



General Instructions



- Only write with pen. Your calculator should be non-programmable.
- This theoretical exam booklet contains **71 pages**, not including the general instructions.
- This examination has **9 problems**.
- You will have **5 hours** to complete 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 working 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 (eg broken calculator, dunny visit), 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	$P_{\text{atm}} = 1.01325 \times 10^5 \text{ Pa} = 760 \text{ mmHg} = 760 \text{ torr}$
Zero of the Celsius scale	273.15 K
1 picometer (pm)	$10^{-12} \text{ m}; 1 \text{ Å} = 10^{-10} \text{ m}$
1 nanometer (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	
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	$y = mx + n$
Lambert-Beer equation	$A = \varepsilon lc$



Periodic Table of Elements

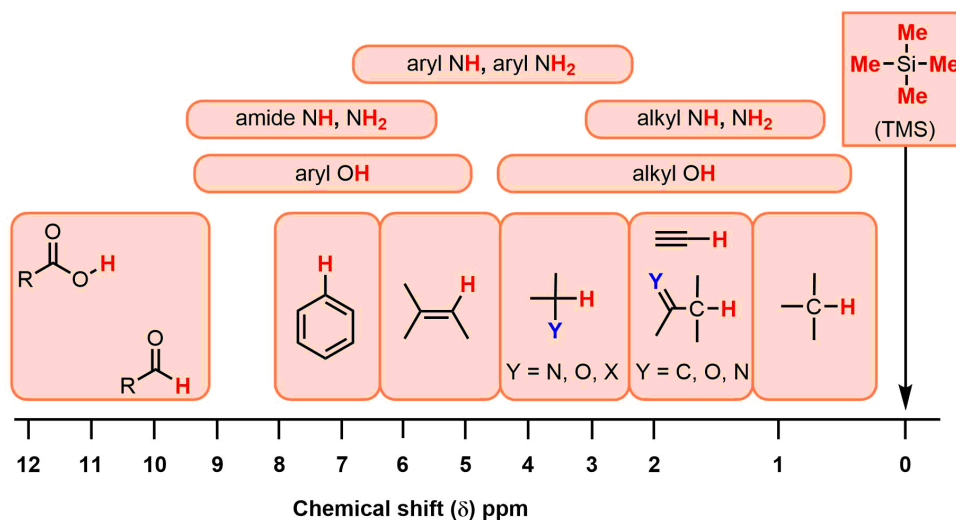
1																	18																		
<div>1 H 1.008</div>		2		<div><div>atomic number</div><div>Symbol</div><div>atomic weight</div></div>														13		14		15		16		17		<div>2 He 4.003</div>							
<div>3 Li 6.94</div>		<div>4 Be 9.01</div>																<div>5 B 10.81</div>		<div>6 C 12.01</div>		<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 -

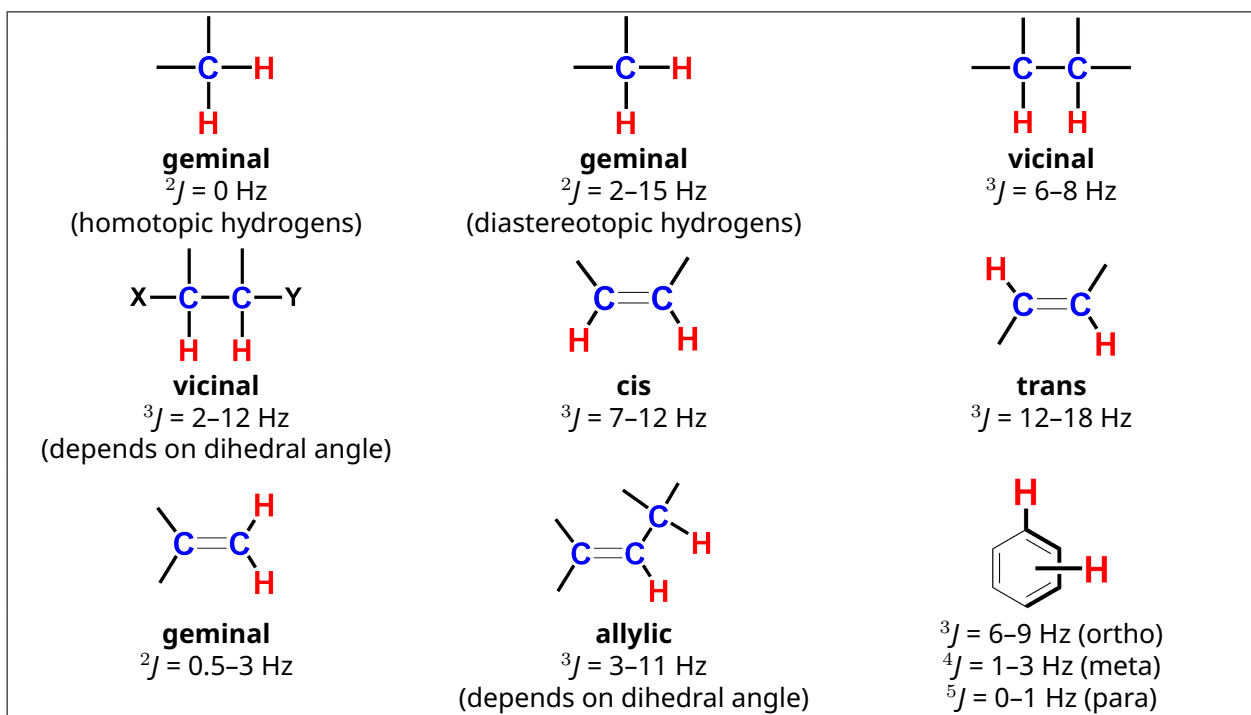


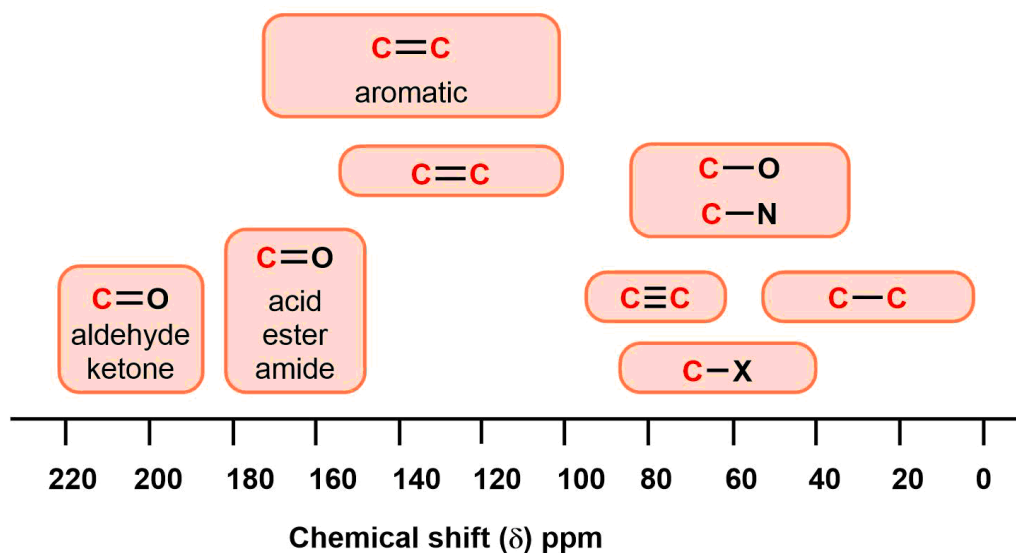
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¹H-NMR Chemical Shifts

Typical Coupling Constants



¹³C-NMR Chemical Shifts



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	

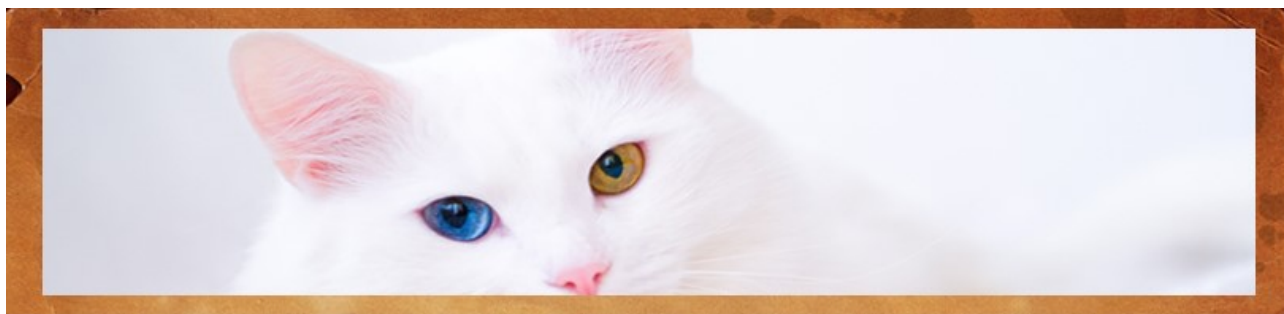


IR Absorption Frequency Table

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 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

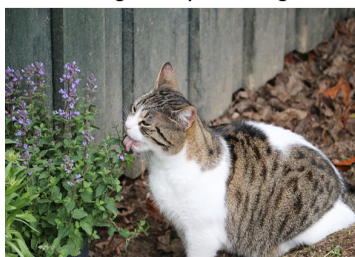


Ankara cat

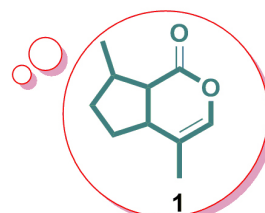
*Nepeta cataria* (catnip)

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



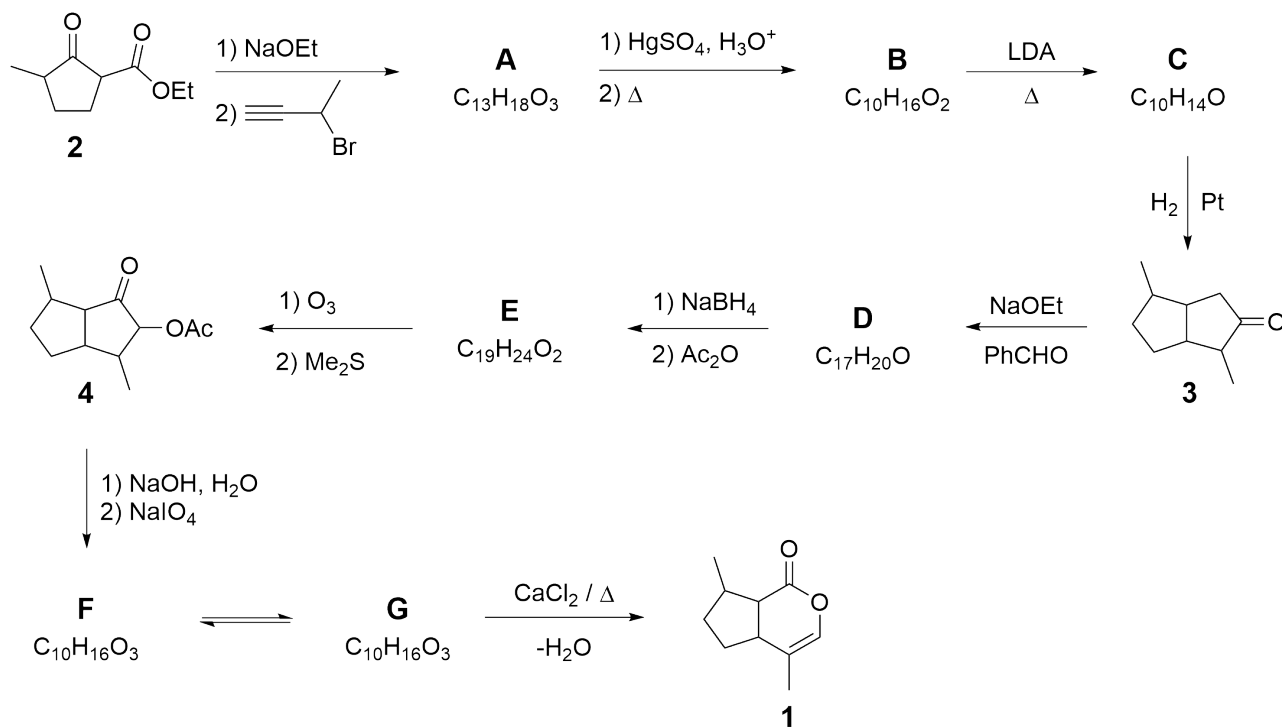
Cat's dream



Nepetalactone



Total synthesis of nepetalactone:



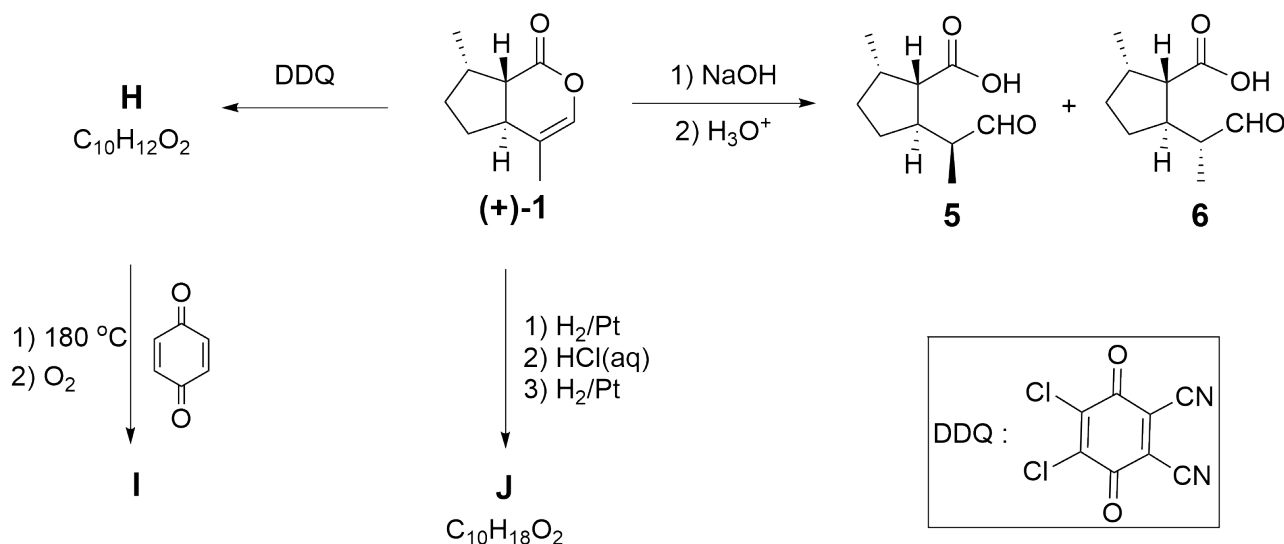
1.1 The above scheme describes the total synthesis of nepetalactone. **Draw** the structures of **A–G**, ignoring stereochemistry. 14.0pt

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

- 1.2** For the relationship between **5** and **6**, which of the following is/are true? Tick 4.0pt
the box(es) next to the correct answer(s) on your answer sheets.

The reaction of **1** with DDQ gives highly conjugated compound **H**. Also, the thermal reaction of compound **H** with *p*-quinone gives **I**, which has 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 its 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 (Australian) (Australia)

1.2 (4.0 pt)

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

1.3 (6.0 pt)

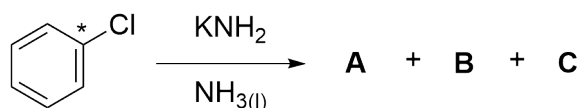
H	I
J	



A Tale of a Reactive Intermediate

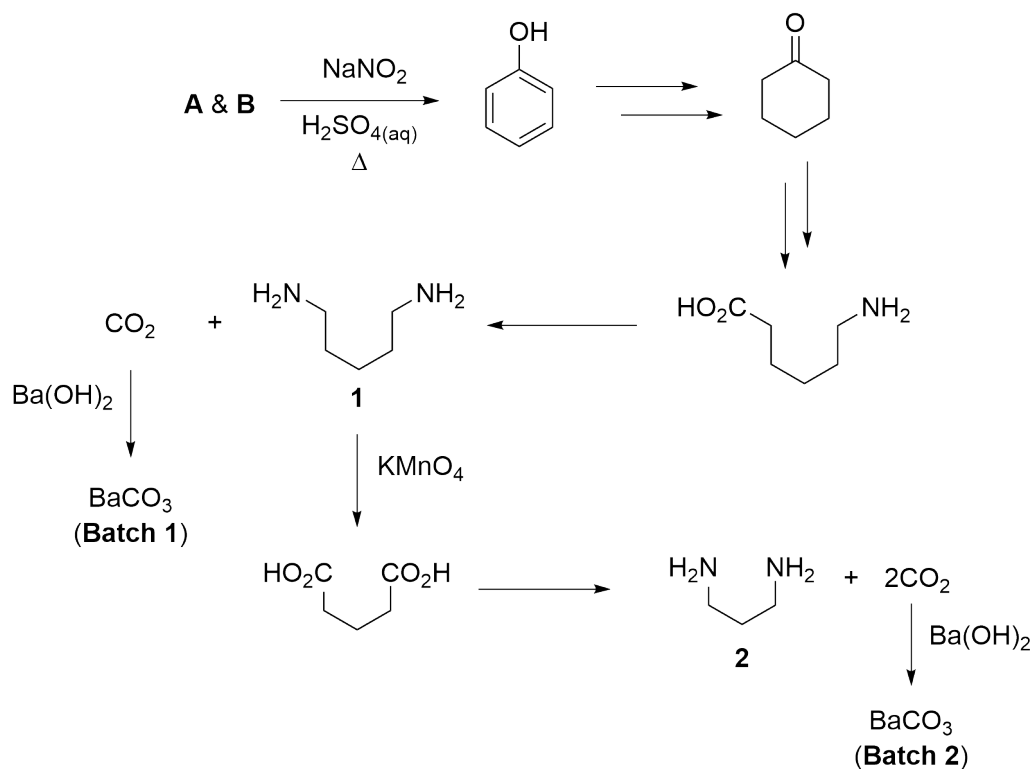
Arynes constitute a special class of reactive intermediates. The first experimental evidence for the structure of an aryne (benzyne) was demonstrated in 1953 via the elegant labeling experiments by John D. Roberts and coworkers.


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 -labeled 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). The radioactivity of each intermediate and final product was examined.





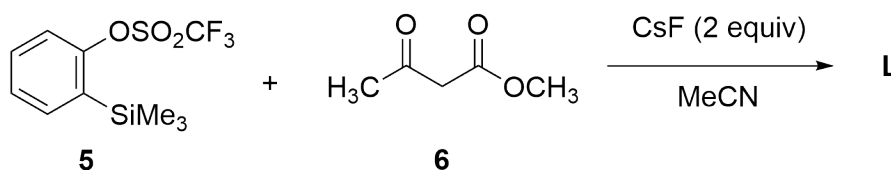
- Combustion analysis of **E** revealed the following elemental proportions: 75.8% carbon, 5.8% hydrogen, and 18.4% oxygen.
- **E** does not have a proton that is exchangeable with D₂O in ¹H-NMR spectroscopy.
- **F** is an ionic compound.

2.3 Determine the structures of **E**, **F**, and **G** ignoring stereochemistry. 8.0pt

- **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

- 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

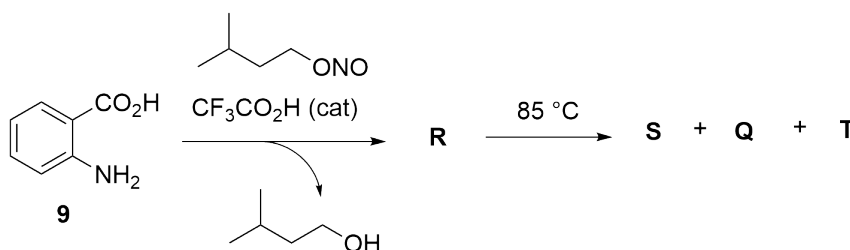
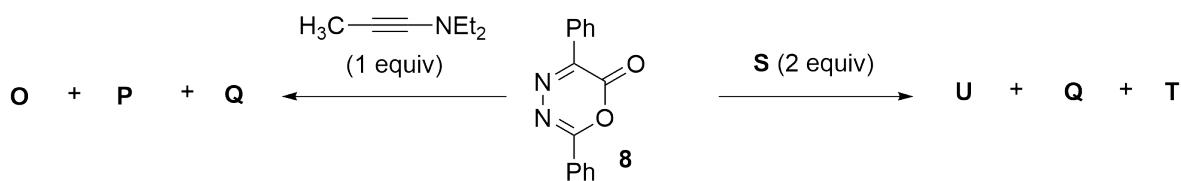
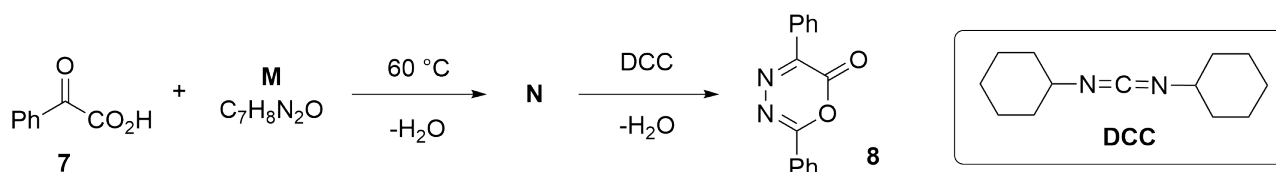
2.6 In the reaction shown in task **2.5**, which of the statement(s) in the answer sheet describe(s) the function of CsF?

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**.

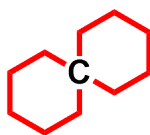


2.7 (28.0 pt)

M	N
O and P	Q
R	S
T	U

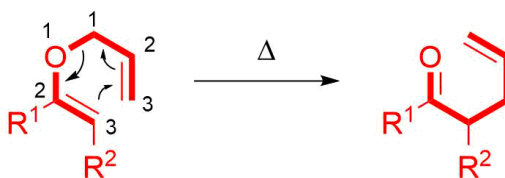
**(±)-Coerulescine**

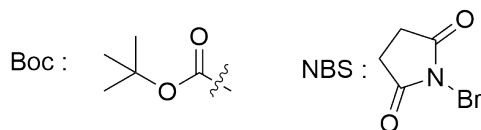
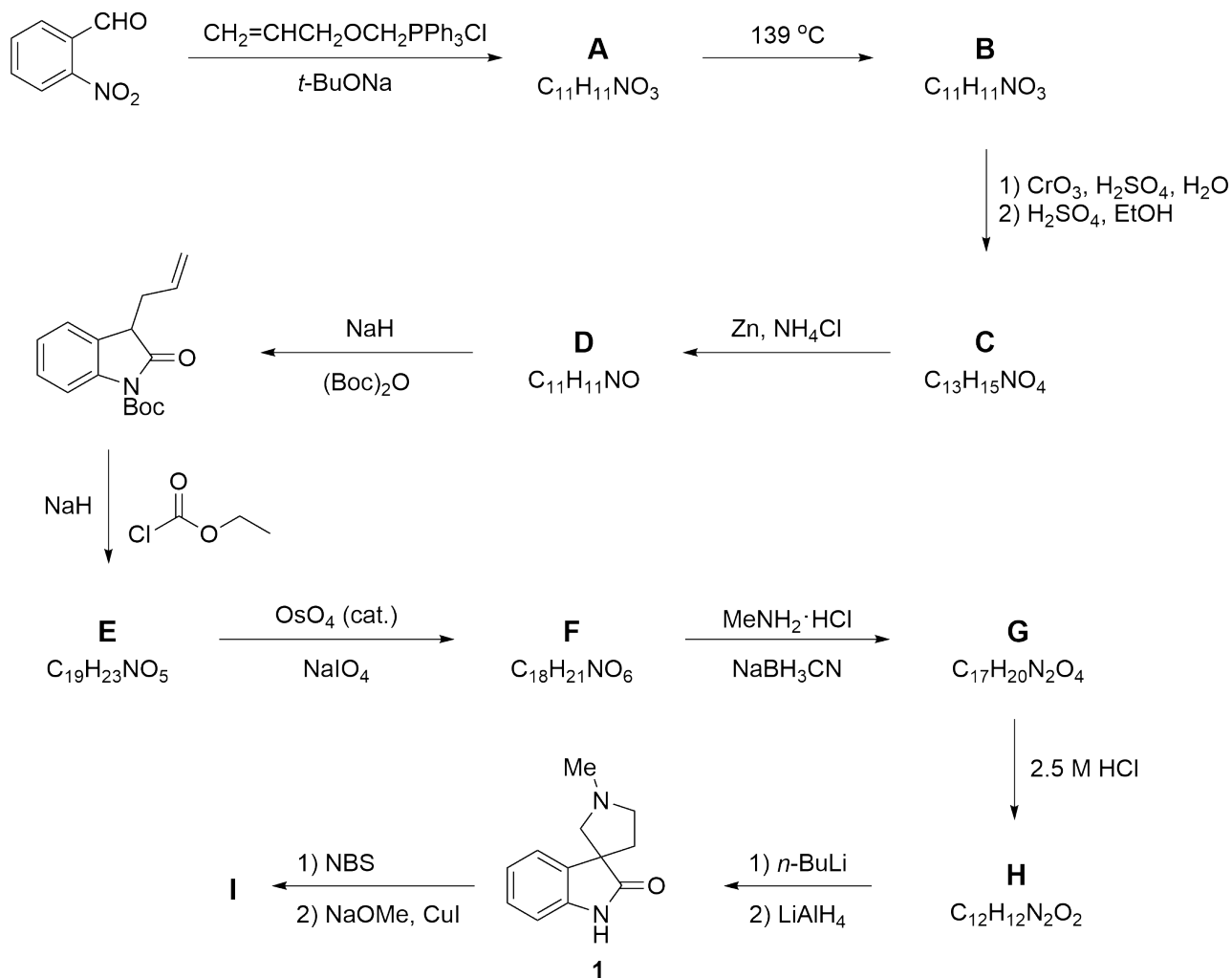
A spiro compound is typically an organic compound containing rings linked together by one common atom (spiroatom), eg the bolded carbon atom in the figure below. The spiro[pyrrolidin-3,3'-oxindole] ring system is a structural framework incorporated in several cytostatic alkaloids and unnatural compounds.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



Claisen rearrangement, which is a [3,3]-sigmatropic rearrangement, is a powerful carbon-carbon bond-forming reaction in which an allyl vinyl ether is converted thermally to an unsaturated carbonyl compound as shown in the scheme below. When compound **A** is heated, it undergoes a Claisen rearrangement to give carbonyl compound **B**.

For this entire task, your answers can be given ignoring stereochemistry.







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

8.0pt

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

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

16.0pt

- **D–F** have a bicyclic structure.

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 formed upon treatment with *n*-BuLi in the step **H** → **coerulescine (1)**.

5.0pt

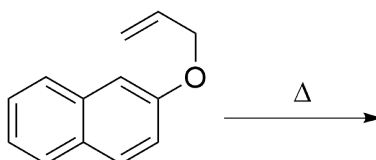
Coerulescine (1), on treatment with *N*-bromosuccinimide (NBS), gives the bromo derivative, which upon heating with sodium methoxide in the presence of cuprous iodide gives **horsfiline (I)** in 60% yield.

3.6 **Choose** the correct structure for compound **I** consistent with the following selected $^1\text{H-NMR}$ 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)

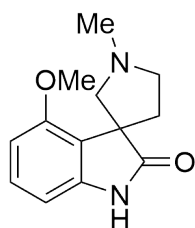
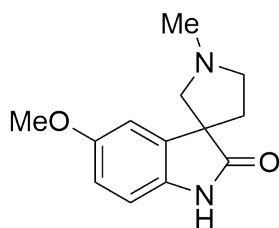
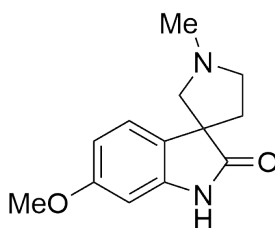
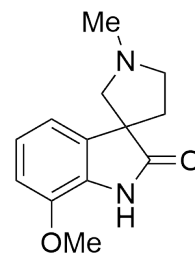
G

H

3.5 (5.0 pt)



3.6 (5.0 pt)

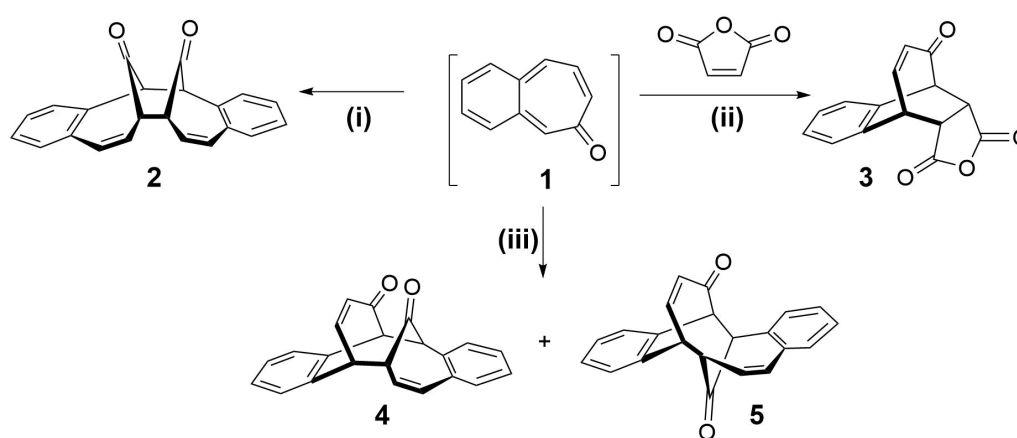
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3.7 (5.0 pt)



Symmetry Does Matter!

There are numerous reactions in organic chemistry that proceed through cyclic transition states and these are classified as pericyclic reactions. Woodward–Hoffmann rules, developed by Robert B. Woodward and Roald Hoffmann, are used to rationalise the stereochemistry and 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	Favoured	Disfavoured

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

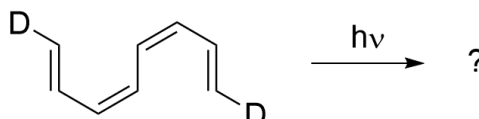
12.0pt

There are three possible benzotropone isomers. Although two of the benzotropone isomers have been 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.

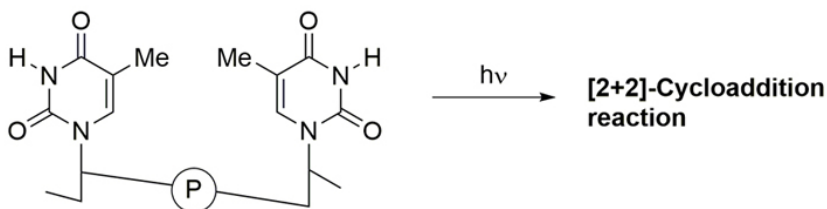
4.2 **Draw** the structures of stable benzotropone isomers **A** (with 6 signals in its ^{13}C -NMR) and **B** (with 11 signals in its ^{13}C -NMR). 6.0pt



- 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

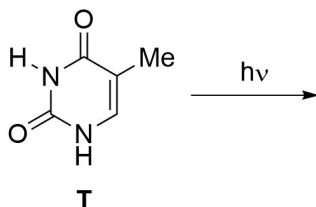


Prof. Dr. Aziz Sancar



The 2015 Nobel Prize in Chemistry was awarded jointly to the Turkish scientist Aziz Sancar, Swedish scientist Tomas Lindahl, and American scientist Paul Modrich for their “mechanistic studies of DNA repair”. Pyrimidine bases found in DNA may undergo a photochemical **[2+2]-cycloaddition reaction** (see above figure) with UV light that reaches a person’s skin, causing damage to DNA, which may ultimately lead to skin cancer. The research by Professor Aziz Sancar focused on the DNA repair mechanism for this type of damage.

Thymine 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.



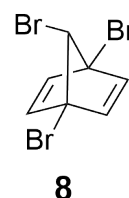
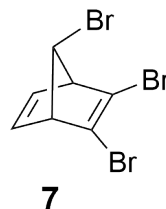
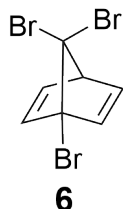
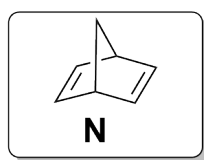
- 4.4** Considering stereochemistry, **draw** the structures of **all possible products** of this reaction between two free thymine molecules. **Circle** the compound(s) which is/are chiral. Drawing only one enantiomer of an enantiomeric pair is sufficient. Please note that only C=C bonds participate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

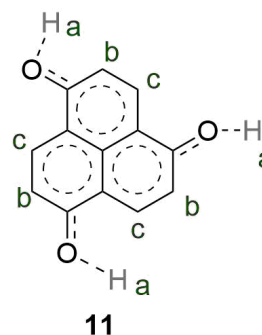
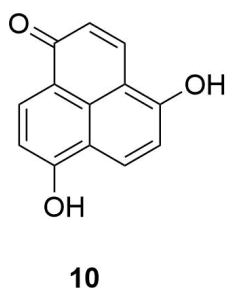
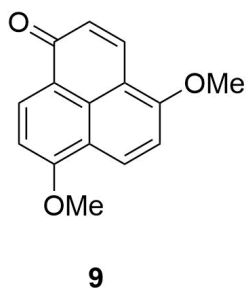
English (Australian) (Australia)



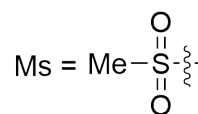
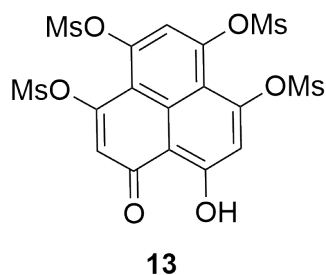
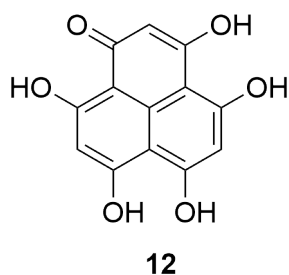
4.5 How many signals do you expect from the ^{13}C -NMR spectra of isomers **6**, **7**, and **8**? **Fill in** the following boxes. 9.0pt

4.6 **Draw** the structures of the remaining achiral (meso) tribromo-norbornadiene ($\text{C}_7\text{H}_5\text{Br}_3$) achiral (meso) isomers (**C**, **D**, and **E**) in addition to **6–8** over the given figures in the boxes. 9.0pt

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



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





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

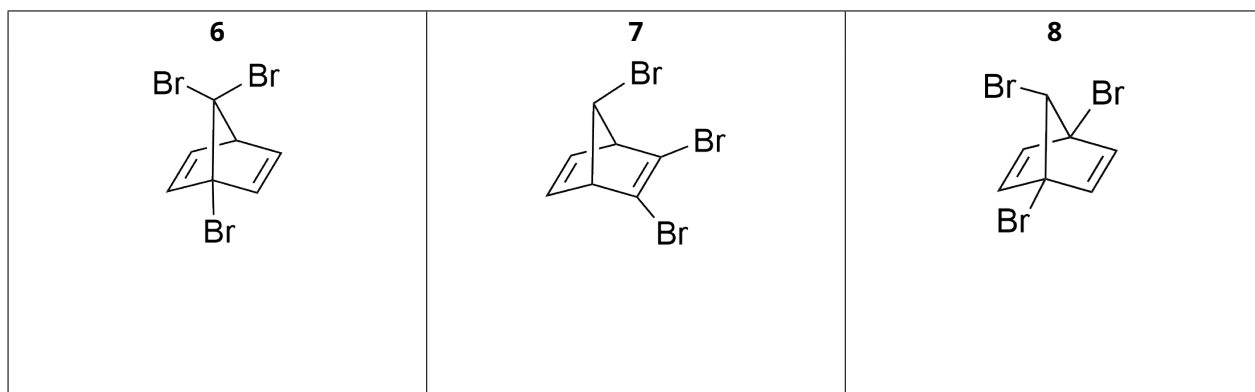
**4.3** (6.0 pt)

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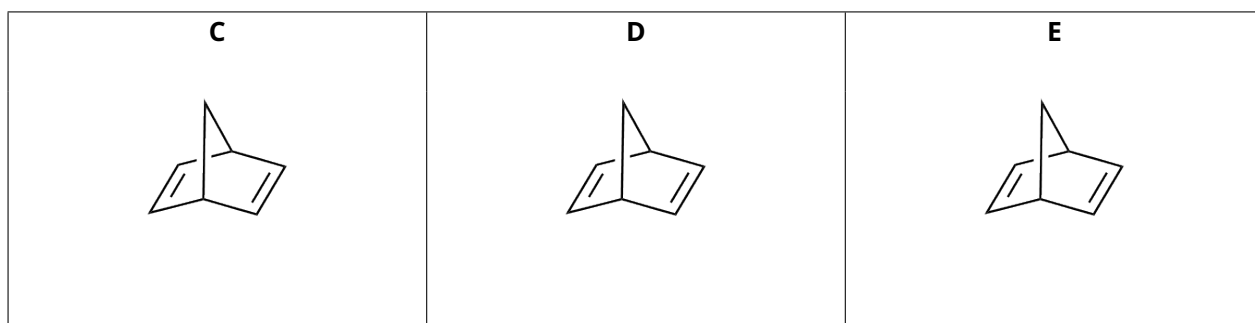
4.4 (16.0 pt)



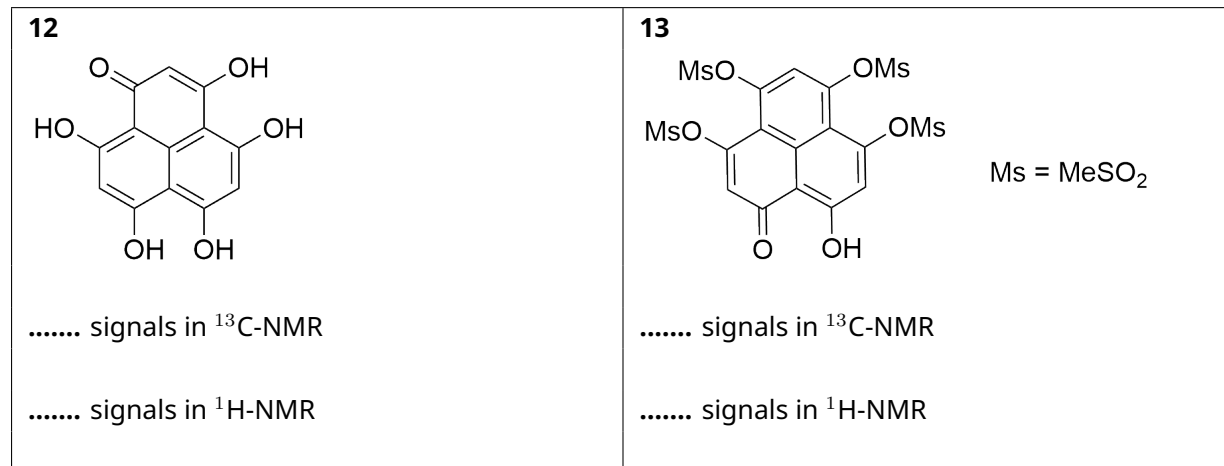
4.5 (9.0 pt)



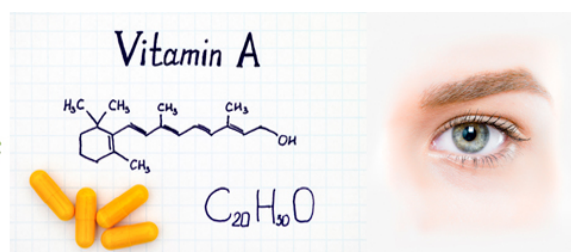
4.6 (9.0 pt)



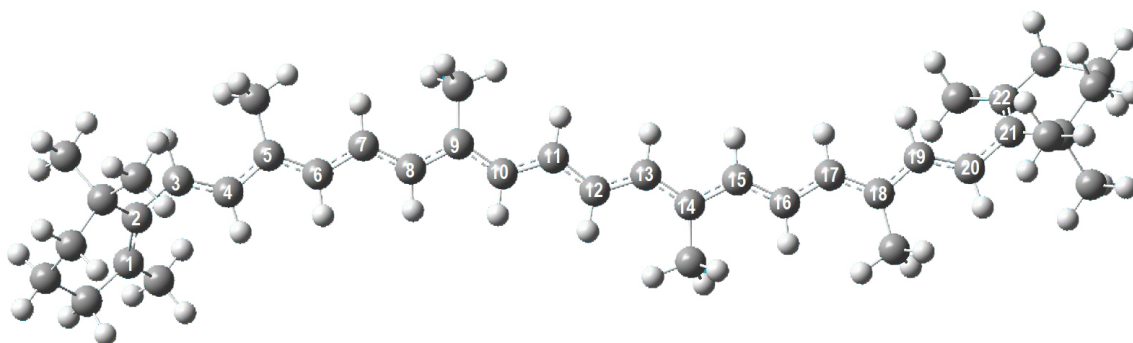
4.7 (8.0 pt)



A large, ornate mosque with a prominent green dome and minarets, surrounded by a well-maintained green lawn and trees. The mosque features intricate architectural details and is set against a clear blue sky. The foreground is a lush green lawn with several small trees and shrubs.



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



As 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 inside the molecule, moving along the x-axis in one dimension. These characteristics of π-electrons make them eligible for being treated by the simplest model called the **particle in a one-dimensional box** model.



Q5-2

English (Australian) (Australia)

The wave function 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 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 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, 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 above are correct? **Tick** only one answer 13.0pt which includes the correct sentences on your answer sheet.

The β -carotene molecule is orange in color because:

- i) it absorbs in the visible region of the electromagnetic spectrum.
- ii) HOMO \rightarrow LUMO transition occurs by absorption of 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 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 is the number of carbon atoms in the conjugated segment.

Use this information to answer questions 5.2–5.6.

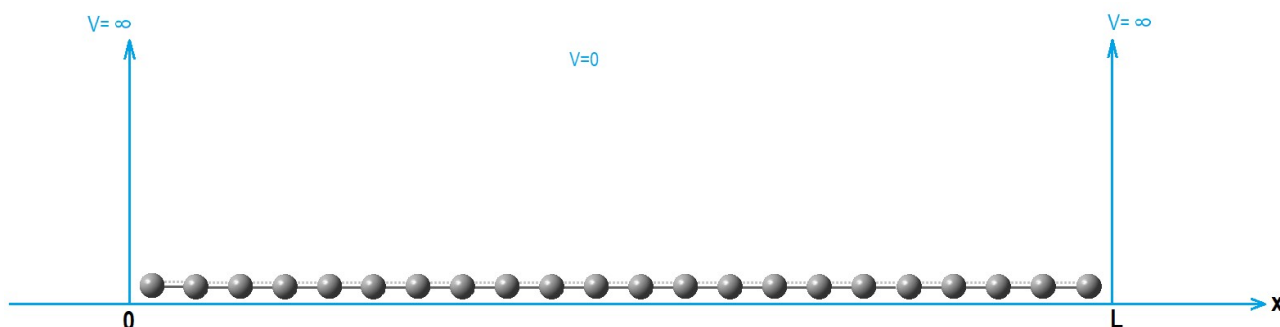


Figure 2. Schematic representation of the conjugated line segment made up of the carbon atoms of β -carotene in a one-dimensional box of length L .



Q5-3

English (Australian) (Australia)

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, properly labelling the x-axis. 15.0pt

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

5.5 **Calculate** 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.

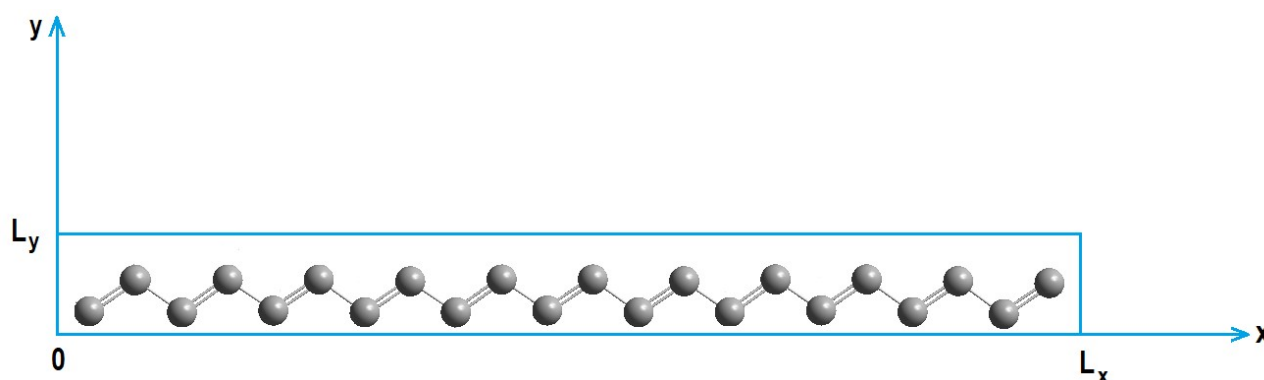


Figure 3. Schematic representation of the conjugated carbon atoms of β -carotene in a two-dimensional box.

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 a two-dimensional rectangular box with dimensions of $L_x = 26.0$ 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 $\lambda_{max} = 455$ nm if L_y is kept constant at 3.0 Å. (Assume that the quantum numbers for HOMO and LUMO are the same as in 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:



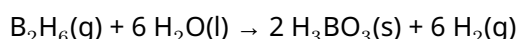
5.8 (12.0 pt)



Thermodynamics through an Interstellar Journey

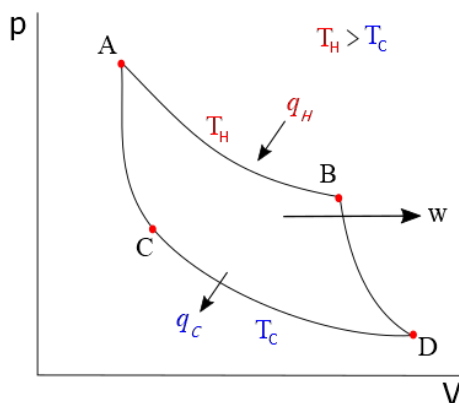
Part 1

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 a 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.

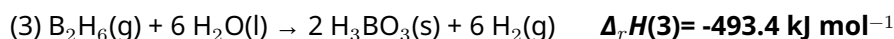
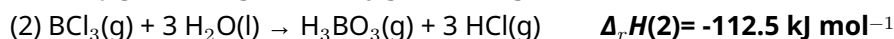
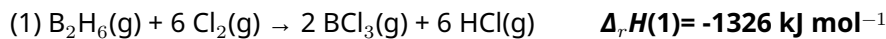


After heat transfers, the remaining energy is released as work (w). Also, q_H and q_C are related to T_C and T_H as follows:

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

The efficiency of the cycle is given by the work released by the cycle (w) divided by the heat absorbed by the cycle (q_H).

You are provided with the change in enthalpy for 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 $\Delta_r U$ (internal energy change) (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 amount of overall work produced by the 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) for the $A \rightarrow B$ and $D \rightarrow C$ processes in the heat engine (in J K^{-1}). 6.0pt

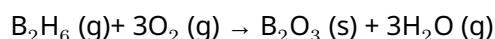
6.6 **Calculate** the Gibbs free energy change (ΔG) (in J) for the $A \rightarrow B$ and $D \rightarrow C$ processes in the heat engine. 6.0pt

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 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 embarked upon by using diborane as rocket fuel. The combustion reaction of diborane is shown below:



Combustion of diborane is performed in a 100 L closed container at different temperatures and the equilibrium conditions recorded.



Q6-3

English (Australian) (Australia)

	8930 K	9005 K
$\text{B}_2\text{H}_6(\text{g})$	0.38 mol	0.49 mol
H_2O	0.20 mol	0.20 mol

Partial pressure of $\text{O}_2(\text{g})$ was stabilized to 1 bar and kept constant for each of the above 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 $\text{B}_2\text{O}_3(\text{s})$ does not change with pressure, all the gas species behave as ideal gases, and 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 $\Delta_r G^\circ$ of the reaction (in kJ mol^{-1}) at 8930 K and 9005 K. (If you failed to find K_p , please use K_p (8930 K) = 2, K_p (9005 K) = 0.5) 6.0pt

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 combustion reaction at 298 K. (If you failed to find K_p , please use K_p (8930 K) = 2, K_p (9005 K) = 0.5) 6.0pt

6.12 Tick the correct answers in the table by determining whether the combustion reaction is favoured or not at each of the given temperatures below, at standard pressure (1 bar). 8.0pt

6.13 Calculate the $\Delta_f H$ (in kJ mol^{-1}) and S° (in $\text{kJ mol}^{-1}\text{K}^{-1}$) of $\text{H}_2\text{O}(\text{g})$ using the values given in the table below. ($\Delta_f H$ = enthalpy of formation, S° = standard entropy) (If you fail to find $\Delta_r H^\circ$ and $\Delta_r S^\circ$ of the combustion reaction, please use $\Delta H^\circ = 1000 \text{ kJ mol}^{-1}$, $\Delta S^\circ = 150 \text{ J K}^{-1} \text{ mol}^{-1}$) 6.0pt

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



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)

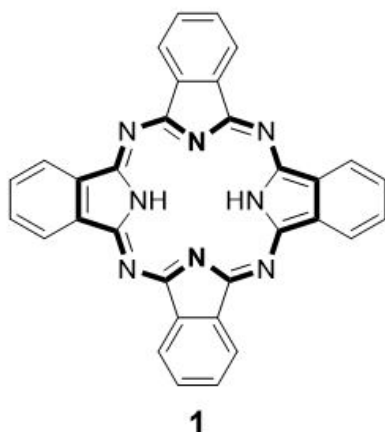
	Favoured	Unfavoured
298 K	<input type="checkbox"/>	<input type="checkbox"/>
8930 K	<input type="checkbox"/>	<input type="checkbox"/>
9005 K	<input type="checkbox"/>	<input type="checkbox"/>
9100 K	<input type="checkbox"/>	<input type="checkbox"/>

6.13 (6.0 pt)

Show your calculation:



Phthalocyanines

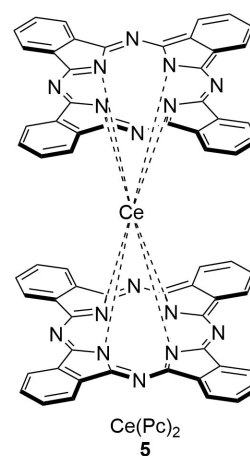
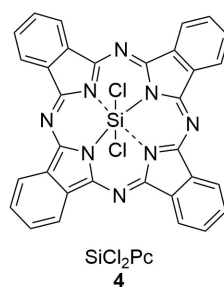
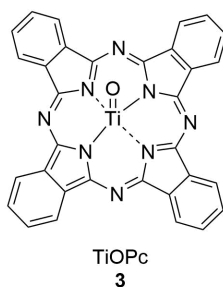
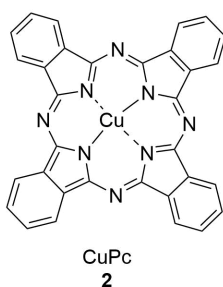


*Emeritus Professor Özer
Bekaroğlu*

The term phthalocyanine (Pc) takes its origin from the Greek “naphtha”, which means rock oil, and “cyanine”, which means dark blue. 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 $(\text{C}_8\text{H}_4\text{N}_2)_4\text{H}_2$.

7.1 How many π -electrons are there in the bold region of the H_2Pc molecule in compound **1** shown above? 4.0pt





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 each 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 **2, 3, and 5**. 6.0pt

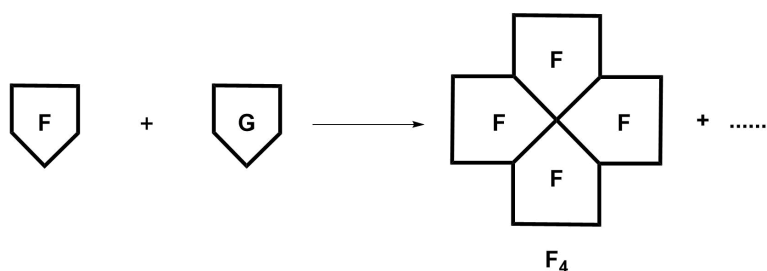
7.4 **Complete** the table in your answer sheet by determining the geometry of compounds **2-5**. 8.0pt

7.5 **Complete** the table in your answer sheet by determining the magnetic properties of compounds **2-5**. 8.0pt
 • Use the letter "p" for paramagnetic and the letter "d" for diamagnetic.

7.6 **Write** the ground-state electron configuration of the silicon (Si) 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 cyclotetramerization of phthalonitriles. On the other hand, Pcs having different substituents are called asymmetric, and can be prepared by the statistical cyclization of two different phthalonitriles. This method has no selectivity and the product is a mixture of all possible isomers.

7.7 **Draw** the possible products that may occur in the statistical cyclization method by using **F** and **G**. If there are any stereoisomers, label them as *cis*- or *trans*-. 19.0pt
 • **F** and **G** represent two different symmetrical phthalonitriles.
 • One of the products is **F₄** as given below.
 • Draw other products in a similar format to that of **F₄**.



Pcs are used as photosensitizers in photodynamic therapy (PDT) for cancer treatment due to their strong absorption in the visible spectrum and high molar absorption coefficients. PDT consists of three essential components: **photosensitizer**, light, and oxygen. None of these is individually toxic, but together they



initiate a photochemical reaction resulting in the generation of cytotoxic singlet oxygen ($^1\text{O}_2$) 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 the bond order. 12.0pt

- 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:

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	

7.5 (8.0 pt)

Compound	Magnetic property
2	
3	
4	
5	

7.6 (14.0 pt)

[illegible]



7.7 (19.0 pt)

Products:



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7.8 (12.0 pt)

MO diagram:

Bond order:

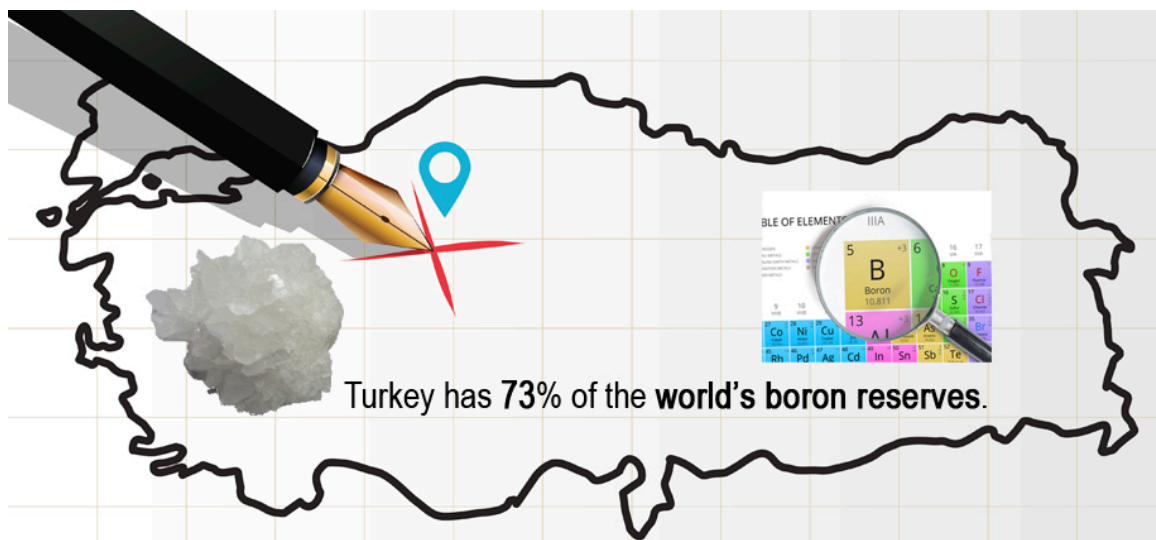
7.9 (6.0 pt)

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 ETI Mining Company in Turkey. NaBH_4 can be synthesized by the reduction of anhydrous borax with metallic sodium under high-pressure hydrogen gas in the presence of silicon dioxide (silica) at $700\text{ }^\circ\text{C}$, namely 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 synthesized by the reaction of NaBH_4 and ammonium sulfate in dry tetrahydrofuran (THF) at $40\text{ }^\circ\text{C}$ (**Hint:** BNH_6 synthesis must be conducted in a well-ventilated fume-hood because flammable gas is generated as one of the by-products). While NaBH_4 is an ionic compound, ammonia borane is a Lewis acid-base adduct.

8.1 Write a balanced chemical equation for the synthesis of NaBH_4 from anhydrous borax. 3.0pt

8.2 Write a balanced chemical equation for the synthesis of ammonia borane from NaBH_4 . 3.0pt

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

8.4 Calculate 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 solvolysis reactions in the presence of a suitable catalyst at room temperature. In the hydrolysis reactions, 4 and 3 moles of H_2 gas are released



from the hydrolysis of 1 mole of NaBH_4 and BNH_6 , respectively, along with a metaborate anion including 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) and in higher borates such as $\text{B}_3\text{O}_6^{3-}$, cyclic structures containing B-O-bonds can be formed. Since B_2O_3 is an acidic compound, it is easily reacted with water to produce boric acid (H_3BO_3). On the other hand, the high temperature and high-pressure reaction of B_2O_3 with ammonia yields two-dimensional boron nitride, which consists of planar graphite-like sheets of alternating B and N atoms.

8.6 **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. **Hint:** 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 synthesized 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. Therefore, it is not possible to isolate it as BH_3 under ordinary conditions. However, it can be stabilized via its reaction with carbon monoxide to yield the compound 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 **Sketch** the Lewis dot structure of BH_3CO molecule, showing the formal charges. 3.0pt

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

Borazine consists of single and double bonded cyclic B—N units and hydrogen atoms attached to these atoms with the molecular formula $\text{B}_3\text{N}_3\text{H}_6$. It is isostructural with benzene. Borazine can be synthesized by using a two-step procedure involving 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, and then 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). **Hint:** THF stabilizes 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 accelerate the rate of reactions by allowing them to proceed via a lower energy pathway. The catalytic activity of catalysts is generally determined by the turnover frequency (TOF), which is calculated by dividing the moles of the product by the moles of active catalyst and the time ($\text{TOF} = \text{mol product}/(\text{mol catalyst} \times \text{time})$). 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). 67.25 mL of hydrogen gas was generated in 5 minutes.

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

As a result of a detailed crystal analysis of a synthesized Cu_xPt_y alloy nanoparticle (the subscripts indicate molar percentages of the atoms in the alloy structure), it was determined that the Pt atoms form a fcc unit cell, where the Pt atoms on the faces of the fcc unit cell are replaced with Cu atoms to form the 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 structure of the described unit cell of Cu_xPt_y alloy nanoparticles by showing the placement of the atoms in 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 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 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 analyst at 298 K:

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

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

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

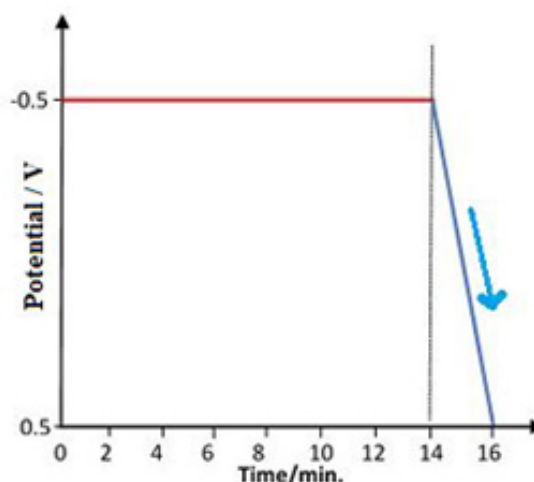
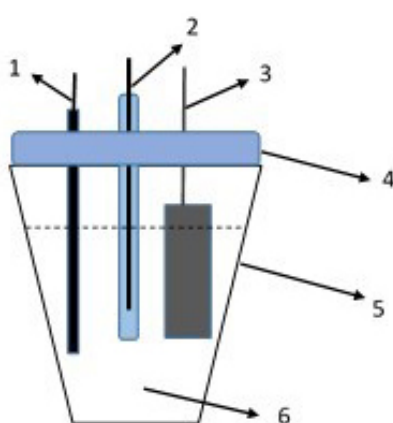


Figure 1. a) Electrochemical cell design; 1) working electrode (Pt wire), 2) reference electrode (Ag/AgCl, 3M KCl), 3) counter electrode (Pt foil), 4) cell tap, 5) electrochemical cell, 6) 10 mL of sample solution. **b)** Potential change of working electrode as a function of time. y-axis: potential/V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

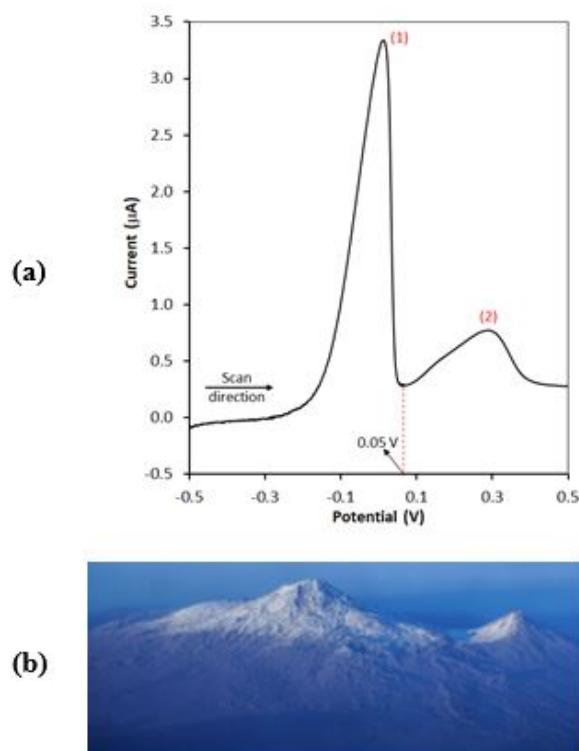


Figure 2. a) Potential scan of the working electrode as a function of current in 0.1 M H_2SO_4 solution after keeping it constant at a potential of -0.50 V in 10 mL of wastewater sample as shown in Figure 1b (horizontal line). y-axis: current/ μA , x-axis: potential/V vs Ag/AgCl, b) A view of Great and 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 minutes 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 is known that 1 mL of the EDTA solution is equivalent to 3.85 mg/mL 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 endpoint.

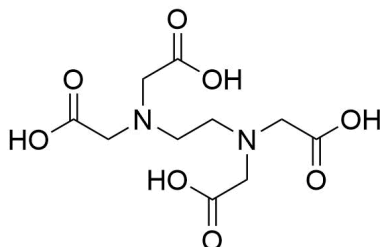


Figure 3. Chemical structure of EDTA (H_4Y).

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

9.2 Which of the statements is expected, if the potential is applied as -1.2 V instead of -0.5 V in *step 1* (horizontal line in Figure 1b)? **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.

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

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

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



Q9-4

English (Australian) (Australia)

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 Ni^{2+} concentration in mg L^{-1} in the wastewater of the factory. *Note:* You must show all working. 25.0pt

9.8 Calculate the minimum pH value for starting the precipitation of Ni^{2+} ions in the solution obtained in *step 5* by passing H_2S gas into the solution until saturation. If you cannot solve question **9.7**, use $20 \text{ mg L}^{-1} \text{ Ni}^{2+}$ 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
- ☐ NO₂ evolution
- ☐ Nitrogen evolution
- ☐ Oxygen evolution
- ☐ Hydrogen evolution

9.3 (8.0 pt)

Show your calculations:

Scan rate = mV/s



9.4 (16.0 pt)

Show your calculations:

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 calculations:

Ni²⁺ concentration: mg L⁻¹:



9.8 (30.0 pt)

Show your calculations:

Minimum pH value: