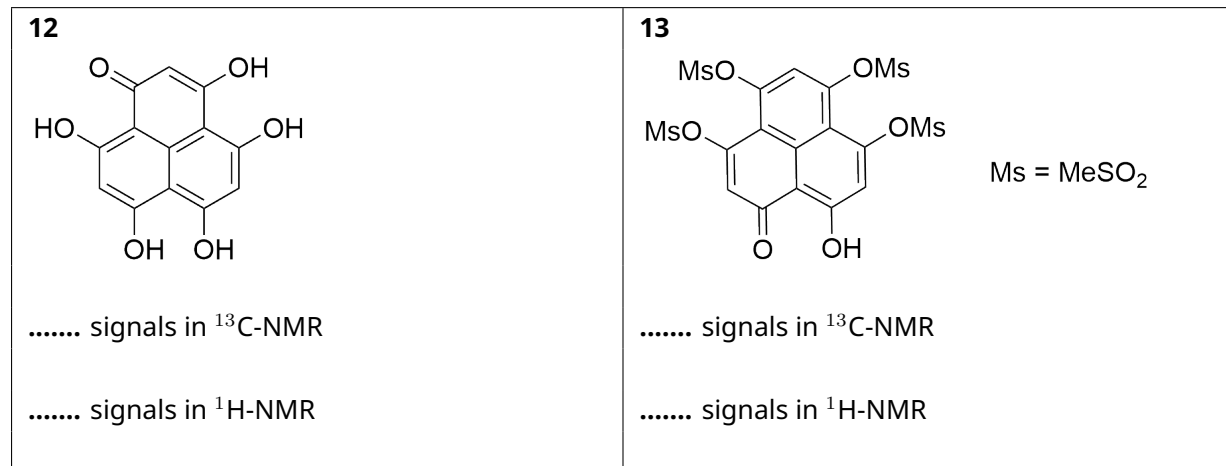
4.5 (9.0 pt)



4.6 (9.0 pt)

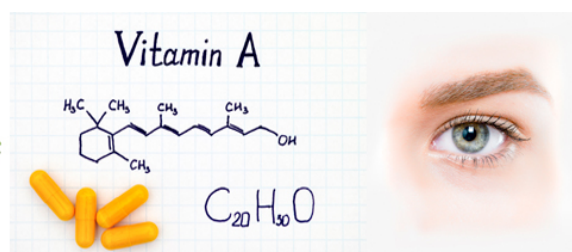


4.7 (8.0 pt)





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 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 normal growth and development, the immune system, and vision function.

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).

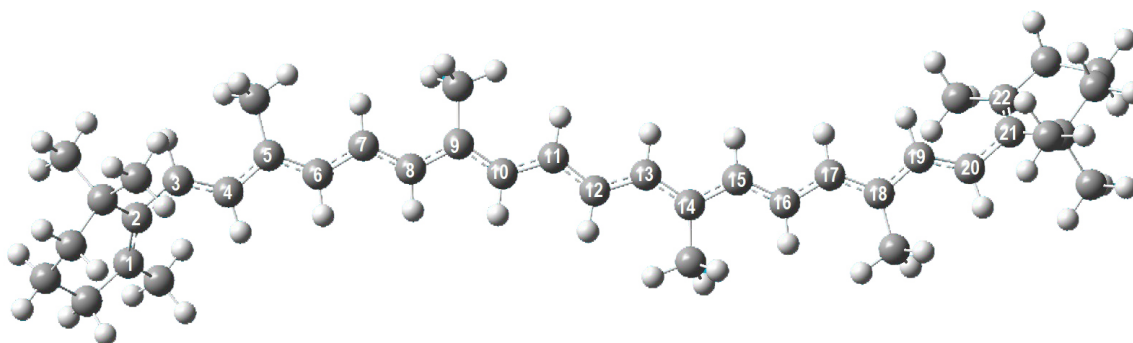


Figure 1. Ball and stick representation of the structure of β -carotene. The gray and white spheres represent the carbon and hydrogen atoms, respectively. The numbered carbon atoms belong to the linear conjugated π -segment of the molecule.

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 to be treated by the simplest model called the **particle in a one-dimensional box** model.



Q5-2

English (Ireland) (Ireland)

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

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

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

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

In two-dimensions, 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:

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

where n_x and n_y are the quantum numbers and they are positive integers. L_x and L_y are the dimensions of the box in the two-dimensional model. They are positive numbers.

5.1 Which two of the sentences given below are correct? **Tick** only one answer 13.0pt corresponding to two correct sentences in your answer sheet.

The β -carotene molecule is orange in colour because:

- i) it absorbs in the visible region of the electromagnetic spectrum.
- ii) a HOMO \rightarrow 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 transmits a red/yellow colour.
- 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 represents the number of carbon atoms in the conjugated segment.

Use this information to answer questions 5.2–5.6.

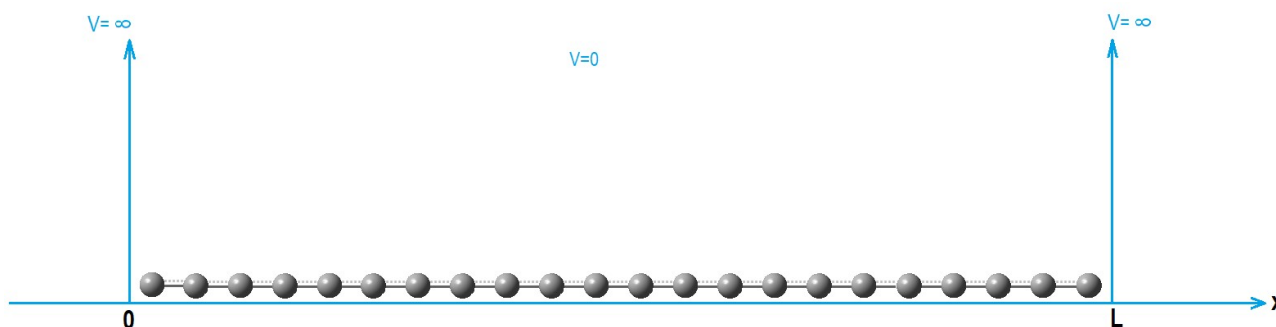


Figure 2. Schematic representation of the conjugated line segment made up of the carbon atoms of β -carotene in a one-dimensional box of length L .



Q5-3

English (Ireland) (Ireland)

5.2	Calculate the energies (in J) of the lowest two energy levels.	13.0pt
5.3	Draw the wavefunctions of the lowest two energy levels with proper labelling of 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.

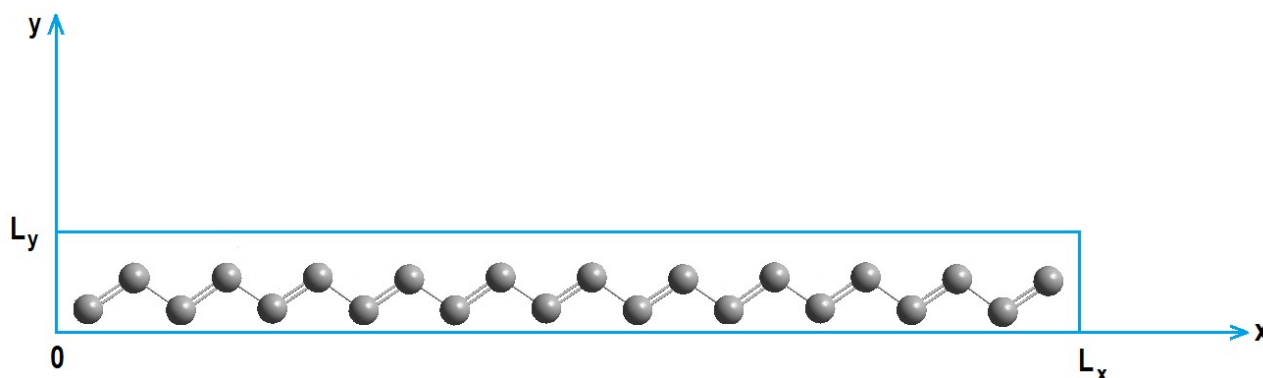


Figure 3. Schematic representation of the conjugated carbon atoms of β -carotene in a two-dimensional box.

Assume that the conjugated segment is made up of carbon atoms that are all-*trans* to each other. The motion of the π -electrons is studied in the two-dimensional rectangular box with the dimensions $L_x = 26.0 \text{ \AA}$ and $L_y = 3.0 \text{ \AA}$ (Figure 3).

5.7	Calculate the energies (in J) of the highest occupied and the lowest unoccupied energy levels and determine the wavelength (in nm) at which the transition between these energy levels occurs.	17.0pt
5.8	What should be the L_x value (in \AA) in order for the molecule to absorb light at the experimental $\lambda_{max} = 455 \text{ nm}$ if L_y is kept constant at 3.0 \AA ? (Assume that the quantum numbers for HOMO and LUMO are the same as in question 5.7).	12.0pt



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

5.1 (13.0 pt)

- | | | | |
|---|--|---|---|
| <input type="checkbox"/> a) i and ii | <input type="checkbox"/> b) i and iii | <input type="checkbox"/> c) i and iv | <input type="checkbox"/> d) i and v |
| <input type="checkbox"/> e) ii and iii | <input type="checkbox"/> f) ii and iv | <input type="checkbox"/> g) ii and v | <input type="checkbox"/> h) iii and iv |
| <input type="checkbox"/> j) iii and v | <input type="checkbox"/> k) iv and v | | |

5.2 (13.0 pt)

Calculation:

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:



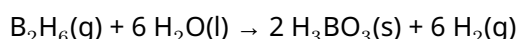
5.8 (12.0 pt)



Thermodynamics through an Interstellar Journey

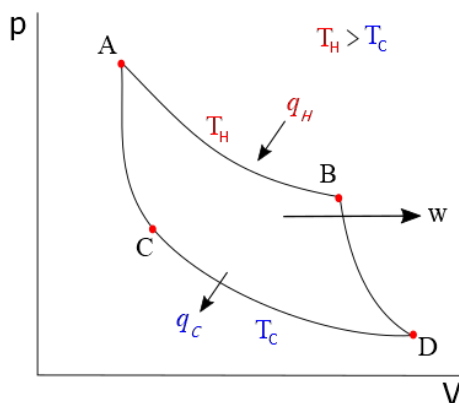
Part 1

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



Assume that in this hypothetical universe, $\text{H}_3\text{BO}_3(\text{s})$ 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.

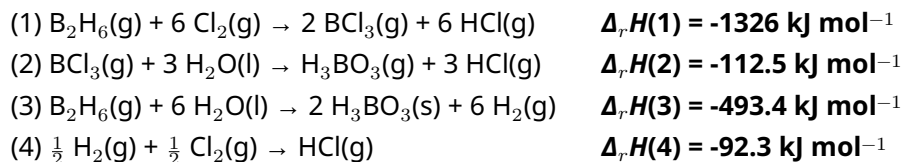


After heat transfers, the remaining energy is released as work (w). Also, q_H and q_C are related to T_C and T_H as follows:

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

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

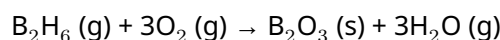
You are provided with the change in enthalpies of the following reactions at 300 K.



- | | | |
|-----|---|--------|
| 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 change ($\Delta_r U$) (in 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). | 12.0pt |
| 6.3 | Calculate the amount of overall work produced by a heat engine ($ w $) (in J) and the amount of overall heat released to the cold sink ($ 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 the $A \rightarrow B$ and $D \rightarrow C$ processes in the heat engine. | 6.0pt |
| 6.6 | Calculate the Gibbs energy change (ΔG) (in J) for the $A \rightarrow B$ and $D \rightarrow C$ processes in the heat engine. | 6.0pt |
| 6.7 | Calculate the ratio of 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 $\text{H}_2(\text{g})$ (in mol) 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:



Combustion of diborane is experimentally carried out in a 100 L closed container at different temperatures and the equilibrium conditions were recorded.



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

- $\Delta_r S^\circ$ and $\Delta_r H^\circ$ are independent of temperature.
- The standard molar entropy (S°) of $B_2O_3(s)$ does not change with pressure.
- All the gaseous species behave as an ideal gas.
- All species remain in the same phase, without any further decomposition before or after reaction, at all temperatures.

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

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

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

6.12 Tick the correct answer in the table by determining whether combustion reac- 8.0pt
tions are favoured or not at the given T below under standard pressure (1 bar)
conditions.

6.13 Calculate $\Delta_f H$ (in kJ mol^{-1}) and S° (in $\text{kJ mol}^{-1} \text{K}^{-1}$) of $H_2O(g)$ using the values 6.0pt
given in the table below. ($\Delta_f H$ = enthalpy of formation, S° = standard entropy).
(If you fail to find $\Delta_r H^\circ$ and $\Delta_r S^\circ$ of the combustion, please use $\Delta H^\circ = 1000 \text{ kJ mol}^{-1}$, $\Delta S^\circ = 150 \text{ J mol}^{-1} \text{K}^{-1}$).

	$\Delta_f H(298 \text{ K})$	$S^\circ(298 \text{ K})$
$B_2H_6(g)$	$36.40 \text{ kJ mol}^{-1}$	$0.23 \text{ kJ mol}^{-1} \text{K}^{-1}$
$O_2(g)$	0.00 kJ mol^{-1}	$0.16 \text{ kJ mol}^{-1} \text{K}^{-1}$
$B_2O_3(s)$	$-1273 \text{ kJ mol}^{-1}$	$0.05 \text{ kJ mol}^{-1} \text{K}^{-1}$



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)

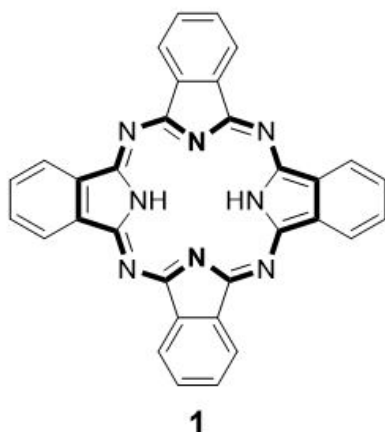
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8930 K	<input type="checkbox"/>	<input type="checkbox"/>
9005 K	<input type="checkbox"/>	<input type="checkbox"/>
9100 K	<input type="checkbox"/>	<input type="checkbox"/>

6.13 (6.0 pt)

Show your calculation:



Phthalocyanines

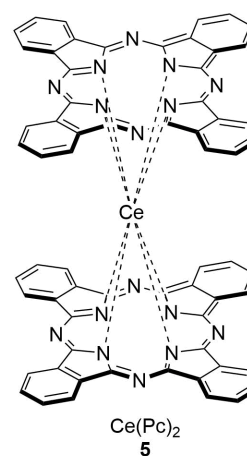
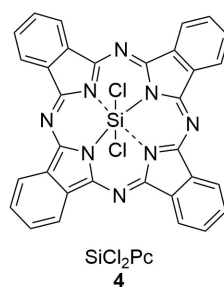
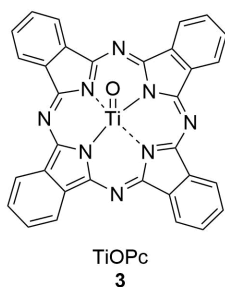
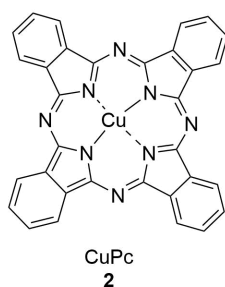


*Emeritus Professor Özer
Bekaroğlu*

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

Metal-free phthalocyanine (**1**, H₂Pc) is a large planar macrocyclic compound with the formula (C₈H₄N₂)₄H₂.

7.1 How many π -electrons are there in the section highlighted in bold in the H₂Pc molecule in compound **1** shown above? 4.0pt





Q7-2

English (Ireland) (Ireland)

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 the central ions in **2-5**. 8.0pt

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

7.4 Complete the table in your answer sheet by determining the geometry of the compounds **2-5**. 8.0pt

7.5 Complete the table in your answer sheet by determining the magnetic property (paramagnetic or diamagnetic) of the compounds **2-5**. 8.0pt

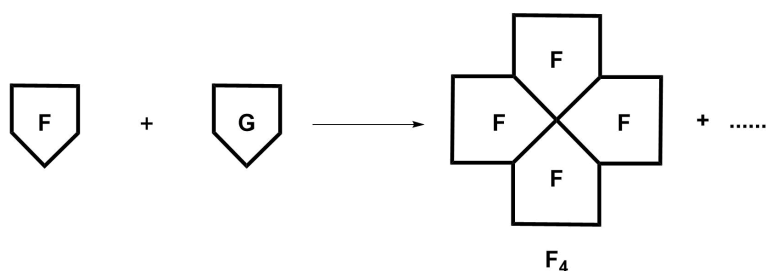
- Use the letter "**p**" to indicate if the compound is paramagnetic and the letter "**d**" to indicate if the compound is diamagnetic.

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

Metal-free phthalocyanine (**1**, H₂Pc) is commonly formed through the cyclotetramerisation of phthalonitriles. On the other hand, Pcs having different substituents are called asymmetric, and 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 as products label these as *cis*- or *trans*-. 19.0pt

- **F** and **G** represent two different symmetrical phthalonitriles.
- One of the products is **F₄** which is represented below.
- When drawing the other products represent them similar to the way product **F₄** is represented below.



Pcs are used as photosensitizers in the photodynamic therapy (PDT) of cancer due to their strong ab-



sorption in the visible spectrum and high molar absorption coefficients. PDT consists of three essential components: a **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 ($^1\text{O}_2$) that can destroy cancer cells.

(multiplicity) $^1\text{O}_2$

- 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 molecular orbital (MO) diagram of the lowest energy singlet state of dioxygen ($^1\text{O}_2$) and calculate its associated bond order. 12.0pt
Note: There are no unpaired electrons in this 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^{-1}) needed for this transition process. 6.0pt



Phthalocyanines

7.1 (4.0 pt)

The number of π -electrons in an H_2Pc :

7.2 (8.0 pt)

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

7.3 (6.0 pt)

Metal in compounds	2	3	5
Oxidation number			

7.4 (8.0 pt)

Geometry	Compound
Octahedral	
Square prism	
Square pyramidal	
Square planar	



A7-3

English (Ireland) (Ireland)

7.7 (19.0 pt)

Products:



A7-4
English (Ireland) (Ireland)

7.8 (12.0 pt)

MO diagram:

Bond order:

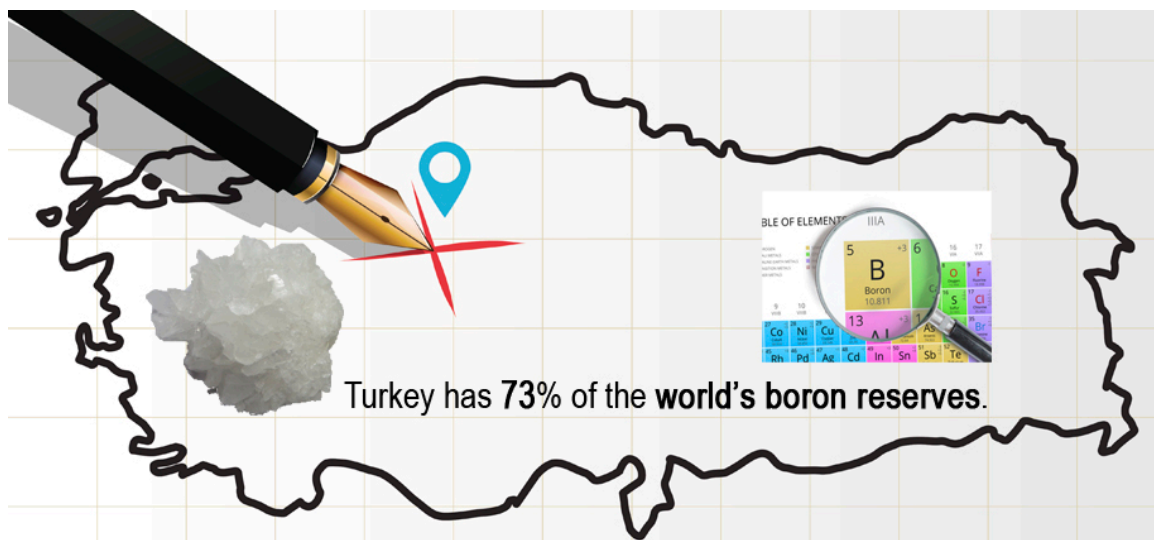
7.9 (6.0 pt)

Show your calculation:

Energy = kJ mol^{-1}



Boron Compounds and Hydrogen Storage



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 ($\text{Na}_2\text{B}_4\text{O}_7 \cdot n\text{H}_2\text{O}$) 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 under high-pressure hydrogen gas in the presence of silicon dioxide (silica) at 700°C . This is the Bayer process. In this process, all hydrogen is stored in NaBH_4 . On the other hand, it has been shown that ammonia borane (BNH_6) can be synthesised by the reaction of NaBH_4 and ammonium sulfate in dry tetrahydrofuran (THF) at 40°C .

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

While sodium borohydride (NaBH_4) is an ionic compound, in contrast, ammonia borane (BNH_6) is a Lewis acid–base adduct.

8.1 **Write** a balanced chemical equation for the synthesis of sodium borohydride (NaBH_4) from anhydrous borax. 3.0pt

8.2 **Write** a balanced chemical equation for the synthesis of ammonia borane (BNH_6) from sodium borohydride (NaBH_4). 3.0pt

8.3 **Draw** the molecular geometries of the BH_4^- ion and the BNH_6 molecule. 4.0pt

8.4 **Calculate** the hydrogen content as a percentage by mass (wt%) in NaBH_4 and in BNH_6 . 4.0pt



The hydrogen stored in both compounds can be released via hydrolysis reactions in the presence of a suitable catalyst at room temperature. Under the hydrolysis reactions, 4 and 3 mol of H_2 gas are released from the hydrolysis of 1 mol 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 $\text{B}_3\text{O}_6^{3-}$ which have cyclic structures containing B-O-bonds, also exist. Since B_2O_3 is an acidic compound, it easily reacts with water to form boric acid (H_3BO_3). On the other hand, the high temperature and high pressure reaction of B_2O_3 with ammonia (NH_3) 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 $\text{B}_3\text{O}_6^{3-}$ ion, boric acid, and a single two-dimensional boron nitride sheet. 6.0pt

Hint: Show at least 10 B atoms in the boron nitride structure.

Furthermore, B-H compounds, called boranes, are an important class of boron-containing 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 . 3.0pt

Hint: Both products are boron-containing compounds.

8.9 **Draw** the molecular geometry of the diborane molecule. 2.0pt

Hint: There is no B-B bond in the structure of diborane.

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 stabilised via its reaction with carbon monoxide (CO) to form borane carbonyl (BH_3CO), which is an adduct of borane. The synthesis 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 **Sketch** the Lewis (electron-dot) structure of the BH_3CO molecule and indicate the formal charges present. 3.0pt

8.11 Which of the statements given in the answer sheet is observed in the C—O bond of a CO molecule upon the formation of a bond between BH_3 and CO? 2.0pt

Tick the correct box.

Borazine consists of single and double bonded cyclic B—N units and hydrogen atoms attached to these atoms with the molecular formula $\text{B}_3\text{N}_3\text{H}_6$ and is found to be isostructural to benzene. Borazine can be synthesised by using a two-step procedure which involves the synthesis of symmetrically trisubstituted chlorine derivatives of borazine ($\text{B}_3\text{N}_3\text{H}_3\text{Cl}_3$) from the reaction of ammonium chloride and boron



trichloride, followed by reduction of $\text{B}_3\text{N}_3\text{H}_3\text{Cl}_3$ 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). 4.0pt
Hint: THF stabilises 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. 4.0pt

Catalysts are substances that accelerate 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:

$\text{TOF} = \text{moles of product} / (\text{moles of catalyst} \times \text{time})$

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** Assuming the catalytic reaction is performed under standard conditions (1 atm and 273.15 K), **calculate** the TOF (in 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. 4.0pt

As a result of a detailed crystal structure analysis of a synthesised Cu_xPt_y alloy nanoparticle (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. Using this information, answer the following questions:

- 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 the atoms within the unit cell. 2.0pt

- 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 note that 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)

$\text{B}_3\text{O}_6^{3-}$	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 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 .

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) 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 min. using a magnetic stirrer.

Step 2) 10-mL of the 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 min. was applied as seen in Figure 1b (horizontal line). It is assumed that 14 min. is sufficient to complete the expected electrochemical reactions.

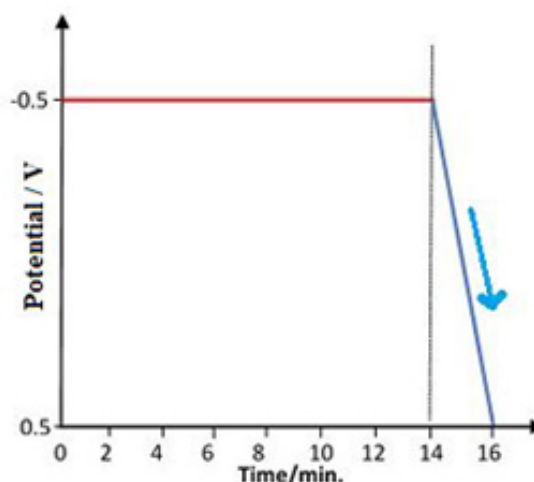
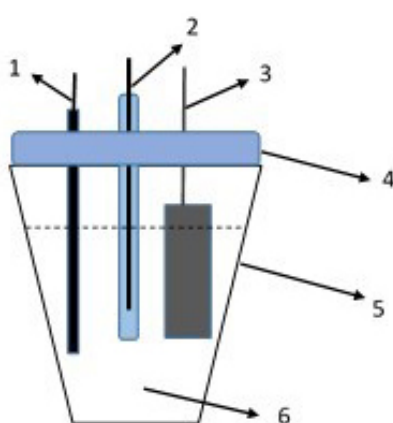


Figure 1. a) Electrochemical cell design; 1) Working electrode (Pt wire), 2) reference electrode (Ag/AgCl, 3M KCl), 3) counter electrode (Pt foil), 4) cell tap, 5) electrochemical cell, 6) 10-mL of sample solution. **b)** Potential change of working electrode as a function of time. y-axis: Potential/V 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 the 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 represented in Figure 2a, which is like an excellent view of *Mount Ararat (Ağrı Dağı)*, the highest mountain in Turkey (Figure 2b).

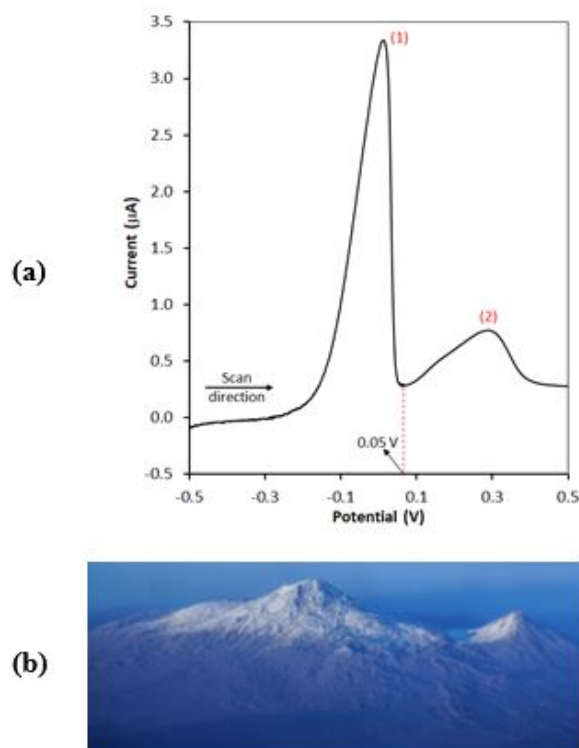


Figure 2. a) Potential scan of the working electrode as a function of current in 0.1 M H_2SO_4 solution after keeping it constant at a potential of -0.50 V in 10-mL of wastewater sample as seen in Figure 1b (horizontal line). y-axis: Current/ μA , x-axis: Potential/V vs Ag/AgCl, b) A view of Great and 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) 5-mL of ethylenediaminetetraacetic acid (EDTA, H_4Y) (Figure 3) solution was added to the solid obtained in *step 6* and it was shaken to dissolve it. It is known that 1-mL of EDTA solution is equivalent to 3.85 mg mL^{-1} BaCO_3 . Then, the pH of the solution was adjusted to 10.0. Excess EDTA was titrated with standard 0.0010 M $\text{Ni}(\text{NO}_3)_2$ solution and it was observed that 95.60 mL of $\text{Ni}(\text{NO}_3)_2$ solution was consumed up to the end-point.

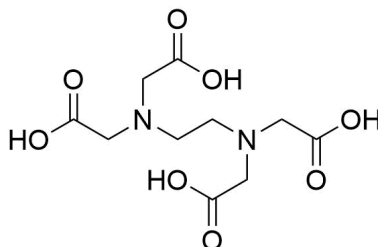


Figure 3. Chemical structure of EDTA (H_4Y).

- 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 can be considered for peak 1 and peak 2 in Figure 2a, respectively? 5.0pt
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? 5.0pt
Tick the correct box on the answer sheet.

9.3 **Calculate** the scan rate (in $mV s^{-1}$) of the data represented in Figure 2a at 298 K. 8.0pt

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

$Pt, H_2 (0.92 \text{ bar}) | HCl(1.50 \times 10^{-2} M), AgCl(sat) | Ag$

9.4 **Calculate** the standard electrode potential value (in V) at 298 K of the half-cell corresponding to: $AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$ 16.0pt
Note: You must show all the steps involved in your calculation.

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



Q9-4

English (Ireland) (Ireland)

9.6 **Write** net ionic equations for the complexation and the back-titration reactions of *step 7* on the answer sheet. 6.0pt

9.7 **Calculate** the Ni^{2+} concentration (in mg L^{-1}) in the wastewater of the factory. 25.0pt
Note: You must show all the steps involved in your calculation.

9.8 **Calculate** the minimum pH value for starting the precipitation of Ni ions in the solution obtained in *step 5* by passing saturated HS gas into the solution until saturation is achieved. 30.0pt
If you cannot solve question **9.7**, use 20 mg L Ni^{2+} *sample* for this question.
Note: You must show all the steps involved in your calculation.

**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
- ☐ NO₂ evolution
- ☐ Nitrogen evolution
- ☐ Oxygen evolution
- ☐ Hydrogen evolution

9.3 (8.0 pt)

Show your calculation:

Scan rate = mV s⁻¹



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:

Ni²⁺ concentration: mg L⁻¹:



9.8 (30.0 pt)

Show your calculation:

Minimum pH value: