

IChO 2020

Theory problems and solutions · Istanbul, Turkey (held remotely) · 9 theory problems with complete solutions

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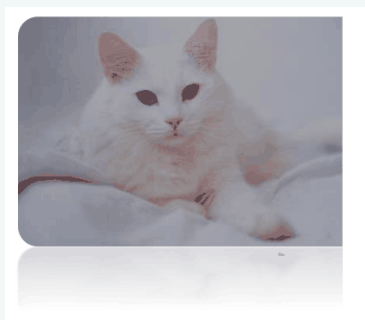
Problem 1: Two Beauties of Turkey: the Van Cat and the Ankara Cat



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



Van cat



Ankara cat

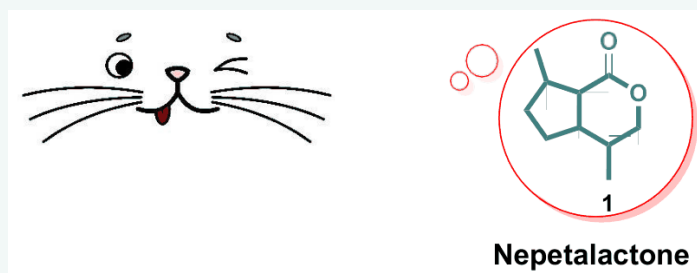


Nepeta cataria (catnip)

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

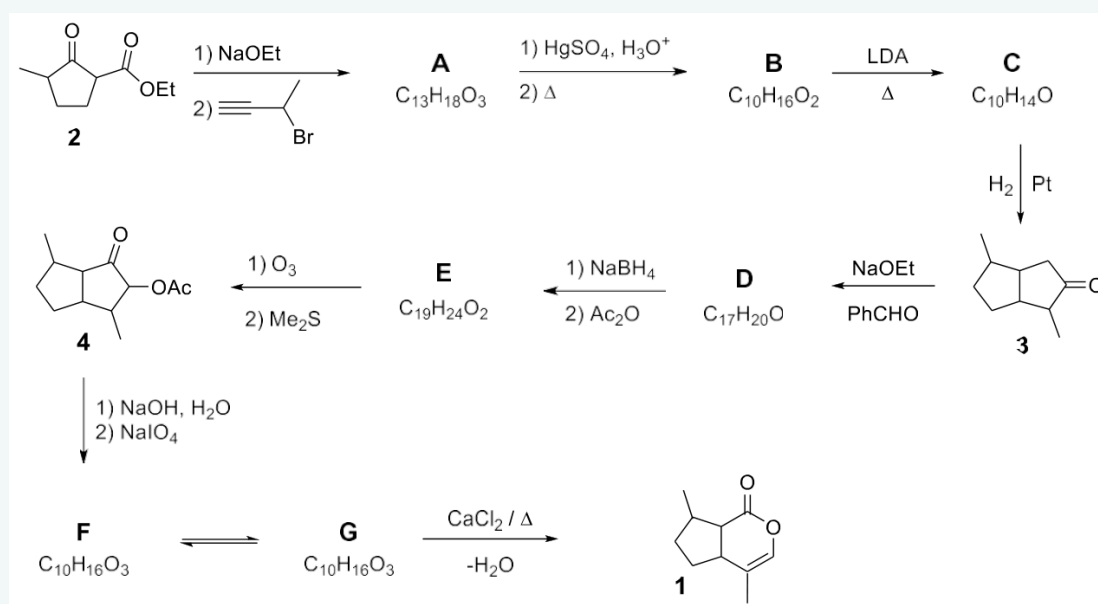


Cat eCat eating catnip in the garden



Cat's dream

Total synthesis of nepetalactone:

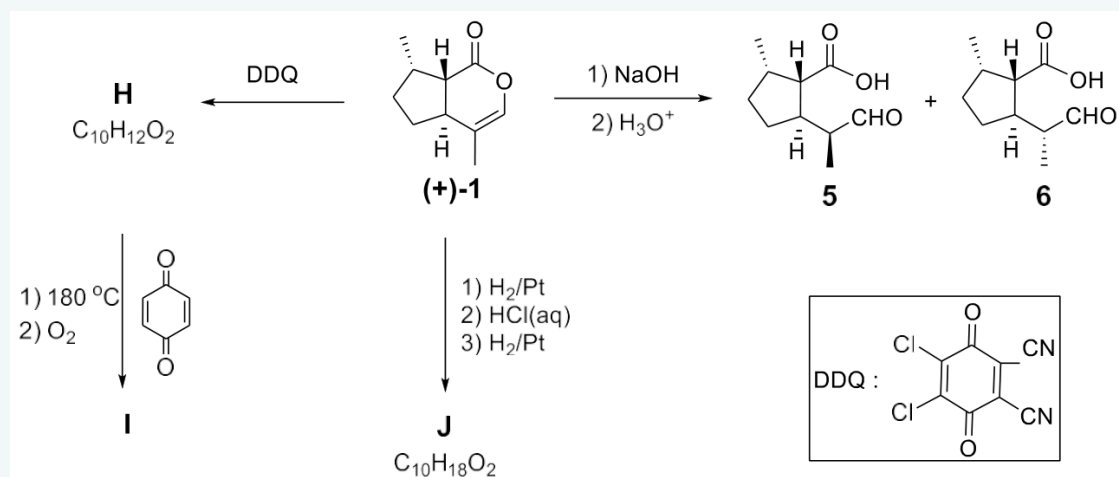


1.1 The above scheme describes the total synthesis of nepetalactone. Draw structures of **A–G**, without stereochemical details.

Hints:

- Compound **A** has strong and sharp band at 3300 cm^{-1} in the IR spectrum.
- **A**, **B**, and **F** are monocyclic, while **C**, **D**, **E**, and **G** are bicyclic compounds.
- **F** has one doublet at $\sim 9.8\text{ ppm}$ 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 the box next to the correct answer(s) on your answer sheets.

☐	Enantiomers
☐	Diastereomers
☐	Identical
☐	Stereoisomers

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

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

Hints:

- During the formation of **I**, sequential pericyclic reactions and an oxidation reaction (due to the presence of O₂) 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.

Official English text of the problem.

Answers

- 1.1**

Stereochemistry is intentionally unspecified.

Compound	Name	SMILES
A	Ethyl 1-(but-3-yn-2-yl)-3-methyl-2-oxocyclopentane-1-carboxylate	CCOC(=O)C1(C(C)C#C)CCC(C)C1=O
B	2-Methyl-5-(3-oxobutan-2-yl)cyclopentan-1-one	CC(=O)C(C)C1CCC(C)C1=O
C	4,8-Dimethylbicyclo[3.3.0]oct-1-en-3-one	CC1CCC2C(C)C(=O)C=C12
D	4-Benzylidene-2,6-dimethylbicyclo[3.3.0]octan-3-one	CC1CCC2C(C)C(=O)C(=Cc3ccccc3)C12
E	4-Benzylidene-2,6-dimethylbicyclo[3.3.0]octan-3-yl acetate	CC1CCC2C(C)C(OC(C)=O)C(=Cc3ccccc3)C12

Compound	Name	SMILES
F	2-(1-Formylethyl)-5-methylcyclopentane-1-carboxylic acid	<chem>CC1CCC(C(C)C=O)C1C(=O)O</chem>
G	4-Hydroxy-5,9-dimethyl-3-oxabicyclo[4.3.0]nonan-2-one	<chem>CC1CCC2C(C)C(O)OC(=O)C12</chem>

• 1.2

Tick **Diastereomers** and **Stereoisomers**. Compounds **5** and **6** are epimers at the side-chain carbon adjacent to the aldehyde group.

• 1.3

Compound	Name	Stereochemical SMILES
H	(9S)-5,9-Dimethyl-3-oxabicyclo[4.3.0]nona-1(6),4-dien-2-one, the conjugated α -pyrone	<chem>C[C@H]1CCC2=C1C(=O)OC=C2C</chem>
I	(3S)-3,7-Dimethyltricyclo[7.4.0.0 ^{2,6}]trideca-1(9),2(6),7,11-tetraene-10,13-dione, a cyclopenta-fused 1,4-naphthoquinone	<chem>C[C@H]1CCc2c1c1C(=O)C=CC(=O)c1cc2C</chem>
J	(1S,2S,5R)-2-Methyl-5-(propan-2-yl)cyclopentane-1-carboxylic acid	<chem>C[C@H]1CC[C@H](C(C)C)[C@H]1C(=O)O</chem>

In drawings of **H** and **I**, retain the dashed methyl bond at the surviving stereocentre of the cyclopentane ring. In **J**, the carboxyl group and ring methyl group are **cis**, and the isopropyl group is **trans** to both.

Solution

The names and SMILES of **A–J** are given above. Small molecules appearing in the balances include water O, hydrogen [H][H], oxygen O=O, carbon dioxide O=C=O, and ethanol CCO. Spectator ions are omitted where appropriate.

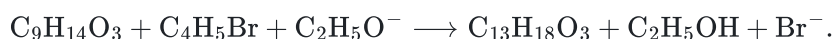
1.1 — Identification of A–G

Formation of A: alkylation of a β -keto ester.

Starting compound **2** is ethyl 3-methyl-2-oxocyclopentane-1-carboxylate, CCOC(=O)C1CCC(C)C1=O.

Ethoxide, CC[O-], removes the proton from the ring carbon between the ketone and ester carbonyl groups. The resulting carbon nucleophile attacks the bromine-bearing carbon of **3-bromobut-1-yne**, C#CC(C)Br, displacing bromide, [Br-].

Consequently, that ring carbon acquires a but-3-yn-2-yl substituent:



The terminal alkyne remains intact. Its $\text{C}\equiv\text{C}-\text{H}$ stretching vibration accounts for the **strong, sharp absorption near 3300 cm⁻¹**. The product is monocyclic, as required.

A $\rightarrow$ B: alkyne hydration, ester hydrolysis, and decarboxylation.

Mercury(II)-catalyzed hydration of the terminal alkyne gives the Markovnikov enol, which tautomerizes to a methyl ketone. Thus the side chain changes from a but-3-yn-2-yl group to a 3-oxobutan-2-yl group.

Acidic ester hydrolysis gives a β -keto acid, which loses carbon dioxide on heating. The overall balance is



The product **B** therefore has a cyclopentanone ring with one methyl substituent and one $-\text{CH}(\text{CH}_3)\text{COCH}_3$ side chain. It remains monocyclic.

B → C: intramolecular aldol condensation.

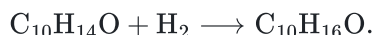
LDA—lithium diisopropylamide, $[\text{Li}^+]\cdot\text{CC}(\text{C})[\text{N}^-]\text{C}(\text{C})\text{C}$ —forms the enolate at the terminal methyl group of the side-chain ketone. That enolate carbon attacks the cyclopentanone carbonyl carbon, forming a new five-membered ring.

Dehydration produces the fused α,β -unsaturated ketone **C**:



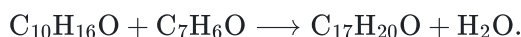
For the drawing, place the new double bond between the former cyclopentanone carbonyl carbon, now a ring-junction carbon, and the adjacent carbon derived from the terminal methyl group.

Hydrogenation then gives compound **3**, **2,6-dimethylbicyclo[3.3.0]octan-3-one**, CC1CCC2C(C)C(=O)CC12:



3 → D: condensation with benzaldehyde.

The α -methylene carbon of **3** undergoes aldol condensation with **benzaldehyde**, O=Cc1ccccc1. Loss of water gives the exocyclic benzylidene group in **D**:



Thus the double bond is between the original α -methylene carbon and the former aldehyde carbon. The ketone carbonyl remains intact.

D → E: carbonyl reduction and acetylation.

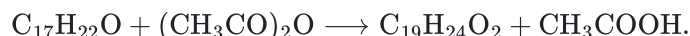
Sodium borohydride reduces the ketone carbonyl while retaining the benzylidene double bond. The intermediate is **4-benzylidene-2,6-dimethylbicyclo[3.3.0]octan-3-ol**, CC1CCC2C(C)C(O)C(=Cc3ccccc3)C12.

A balanced representation with aqueous work-up is



Here borohydride is $[\text{BH}_4^-]$ and tetrahydroxyborate is $[\text{B}^-](\text{O})(\text{O})(\text{O})\text{O}$.

The alcohol is then acetylated by **acetic anhydride**, CC(=O)OC(C)=O, giving **E** and **acetic acid**, CC(=O)O:



E → 4: reductive ozonolysis.

Ozonolysis cleaves the exocyclic benzylidene double bond. Its ring carbon becomes a ketone carbonyl, while its phenyl-bearing carbon gives benzaldehyde.

Compound **4** is **2,6-dimethyl-4-oxobicyclo[3.3.0]octan-3-yl acetate**, CC1CCC2C(C)C(OC(C)=O)C(=O)C12.

With ozone, $[\text{O}^-][\text{O}^+]=\text{O}$, and dimethyl sulfide, CSC, the balanced reaction is



The sulfur-containing product is **dimethyl sulfoxide**, CS(C)=O.

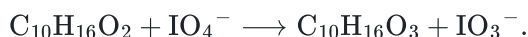
4 → F: deacetylation and periodate cleavage.

Hydroxide, $[\text{OH}^-]$, hydrolyzes the acetate ester:



The products are **3-hydroxy-4,8-dimethylbicyclo[3.3.0]octan-2-one**, CC1CCC2C(C)C(O)C(=O)C12, and acetate, CC(=O)[O-].

Periodate then cleaves the bond between the adjacent ketone and alcohol carbons. The ketone carbon becomes a carboxyl carbon; the alcohol carbon, which bears hydrogen, becomes an aldehyde carbon. This opens the second five-membered ring:

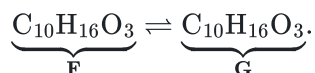


Periodate is $[\text{O}^-]\text{I}(=\text{O})(=\text{O})=\text{O}$; iodate is $[\text{O}^-]\text{I}(=\text{O})=\text{O}$.

The resulting **F** is therefore a monocyclic aldehyde–carboxylic acid. Its aldehyde proton couples to the single proton on the adjacent $\text{CH}(\text{CH}_3)$ carbon, explaining the **doublet near 9.8 ppm**.

F $\rightleftharpoons$ G $\rightarrow$ 1: ring closure and dehydration.

The carboxyl hydroxyl oxygen of **F** attacks its aldehyde carbon intramolecularly. Proton transfer gives the six-membered hydroxy-lactone **G**, without changing the molecular formula:



For the drawing of **G**, the newly formed ring contains, in order:

- the carboxyl-bearing cyclopentane carbon;
- the ester carbonyl carbon;
- the ring oxygen;
- the former aldehyde carbon, now bearing hydroxyl;
- the methyl-bearing side-chain carbon;
- the adjacent cyclopentane carbon.

Heating with calcium chloride promotes dehydration between the hydroxyl-bearing carbon and its methyl-bearing neighbour:



This gives **nepetalactone 1**, with unspecified stereochemistry for this part: CC1CCC2C(C)=COC(=O)C12.

The formula and ring-count checks are:

Compound	Formula	Number of rings
A	$\text{C}_{13}\text{H}_{18}\text{O}_3$	1
B	$\text{C}_{10}\text{H}_{16}\text{O}_2$	1
C	$\text{C}_{10}\text{H}_{14}\text{O}$	2
D	$\text{C}_{17}\text{H}_{20}\text{O}$	2
E	$\text{C}_{19}\text{H}_{24}\text{O}_2$	2
F	$\text{C}_{10}\text{H}_{16}\text{O}_3$	1
G	$\text{C}_{10}\text{H}_{16}\text{O}_3$	2

1.2 — Relationship between 5 and 6

Hydrolysis opens the enol-lactone ring. The resulting enol tautomerizes to an aldehyde, creating a stereocentre at the side-chain carbon bearing methyl. Either configuration can form there, while the three pre-existing cyclopentane stereocentres retain their spatial configurations.

The neutral overall hydrolysis balance, for either product, is



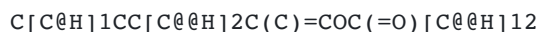
The two structures are:

Compound	Name	Stereochemical SMILES
5	(1S,2R,5S)-2-[(1S)-1-Formylethyl]-5-methylcyclopentane-1-carboxylic acid	<chem>C[C@H]1CC[C@H]([C@H](C)C=O)[C@H]1C(=O)O</chem>
6	(1S,2R,5S)-2-[(1R)-1-Formylethyl]-5-methylcyclopentane-1-carboxylic acid	<chem>C[C@H]1CC[C@H]([C@@H](C)C=O)[C@H]1C(=O)O</chem>

They have identical connectivity and differ at exactly one of four stereocentres. They are therefore **epimers**, hence **diastereomers** and **stereoisomers**. They are neither identical nor enantiomers.

1.3 — Identification and stereochemistry of H, I, and J

The stereochemical starting structure shown in the question is **(+)-nepetalactone 1**:

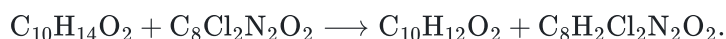


Formation of H.

DDQ removes the two ring-junction hydrogens, introducing a double bond along the shared edge of the five- and six-membered rings. Together with the existing alkene and lactone carbonyl, this gives the conjugated **α -pyrone H**.

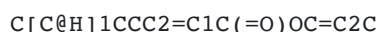
DDQ is **2,3-dichloro-5,6-dicyano-1,4-benzoquinone**, N#CC1=C(C#N)C(=O)C(Cl)=C(Cl)C1=O. Its reduced product is **2,3-dichloro-5,6-dicyanohydroquinone**, N#CC1C(C#N)C(O)C(Cl)C(Cl)C1O.

The balanced dehydrogenation is



Both ring-junction atoms become trigonal and cease to be stereocentres. The methyl-bearing cyclopentane stereocentre retains its *S* configuration.

Thus **H** is:



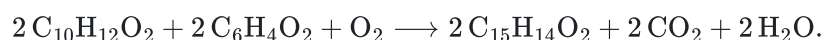
Formation of I.

The other reactant is **1,4-benzoquinone**, O=C1C=CC(=O)C=C1.

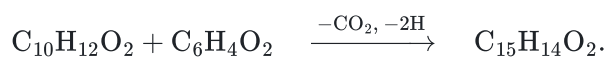
The sequence is:

1. **Diels–Alder cycloaddition.** The four-carbon conjugated diene of the α -pyrone reacts with one double bond of benzoquinone.
2. **Retro-Diels–Alder fragmentation.** The bridged lactone unit is expelled as **carbon dioxide**, O=C=O. Its carbon atom is the original lactone carbonyl carbon, and its oxygen atoms are both original lactone oxygens.
3. **Oxidative aromatization.** Oxygen removes two hydrogen atoms from the newly formed six-membered ring, giving the fused aromatic ring of **I**.

The overall balanced equation is



The formula can also be followed directly:



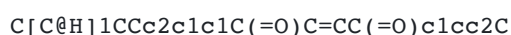
Using conventional atomic molar masses,

$$\begin{aligned} M(\text{I}) &= 15(12.011) + 14(1.008) + 2(15.999) \\ &= 226.275 \text{ g mol}^{-1} \\ &\approx \boxed{226.28 \text{ g mol}^{-1}}, \end{aligned}$$

matching the given value.

For the drawing, retain the cyclopentane ring and its stereogenic methyl-bearing carbon. The four diene carbons of **H** and the two reacting alkene carbons of benzoquinone form the new aromatic ring. The two quinone carbonyl groups and its other alkene remain intact.

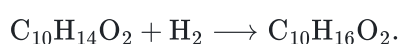
The precise structure is:



The original *S* stereocentre survives; the transient stereocentres introduced during cycloaddition disappear during fragmentation and aromatization.

Formation of J.

The first hydrogenation saturates the enol-lactone double bond:



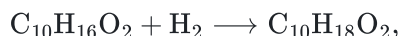
The intermediate is **dihydronepetalactone**:



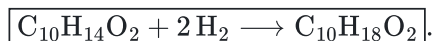
The newly created methyl-bearing stereocentre is left unspecified here because its configuration does not affect the final product.

Acid-promoted opening and the final hydrogenolysis cleave the lactone's alkyl carbon–oxygen linkage overall. The ester carbonyl becomes a carboxyl group, and the terminal oxygen-bearing carbon becomes a methyl group. Consequently, the side chain becomes isopropyl.

The combined balance for these last operations is



and the complete sequence has the net balance



The very broad $3300\text{--}2500\text{ cm}^{-1}$ band identifies the hydrogen-bonded hydroxyl group of a **carboxylic acid**. The formula gives

$$\text{DBE} = \frac{2(10) + 2 - 18}{2} = 2,$$

accounted for by the cyclopentane ring and the carboxyl carbonyl.

Thus **J** is **(1S,2S,5R)-2-methyl-5-(propan-2-yl)cyclopentane-1-carboxylic acid**:

C[C@H]1CC[C@H](C(C)C)[C@H]1C(=O)O

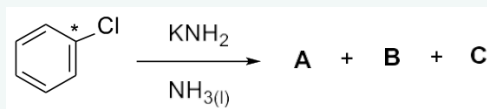
All three cyclopentane stereocentres retain their spatial configurations. The side-chain carbon is no longer stereogenic because it now bears two identical methyl groups.

The answers were checked against the official answers published by the organisers.

Problem 2: A Tale of a Reactive Intermediate

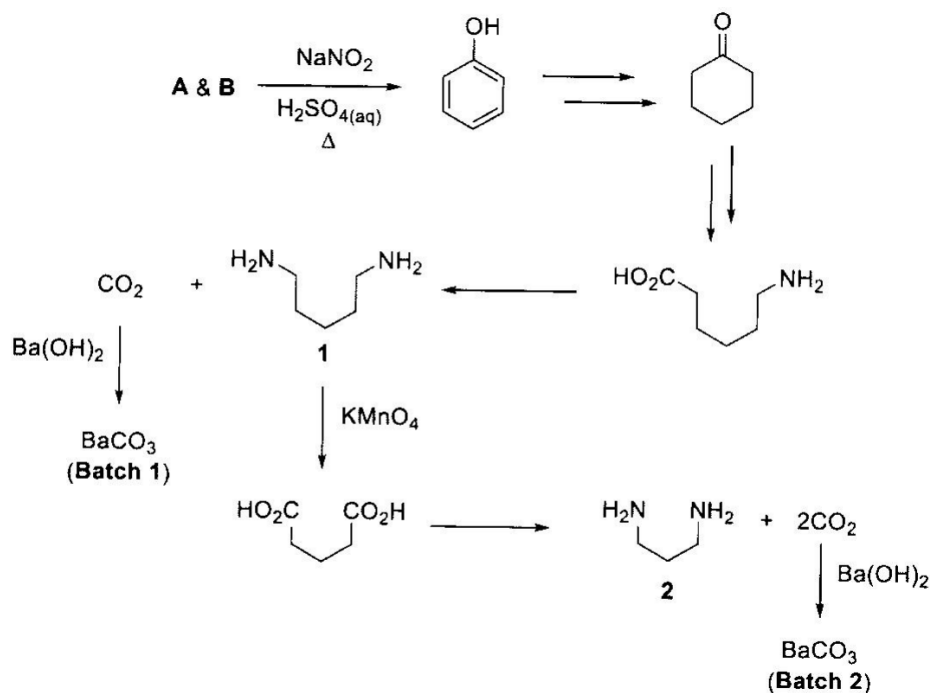
Arynes constitute a special class of reactive intermediates. The first experimental evidence for the structure of an aryne (benzyne) was demonstrated in 1953 via the elegant labeling experiments by John D. Roberts and coworkers.

In one such experiment, chlorobenzene, whose carbon at position 1 was labeled with radioactive ^{14}C , was reacted with KNH_2 in liquid NH_3 to give nearly equal amounts of isotopic isomers **A** and **B** along with the inorganic salt **C**. This reaction proceeds via the formation of aryne intermediate **D**.



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

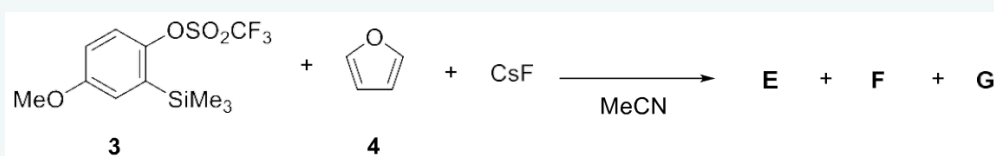
Analysis of the ^{14}C -labeled product(s) was achieved via degradation experiments (the ^{14}C -labeled carbons are not shown on the structures). Radioactivities of the intermediates and final products were examined.



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

Considering only A :	Considering only B :
☐ Compound 1	☐ Compound 1
☐ BaCO ₃ (Batch 1)	☐ BaCO ₃ (Batch 1)
☐ Compound 2	☐ Compound 2
☐ BaCO ₃ (Batch 2)	☐ BaCO ₃ (Batch 2)

With the aim of facilitating aryne formation, Kobayashi and co-workers developed a fluoride-induced aryne generation protocol. Using this method, benzene derivative **3** is reacted with furan (**4**) in the presence of CsF, resulting in the formation of **E**, **F**, and **G**.



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

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

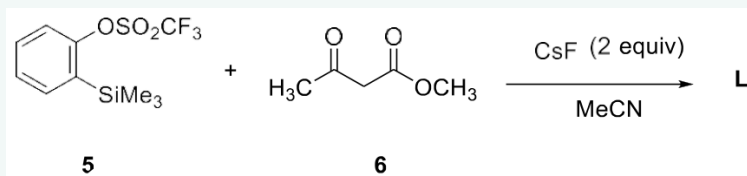
In the absence of a nucleophile or a trapping agent, arynes can undergo [2+2]-type cyclodimerization or [2+2+2]-type cyclotrimerization reactions under suitable conditions. The aryne derivative that is obtained when **3** is treated with one equivalent of CsF in MeCN can give, in principle, four different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

- H** has two planes of symmetry.
- I** is expected to exhibit 21 signals in its ¹³C-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.

When **5** is reacted with β -ketoester **6** in the presence of 2 equivalents of CsF at 80 °C, **L** is obtained as the major product. The ^1H -NMR and ^{13}C -NMR data for **L**, in CDCl_3 , are as follows:

- ^1H -NMR: δ 7.79 (dd, $J = 7.6, 1.5$ Hz, 1H), 7.47–7.33 (m, 2H), 7.25–7.20 (m, 1H), 3.91 (s, 2H), 3.66 (s, 3H), 2.56 (s, 3H) ppm.
- ^{13}C -NMR: δ 201.3, 172.0, 137.1, 134.4, 132.8, 132.1, 130.1, 127.5, 51.9, 40.2, 28.8 ppm.



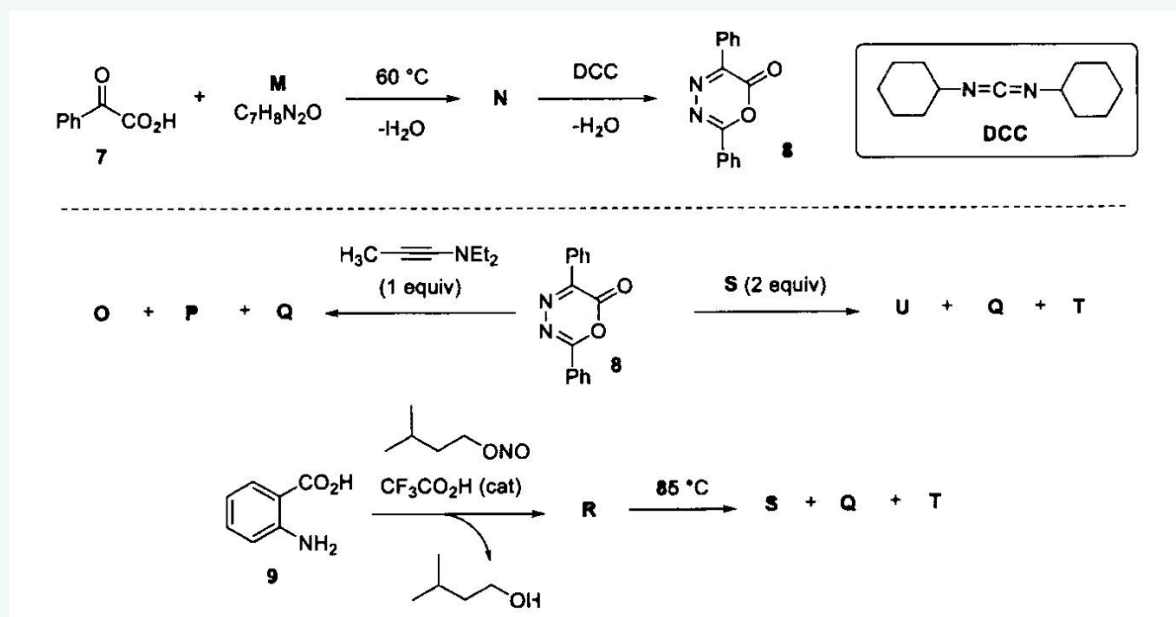
2.5 Determine the structure of L.

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

- The pK_a values of HF and β -ketoester **6** in dimethyl sulfoxide (DMSO) are about 15 and 14, respectively.
- ☐ F^- hydrolyzes the trifluoromethanesulfonate (O_3SCF_3) group of **5**
- ☐ F^- attacks the $-\text{SiMe}_3$ group of **5**.
- ☐ F^- acts as a base to deprotonate **6**.
- ☐ F^- acts as a nucleophile and attacks the ester group of **6**.

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.

Official English text of the problem.

Answers

• 2.1

The following convention defines **A** and **B** throughout this solution.

Species	Identification and position of the asterisk	SMILES
A	Aniline-1- ¹⁴ C: put * on the carbon bearing NH ₂ .	<chem>N[14c]1ccccc1</chem>
B	Aniline-2- ¹⁴ C: put * on a carbon immediately adjacent to the carbon bearing NH ₂ .	<chem>Nc1[14cH]cccc1</chem>
C	Potassium chloride, KCl.	<chem>[K+] . [Cl-]</chem>
D	Benzyne with one ¹⁴ C atom at an endpoint of its formal triple bond; put * on that endpoint.	<chem>[14C]1#CC=CC=C1</chem>

Each labeled molecule contains **one** radioactive carbon. Interchanging the names **A** and **B** is equally valid if their columns in 2.2 are also interchanged.

• 2.2

Intermediate or product	Starting from A	Starting from B
Compound 1	☐	☒
BaCO ₃ , Batch 1	☒	☐
Compound 2	☐	☐
BaCO ₃ , Batch 2	☐	☒

1 is pentane-1,5-diamine, NCCCCN; **2** is propane-1,3-diamine, NCCCN. Barium carbonate is [Ba+2] . [O-]C(=O)[O-].

• 2.3

Species	Name	SMILES
E	6-Methoxy-1,4-epoxy-1,4-dihydronaphthalene, the oxygen-bridged benzyne–furan cycloadduct	<chem>COc1ccc2c(c1)C1C=CC2O1</chem>
F	Cesium trifluoromethanesulfonate, CsCF ₃ SO ₃	<chem>[Cs+] . [O-]S(=O)(=O)C(F)(F)F</chem>
G	Fluorotrimethylsilane, Me ₃ SiF	<chem>C[Si](C)(C)F</chem>

For **E**, the oxygen bridge connects positions 1 and 4; the remaining nonaromatic double bond connects positions 2 and 3. Stereochemistry is omitted as requested.

• 2.4

Species	Name	SMILES
H	2,7-Dimethoxybiphenylene	<chem>COc1ccc2c(c1)-c1cc(OC)ccc1-2</chem>
I	2,6,11-Trimethoxytriphenylene	<chem>COc1ccc2c(c1)c1cc(OC)ccc1c1ccc(OC)cc21</chem>
J	2,6,10-Trimethoxytriphenylene	<chem>COc1ccc2c(c1)c1ccc(OC)cc1c1ccc(OC)cc21</chem>
K	2,6-Dimethoxybiphenylene	<chem>COc1ccc2c(c1)-c1ccc(OC)cc1-2</chem>

• 2.5

L is **methyl 2-(2-acetylphenyl)acetate**, COC(=O)Cc1ccccc1C(C)=O. The acetyl and CH2CO2Me groups occupy adjacent positions on the benzene ring.

- 2.6

Tick **statements 2 and 3**:

- F^- attacks the $-SiMe_3$ group of **5**.
- F^- acts as a base to deprotonate **6**.

Fluoride ion has SMILES [F-].

- 2.7

O and **P** may be interchanged.

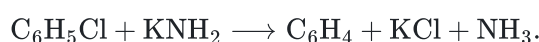
Species	Name or precise identification	SMILES
M	Benzohydrazide	<chem>NNC(=O)c1ccccc1</chem>
N	Phenylglyoxylic acid benzoylhydrazone; shown in the cyclizing <i>Z</i> geometry	<chem>O=C(O)/C(=N\NC(=O)c1ccccc1)c1ccccc1</chem>
O	4-(Diethylamino)-5-methyl-3,6-diphenyl-2H-pyran-2-one	<chem>O=C1OC(c2ccccc2)=C(C)C(N(CC)CC)=C1c1ccccc1</chem>
P	5-(Diethylamino)-4-methyl-3,6-diphenyl-2H-pyran-2-one	<chem>O=C1OC(c2ccccc2)=C(N(CC)CC)C(C)=C1c1ccccc1</chem>
Q	Dinitrogen, N_2	<chem>N#N</chem>
R	Benzenediazonium-2-carboxylate, an internal diazonium-carboxylate salt	<chem>O=C([O-])c1ccccc1[N+]#N</chem>
S	Benzyne	<chem>C1#CC=CC=C1</chem>
T	Carbon dioxide, CO_2	<chem>O=C=O</chem>
U	9,10-Diphenylanthracene	<chem>c1ccc2c(c1)c(-c1ccccc1)c1ccccc1c2-c1ccccc1</chem>

Solution

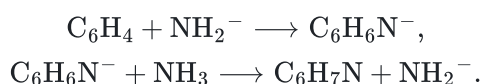
2.1 — Formation and trapping of labeled benzyne

The starting material is chlorobenzene-1- ^{14}C , C1[14c]1ccccc1. Potassium amide, [K+].[NH2-], removes an ortho hydrogen. Elimination of chloride then produces **D**, with the original chlorine-bearing carbon as one endpoint of the aryne bond.

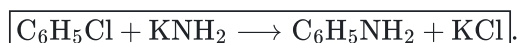
The balanced elimination is



Here, C_6H_4 denotes labeled benzyne **D**. Amide ion can attack either endpoint of its aryne bond. The resulting carbon anion takes a proton from ammonia, N :



Thus the overall substitution is



Attack at the labeled endpoint gives **A**, with the label on the amino-bearing carbon. Attack at the other endpoint gives **B**, with the label adjacent to that carbon. The two aryne endpoints are equivalent apart from the isotope, explaining the nearly equal amounts.

The formal triple bond in the SMILES represents a **strained, bent aryne bond** constrained within a six-membered ring; it does not imply the linear geometry of an ordinary acyclic alkyne.

2.2 — Following the radioactive carbon through degradation

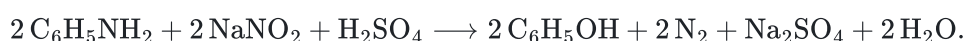
Number the aniline ring so that C_1 bears the amino group, with C_2 and C_6 adjacent to it. Under our convention:

- **A** is labeled at C_1 .
- **B** is labeled at C_2 , equivalently C_6 by reflection.

The relevant structures in the degradation sequence are:

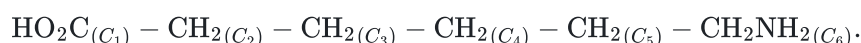
Structure	Name	SMILES
Aromatic hydrolysis product	Phenol	<chem>Oc1ccccc1</chem>
Cyclic ketone	Cyclohexanone	<chem>O=C1CCCCC1</chem>
Amino acid	6-Aminohexanoic acid	<chem>NCCCCC(=O)O</chem>
Oxidation product of 1	Glutaric acid, or pentanedioic acid	<chem>O=C(O)CCCC(=O)O</chem>

Diazotization and hydrolysis replace the amino group with hydroxyl without removing its ring carbon. A balanced overall equation using the stated reagents is



The phenolic carbon becomes the carbonyl carbon of cyclohexanone. Oxime formation, Beckmann rearrangement, and hydrolysis retain that carbon as the carboxyl carbon of 6-aminohexanoic acid.

One orientation of the opened carbon chain is therefore



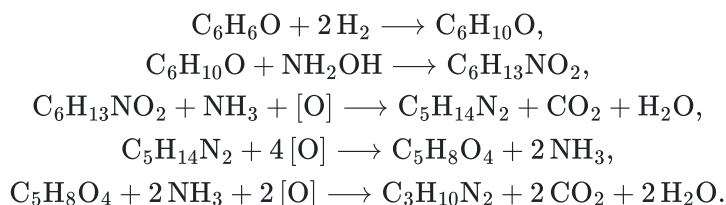
Opening in the opposite direction interchanges C_2 with C_6 and C_3 with C_5 , without changing the conclusions.

The first chain-shortening degradation removes the carboxyl carbon C_1 as carbon dioxide and gives **1**. Oxidation of the two terminal amino-bearing carbons of **1** gives the two carboxyl carbons of glutaric acid. Its subsequent degradation removes those carbons, C_2 and C_6 , and gives **2**.

Stage	Original ring carbons retained or collected
CO_2 , subsequently Batch 1	C_1
Compound 1	C_2, C_3, C_4, C_5, C_6
CO_2 , subsequently Batch 2	C_2, C_6
Compound 2	C_3, C_4, C_5

Consequently, **A** labels only Batch 1. **B** labels compound **1** and Batch 2. Neither starting isotopomer labels compound **2**.

For completeness, the unspecified multistep arrows admit the following balanced overall bookkeeping equations. Here [O] represents an oxygen-atom oxidizing equivalent; these equations do not specify the omitted experimental reagents. Hydroxylamine is NO.



Each carbonate collection follows



Starting from pure **B**, one radioactive carbon is distributed among the two carbon dioxide molecules released in the second degradation. The collected batch therefore exhibits radioactivity even though not every carbonate ion is labeled.

2.3 — Fluoride-induced aryne generation and furan trapping

Compound **3** is 4-methoxy-2-(trimethylsilyl)phenyl triflate:

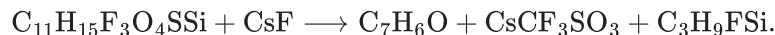
COc1ccc(OS(=O)(=O)C(F)(F)F)c([Si](C)(C)C)c1.

Fluoride attacks silicon. Cleavage of the aryl-silicon bond, followed by elimination of the adjacent triflate group, generates **4-methoxybenzyne**:

C1#CC=C(OC)C=C1.

The silicon-containing product is **G**, fluorotrimethylsilane. The departing triflate combines with cesium to give ionic **F**.

The balanced aryne-generation equation is



Furan, c1ccoc1, traps the aryne in a [4+2] cycloaddition:



To check the composition, take a 100.0 g sample of **E**. Using conventional atomic molar masses,

$$n_{\text{C}} = \frac{75.8}{12.01} = 6.31 \text{ mol}, \quad n_{\text{H}} = \frac{5.8}{1.008} = 5.75 \text{ mol}, \quad n_{\text{O}} = \frac{18.4}{16.00} = 1.15 \text{ mol}.$$

Normalizing to two oxygen atoms gives

$$\text{C} : \text{H} : \text{O} = 10.98 : 10.01 : 2.00 \approx 11 : 10 : 2.$$

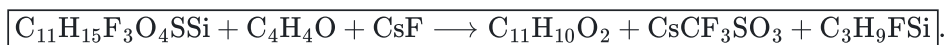
Thus the composition supports $\text{C}_{11}\text{H}_{10}\text{O}_2$, exactly the formula obtained by adding furan to methoxybenzyne. Its calculated composition is

$$75.84\% \text{ C}, \quad 5.79\% \text{ H}, \quad 18.37\% \text{ O},$$

consistent with all three reported percentages.

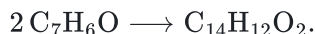
The product contains a methoxy oxygen and a bridging ether oxygen, with **no hydroxyl group**, explaining the absence of a proton exchangeable with D_2O .

The complete balanced reaction is



2.4 — The two dimers and two trimers

The methoxyaryne has formula $\text{C}_7\text{H}_6\text{O}$. Its two possible dimer connectivities are biphenylene derivatives:



Its two possible trimer connectivities are triphenylene derivatives:



The calculated monoisotopic mass of $\text{C}_{21}\text{H}_{18}\text{O}_3$ is approximately 318.126 Da, consistent with the reported molecular-ion $m/z = 318.1$. Therefore, **I** and **J** are the trimers, while **H** and **K** are the dimers.

For the dimers, draw a biphenylene framework with a central four-membered ring and one benzenoid ring on each side:

- In **H**, the two methoxy groups lie on the **same side** of the framework's long axis. This is 2,7-dimethoxybiphenylene. Its skeletal structure has the molecular mirror plane and a second plane perpendicular to it that interchanges the two benzenoid halves.
- In **K**, the methoxy groups occupy diagonally opposed positions. This is 2,6-dimethoxybiphenylene. It lacks that second mirror plane.

For the trimers, the three aryne-derived units can all have the same cyclic orientation, or one can be reversed:

- **J**, 2,6,10-trimethoxytriphenylene, has threefold rotational symmetry. Its 21 carbons form seven sets of three equivalent carbons, predicting **7** ^{13}C -NMR signals.
- **I**, 2,6,11-trimethoxytriphenylene, lacks any symmetry operation that interchanges its carbon atoms. It therefore has **21** distinct carbon environments, as required.

2.5 — Identification of **L** from its NMR spectra

Compound **5** is 2-(trimethylsilyl)phenyl triflate:

C[Si](C)(C)c1ccccc1OS(=O)(=O)C(F)(F)F.

Compound **6** is methyl acetoacetate, or methyl 3-oxobutanoate:

COC(=O)CC(C)=O.

Their reaction gives **L**, methyl 2-(2-acetylphenyl)acetate.

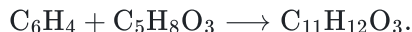
Observed signal	Assignment in L
Four aromatic protons, $\delta_{\text{H}} = 7.79$ to 7.20 ppm	Disubstituted benzene ring
$\delta_{\text{H}} = 3.91$ ppm, s, 2H; $\delta_{\text{C}} = 40.2$ ppm	Benzylic $\text{CH}_2\text{CO}_2\text{Me}$
$\delta_{\text{H}} = 3.66$ ppm, s, 3H; $\delta_{\text{C}} = 51.9$ ppm	Ester methoxy group
$\delta_{\text{H}} = 2.56$ ppm, s, 3H; $\delta_{\text{C}} = 28.8$ ppm	Acetyl methyl group
$\delta_{\text{C}} = 201.3$ ppm	Ketone carbonyl
$\delta_{\text{C}} = 172.0$ ppm	Ester carbonyl
Six resonances from 127.5 to 137.1 ppm	Six inequivalent aromatic carbons

The structure accounts for all eleven carbon resonances and all twelve hydrogens.

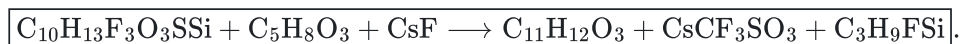
The mechanism explains the adjacent substituents:

1. Fluoride generates benzyne from **5** and forms the enolate of **6**.
2. The enolate carbon attacks one aryne carbon, producing a carbanion at the adjacent aromatic carbon.
3. That carbanion attacks the ketone carbonyl intramolecularly, forming a four-membered alkoxide intermediate.
4. Re-formation of the carbonyl breaks the original bond between the ketone carbonyl carbon and the ester-bearing carbon.
5. Protonation gives **L**.

Thus benzyne is formally inserted into the ketone–methylene carbon–carbon bond of methyl acetoacetate:



Including aryne generation, the balanced net reaction is



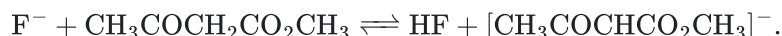
Two equivalents of CsF are used experimentally. One is consumed in aryne generation; the fluoride involved in deprotonation is regenerated in the formal proton-transfer cycle and therefore cancels from the net equation.

2.6 — The two functions of fluoride

The first function is **nucleophilic attack on silicon**, generating the aryne through desilylation and triflate elimination.

The second function is **deprotonation of methyl acetoacetate**. Its carbon-centered enolate can be represented as COC(=O)[CH-]C(C)=O.

The balanced acid–base equilibrium is



Using the supplied pK_{a} values,

$$K \approx 10^{pK_{\text{a}}(\text{HF}) - pK_{\text{a}}(\text{6})} = 10^{15-14} \approx 10.$$

On the quoted DMSO scale, this favors enolate formation. The numerical value is not an independently established equilibrium constant for the reaction solvent, MeCN, but it supports the intended basic role of fluoride.

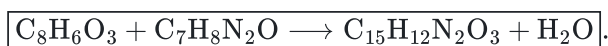
Neither triflate hydrolysis nor attack on the ester carbonyl is needed to account for the observed reaction. Therefore, only statements **2** and **3** are correct.

2.7 — Preparation and reactions of the diazapyrone

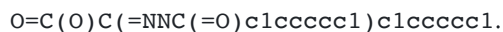
Formation of M and N. Phenylglyoxylic acid **7**, O=C(O)C(=O)c1ccccc1, contains a ketone that can condense with a hydrazide.

The reagent must provide the second phenyl group, both adjacent nitrogen atoms, and the carbon–oxygen unit needed for the heterocycle. Benzohydrazide **M** does exactly this and has the required formula $C_7H_8N_2O$.

Its terminal amino group condenses with the ketone of **7**, giving hydrazone **N**:

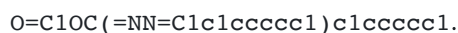


The hydrazone connectivity is



Ring closure requires the carboxyl group and the nitrogen-linked benzoyl group to be on the same side of the hydrazone double bond. The corresponding cyclizing *Z* geometry is the stereochemical SMILES given in the Answers.

Cyclodehydration to 8. Compound **8** is 2,5-diphenyl-6H-1,3,4-oxadiazin-6-one:



Cyclization joins the benzoyl-derived oxygen to the carboxyl carbon, with formal loss of water:



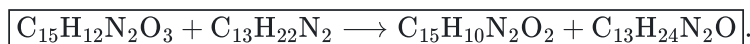
DCC is *N*, *N'*-dicyclohexylcarbodiimide,



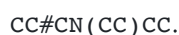
It accepts the elements of water to form *N*, *N'*-dicyclohexylurea,



The balanced equation including the dehydrating reagent is therefore



Formation of O, P, and Q. The alkyne is *N*, *N*-diethylprop-1-yn-1-amine,



The $C=N-N=C$ segment of **8** undergoes cycloaddition with this unsymmetrical alkyne. Extrusion of the adjacent nitrogen atoms as **Q**, N_2 , gives an α -pyrone.

The two alkyne carbons become positions 4 and 5 of the pyrone. Their two possible orientations give:

- **O**: diethylamino at position 4 and methyl at position 5;
- **P**: methyl at position 4 and diethylamino at position 5.

Both retain phenyl groups at positions 3 and 6. The balanced equation applies separately to either regioisomer:



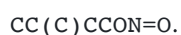
The scheme's **O + P** denotes a mixture of alternative products, rather than one molecule of each being formed from one molecule of **8**.

Dinitrogen fits the IR observation: stretching a homonuclear N_2 molecule does not change its dipole moment, so its fundamental vibration is IR-inactive.

Formation and decomposition of R. Compound **9** is anthranilic acid, or 2-aminobenzoic acid,



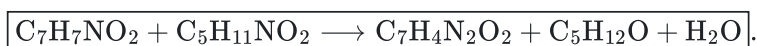
The alkyl nitrite is 3-methylbutyl nitrite,



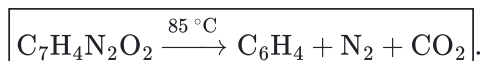
It diazotizes the amino group, producing the internal salt **R**. The alcohol shown is 3-methylbutan-1-ol,



Including the water required by atom balance,



On heating, **R** loses both its diazonium group and its carboxylate carbon:

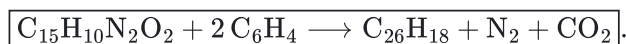


Thus **S** is benzyne, **Q** is dinitrogen, and **T** is carbon dioxide. The equation gives exactly one mole of **S** per mole of **R**, as stated.

Formation of U. Reaction with two benzyne molecules constructs the anthracene framework through successive cycloadditions and loss of N_2 and CO_2 .

Each benzyne contributes one outer benzenoid ring. The two phenyl-bearing carbons of **8** become positions 9 and 10 of the central anthracene ring. Consequently, **U** is **9,10-diphenylanthracene**.

The complete balanced equation is

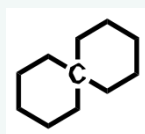


The carbon balance is particularly diagnostic: $15 + 2(6) - 1 = 26$ carbons remain in **U**, while all eighteen hydrogens remain in the organic product.

The answers were checked against the official answers published by the organisers.

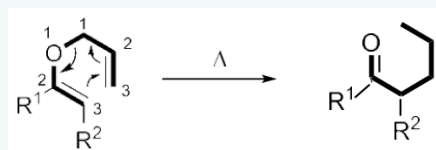
Problem 3: (±)-Coerulescine

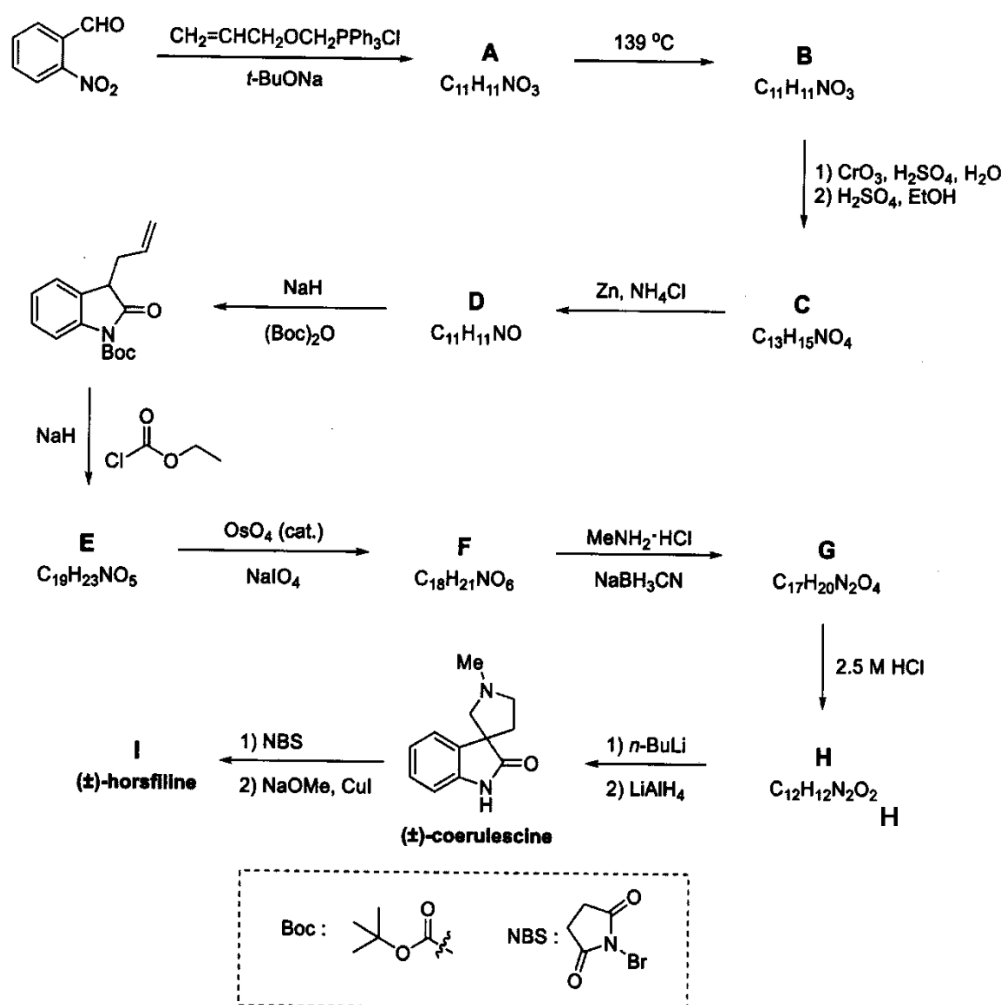
A spiro compound is typically an organic compound containing rings linked together by one common atom (spiroatom) as carbon atom with bold in figure below. The spiro[pyrrolidin-3,3'-oxindole] ring system is a structural framework incorporated in several cytostatic alkaloids and unnatural compounds. Coerulescine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



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

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





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

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

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

- D–F** have a bicyclic structure.

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

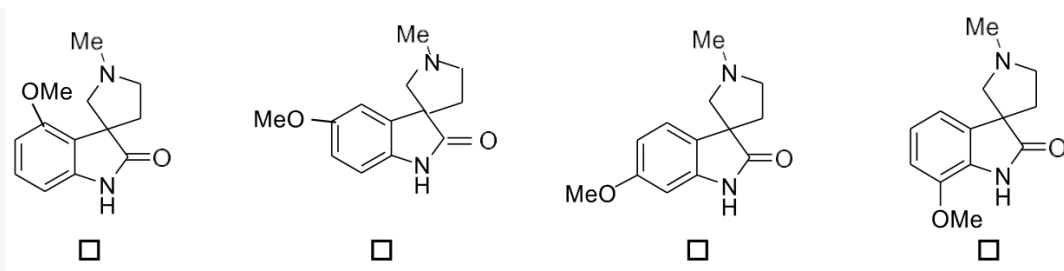
- ☐ Imine formation, then reduction, then amidation
- ☐ Amidation, then imine formation, then reduction
- ☐ Reduction, then amidation, then imine formation

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

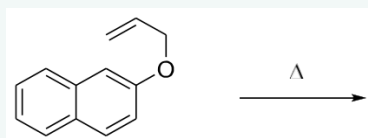
3.5 Draw the structure of the intermediate produced by treatment with *n*-BuLi in the step **H** → coerulescine (1).

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

3.6 Choose the correct structure for compound **I** consistent with the following selected ^1H -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. Tick the relevant box.



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



Official English text of the problem.

Answers

Unprimed positions below belong to the oxindole ring; primed positions belong to the second nitrogen-containing ring. Stereochemistry is omitted where permitted by the problem.

- **3.1**
- **A:** Allyl 2-(2-nitrophenyl)vinyl ether, an *E/Z* mixture.
 E : C=CCO/C=C/c1ccccc1[N+](=O)[O-]
 Z : C=CCO/C=C\c1ccccc1[N+](=O)[O-]
- **B:** 2-(2-Nitrophenyl)pent-4-enal.
O=CC(CC=C)c1ccccc1[N+](=O)[O-]
- **3.2**
- **C:** Ethyl 2-(2-nitrophenyl)pent-4-enoate.
CCOC(=O)C(CC=C)c1ccccc1[N+](=O)[O-]
- **D:** 3-Allylindolin-2-one.
O=C1Nc2ccccc2C1CC=C
- **E:** 1-tert-Butyl 3-ethyl 2-oxo-3-(prop-2-en-1-yl)indoline-1,3-dicarboxylate.
CCOC(=O)C1(CC=C)C(=O)N(C(=O)OC(C)(C)C)c2ccccc21
- **F:** 1-tert-Butyl 3-ethyl 2-oxo-3-(2-oxoethyl)indoline-1,3-dicarboxylate.
CCOC(=O)C1(CC=O)C(=O)N(C(=O)OC(C)(C)C)c2ccccc21
- **3.3** Tick the **first box: imine formation, then reduction, then amidation.**
- **3.4**
- **G:** The oxindole-*N*-Boc derivative of 1'-methylspiro[indoline-3,3'-pyrrolidine]-2,2'-dione.
CN1CCC2(C1=O)c1ccccc1N(C(=O)OC(C)(C)C)C2=O
- **H:** 1'-Methylspiro[indoline-3,3'-pyrrolidine]-2,2'-dione.
CN1CCC2(C1=O)c1ccccc1NC2=O
- **3.5** The **lithium salt of H** formed by deprotonation of its oxindole nitrogen.
CN1CCC2(C1=O)c1ccccc1[N-]C2=O.[Li+]
- **3.6** Tick the **second structure from the left: horsfiline, the 5-methoxy derivative of coerulescine.**
CN1CCC2(C1)c1cc(OC)ccc1NC2=O

- **3.7 1-Allylnaphthalen-2-ol**, also called **1-allyl-2-naphthol**.

C=CCc1c(O)ccc2ccccc12

Solution

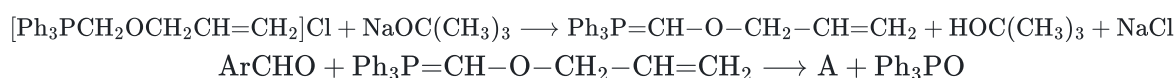
Throughout the solution, **Ar** denotes the **2-nitrophenyl group**. In reduction equations, **[H]** denotes one formal reducing hydrogen equivalent supplied by the stated reagents.

3.1 — Wittig reaction and Claisen rearrangement

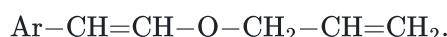
Sodium tert-butoxide removes a proton from the carbon adjacent to phosphorus in the phosphonium salt. This gives the **allyloxymethylene triphenylphosphorus ylide**, represented by the charge-separated SMILES:

C=CCO[CH-][P+](c1ccccc1)(c1ccccc1)c1ccccc1

The activation and Wittig reactions can be written as:

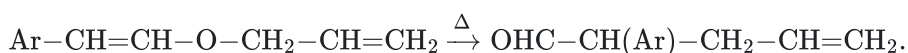


The aldehyde carbon becomes the aryl-bearing carbon of the new double bond. The ylide carbon becomes the oxygen-bearing carbon. Thus **A** has the connectivity



Each alkene carbon bears two different substituents, so *E* and *Z* forms are possible, explaining the stated inseparable *cis/trans* mixture.

At 139 °C, **A** undergoes a concerted Claisen rearrangement:



The six-membered transition-state arrangement produces three simultaneous changes:

1. The oxygen–allyl carbon bond breaks.
2. A new carbon–carbon bond forms between the terminal allyl carbon and the aryl-bearing vinyl carbon.
3. The vinyl ether becomes a carbonyl group, while the allyl double bond shifts.

The oxygen-bearing vinyl carbon originally carries hydrogen, so the carbonyl product is the **aldehyde B**, rather than a ketone. Its aldehyde carbonyl is consistent with the absorption at 1726 cm^{−1}.

Both **A** and **B** have formula C₁₁H₁₁NO₃, as required for an isomerization.

3.2 — Identification of C, D, E, and F

Formation of C. Jones oxidation converts the aldehyde of **B** into **2-(2-nitrophenyl)pent-4-enoic acid**:

O=C(O)C(CC=C)c1ccccc1[N+](=O)[O-]

A balanced oxidation equation is



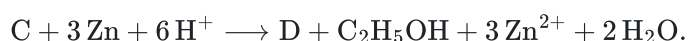
Acid-catalysed esterification with ethanol then gives **C**:



The ethyl ester has formula C₁₃H₁₅NO₄, matching the scheme.

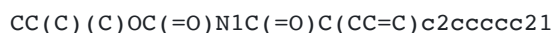
Formation of D. Zinc/ammonium chloride reduces the ortho nitro group to an amino group. The resulting amino group attacks the ester carbonyl intramolecularly. Loss of ethanol closes the five-membered lactam ring, giving **3-allylindolin-2-one, D**.

The balanced net ionic equation, combining reduction and cyclization, is

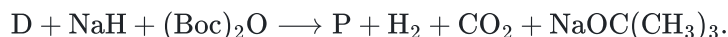


The benzene ring and newly formed lactam ring constitute the required bicyclic structure. The product formula is $C_{11}H_{11}NO$.

Formation of E. First, the oxindole nitrogen is Boc-protected. Call the explicitly drawn protected intermediate **P**, **tert-butyl 3-allyl-2-oxindoline-1-carboxylate**:



A balanced net equation for protection under the stated sodium hydride conditions is

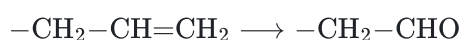


A second treatment with sodium hydride removes the remaining hydrogen at oxindole C3. The resulting enolate attacks **ethyl chloroformate**, CCOC(=O)Cl, installing an ethoxycarbonyl group at C3:



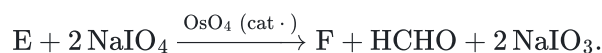
Thus **E** has both an allyl group and an ethoxycarbonyl group attached to C3, while its nitrogen carries Boc. Its formula is $C_{19}H_{23}NO_5$.

Formation of F. Catalytic osmium tetroxide and sodium periodate cleave the terminal alkene:



on the retained molecular fragment. The terminal alkene carbon becomes **methanal (formaldehyde)**, $C=O$.

The balanced net oxidation is



Consequently, the allyl substituent of **E** becomes a **2-oxoethyl substituent** in **F**. The formula changes from $C_{19}H_{23}NO_5$ to $C_{18}H_{21}NO_6$, exactly as printed.

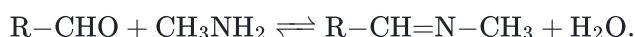
3.3 — Order of the steps from F to G

The correct sequence is **imine formation** → **reduction** → **amidation**.

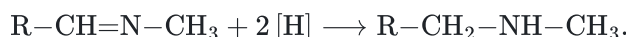
- Imine formation.** Methylamine reacts with the aldehyde group of **F**, eliminating water. The **N-methyl imine of F** is:



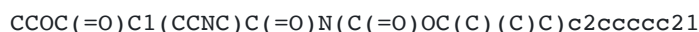
For the aldehyde-containing fragment, the balanced condensation is



- Reduction.** Sodium cyanoborohydride reduces the imine/iminium functionality to a secondary amine:

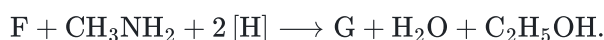


The resulting **2-(methylamino)ethyl derivative of F** is:



- Amidation.** The secondary amine attacks the ethyl ester carbonyl intramolecularly. Ethanol is eliminated, and a five-membered *N*-methyl lactam forms.

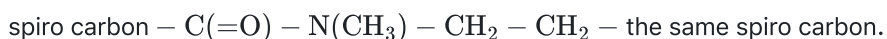
The complete atom-balanced net transformation is



The aldehyde readily undergoes condensation with methylamine. Amidation first would instead produce a much less nucleophilic amide nitrogen, making the proposed subsequent imine formation unfavourable.

3.4 — Structures of G and H

The ring formed during amidation follows this sequence:

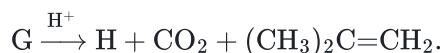


It shares only the original oxindole C3 atom with the oxindole ring, so **G** is a spiro compound. It contains:

- the original oxindole carbonyl;
- the newly formed *N*-methyl lactam carbonyl;
- a Boc group on the oxindole nitrogen.

Its formula is C₁₇H₂₀N₂O₄.

Treatment with 2.5 M hydrochloric acid removes Boc and gives the oxindole N–H compound **H**. Net Boc fragmentation can be written as



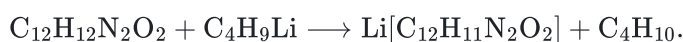
Here the hydrocarbon coproduct is **2-methylpropene**, C=C(C)C. The molecular formula changes by loss of C₅H₈O₂:



Both lactam carbonyls are present in **H**.

3.5 — Intermediate formed with *n*-BuLi

The oxindole nitrogen of **H** bears an acidic hydrogen. *n*-Butyllithium removes this hydrogen, producing the **lithium amidate of H** and butane:



To draw the intermediate, replace the oxindole **N–H** in **H** with N[−] and an associated Li⁺. Both carbonyl groups remain present.

The ionic SMILES in the Answers section records this formal N-deprotonated structure. The amidate charge is delocalized over the nitrogen–carbonyl unit; that SMILES does not specify lithium coordination or aggregation.

Deprotonation makes the oxindole carbonyl less electrophilic. Lithium aluminium hydride then reduces the other, *N*-methyl lactam carbonyl to a methylene group. Work-up restores the oxindole N–H, giving **coerulescine, 1'-methylspiro[indoline-3,3'-pyrrolidin]-2-one**:

CN1CCC2(C1)c1cccc1NC2=O

The overall reduction, including work-up, has the formal balance



3.6 — Identification of horsfiline

The answer is the **second structure from the left**, with methoxy at **oxindole C5**.

Its three aromatic protons are H4, H6, and H7:

Proton	Given signal	Coupling assignment
H4	δ7.05, d, <i>J</i> = 1.4 Hz	Meta coupling to H6
H7	δ6.78, d, <i>J</i> = 8.0 Hz	Ortho coupling to H6
H6	δ6.72, dd, <i>J</i> = 8.0, 1.4 Hz	Ortho coupling to H7 and meta coupling to H4

The large coupling identifies one adjacent proton pair, H6–H7. The small coupling identifies the meta pair H4–H6.

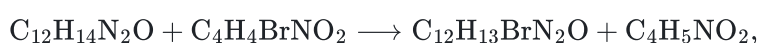
The 4- and 7-methoxy alternatives each leave three consecutive aromatic protons and therefore require two substantial ortho couplings. They do not fit the observed pattern.

The coupling topology alone also permits a 6-methoxy arrangement. The **chemical-shift assignments and reaction regiochemistry** select C5: the lactam nitrogen directs aromatic bromination preferentially to the para position, C5. Copper-assisted methoxylation then replaces bromine at that same carbon.

The intermediate is **5-bromocoerulescine**:

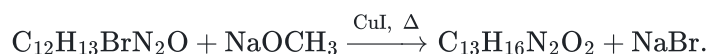
CN1CCC2(C1)c1cc(Br)ccc1NC2=O

The balanced bromination is



where the brominating reagent is **N-bromosuccinimide**, $\text{O}=\text{C1CCC}(=\text{O})\text{N1Br}$, and its coproduct is **succinimide**, $\text{O}=\text{C1CCC}(=\text{O})\text{N1}$.

Methoxylation gives horsfiline:



The stated 60% yield is the isolated yield; it does not change the structural assignment.

3.7 — Claisen rearrangement of the allyl ether of 2-naphthol

The starting material is **2-(allyloxy)naphthalene**:

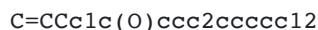


Its preferred aromatic Claisen rearrangement forms the new carbon–carbon bond at **naphthalene C1**, adjacent to the oxygen-bearing C2. This pathway preserves a benzenoid ring during rearrangement.

The immediate keto intermediate is **1-allylnaphthalen-2(1H)-one**:

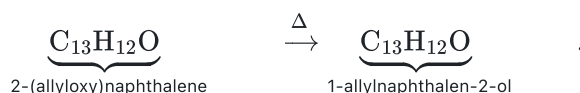


Proton transfer and keto–enol tautomerization restore aromaticity, furnishing **1-allylnaphthalen-2-ol**:



Thus the product to draw is a naphthalene ring with **OH at C2** and **–CH₂–CH=CH₂ at C1**. The double bond remains terminal.

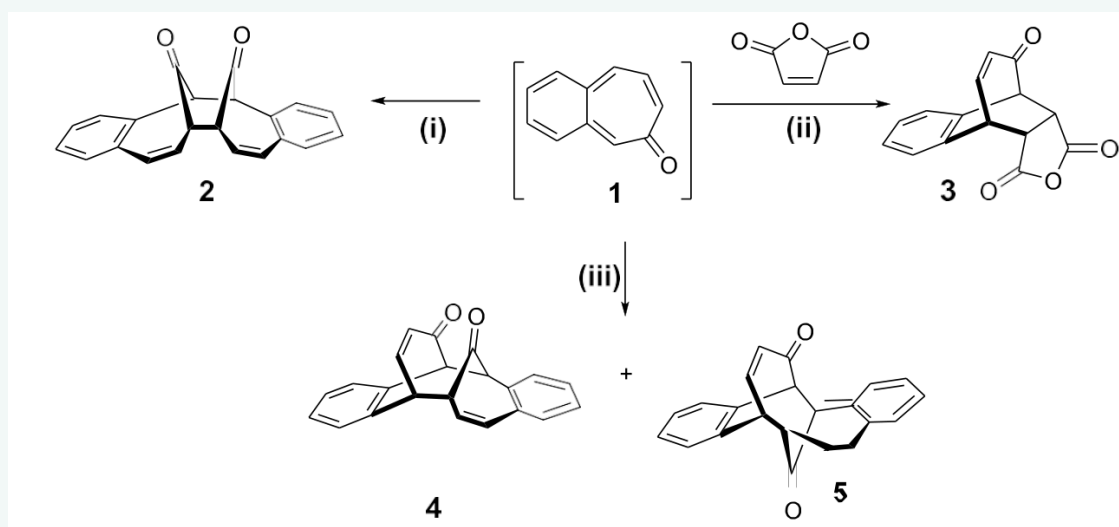
The overall reaction is an atom-conserving isomerization:



The answers were checked against the official answers published by the organisers.

Problem 4: Symmetry Does Matter!

There are numerous reactions in organic chemistry that proceed through cyclic transition states and these are classified as pericyclic reactions. Woodward–Hoffmann rules, developed by Robert B. Woodward and Roald Hoffmann, are used to rationalize stereochemical aspects and the activation energy of pericyclic reactions.



Woodward–Hoffmann rules

Number of electrons	Electrocyclic reactions: Thermal (Δ)	Electrocyclic reactions: Photochemical ($h\nu$)	Cycloadditions: Thermal (Δ)	Cycloadditions: Photochemical ($h\nu$)
$4n$, ($n = 1, 2, \dots$)	Conrotatory (con)	Disrotatory	Disfavored	Favored
$4n + 2$, ($n = 1, 2, \dots$)	Disrotatory (dis)	Conrotatory	Favored	Disfavored

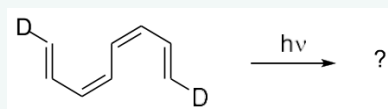
4.1 Fill in the table for reactions (i)–(iii) or products **2–5**:

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

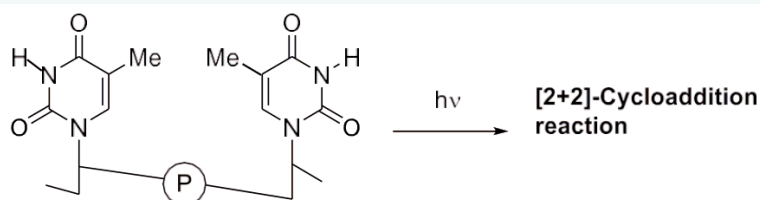
There are three possible benzotropone isomers. Although two of the benzotropone isomers were isolated, 3,4-benzotropone (**1**) has not been isolated. Its instability is attributed to the *o*-quinoidal structure of **1** because it has no sextet electron system in the benzene ring.

4.2 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).

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.



☐		☐	
☐		☐	
☐		☐	

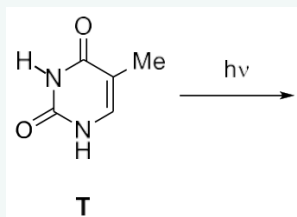


Prof. Dr. Aziz Sancar

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

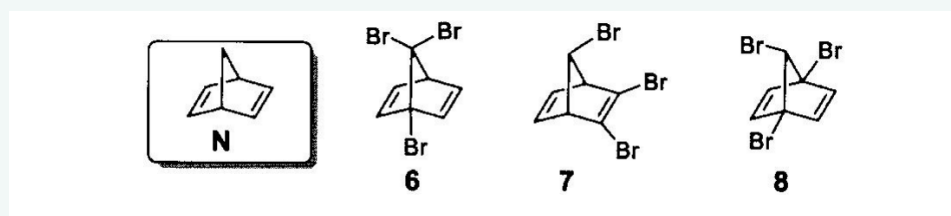
that reaches a person's skin, causing damage to DNA, which may ultimately lead to skin cancer. The research by Professor Aziz Sancar focused on the DNA repair mechanism for this type of damage.

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.

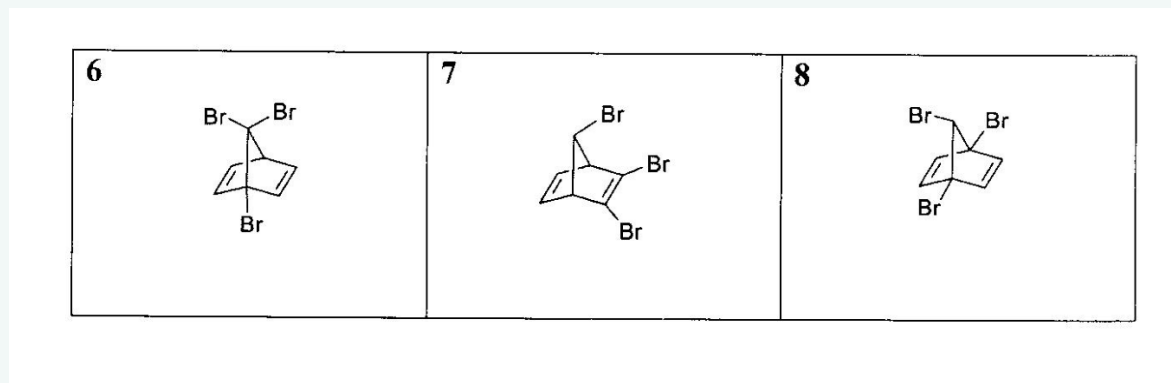


4.4 Considering stereochemistry, draw the structures of all possible products of this reaction between two free thymine (**T**) molecules. Circle the compound(s) which is/are chiral. A drawing only one enantiomer of an enantiomeric pair is sufficient. Please note that only C=C bonds participate in this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

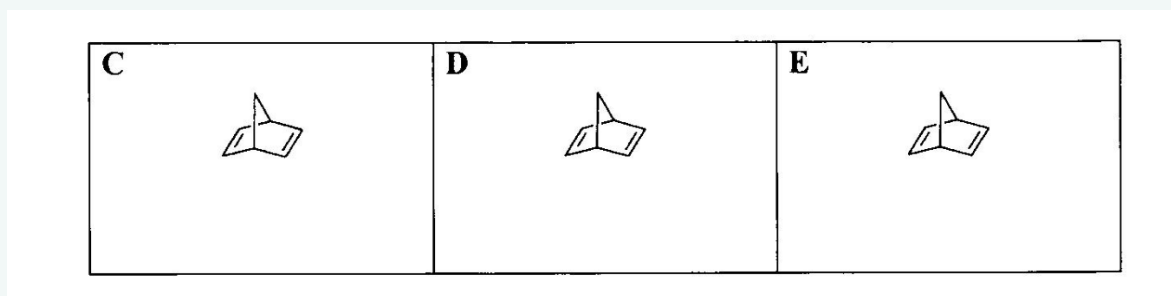
A broad range of halogenated derivatives of norbornadiene (**N**) are known in the literature. Tribromo-norbornadiene ($C_7H_5Br_3$) has six achiral (meso) isomers. Three of these isomers (**6**, **7** and **8**) are given below.



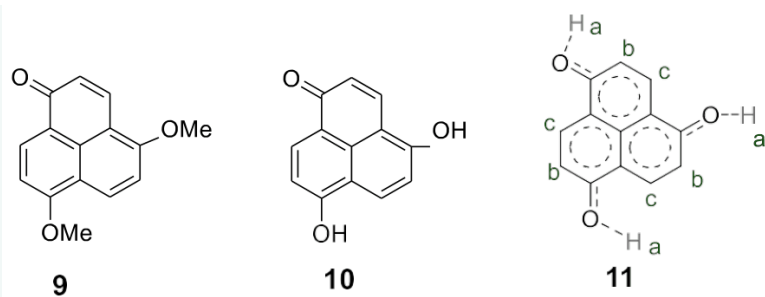
4.5 How many signals do you expect from the ^{13}C -NMR spectra of **6**, **7**, and **8**? Fill in the following boxes.



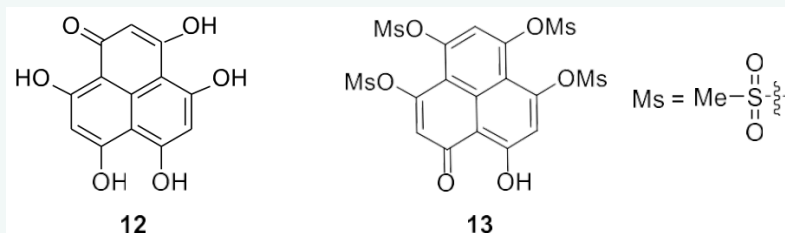
4.6 Draw structures of the remaining achiral (meso) tribromo-norbornadiene ($C_7H_5Br_3$) isomers (**C**, **D**, and **E**) in addition to **6** – **8** over the given figures in the boxes.



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**?



Official English text of the problem.

Answers

• 4.1

Reaction	Product	Cycloaddition	Condition
i	2	[6 + 6]	$h\nu$
ii	3	[4 + 2]	Δ
iii	4	[6 + 4]	Δ
iii	5	[6 + 4]	Δ

• 4.2

A: 4,5-benzotropone — O=C1C=Cc2ccccc2C=C1

B: 2,3-benzotropone — O=C1c2ccccc2C=CC=C1

- **4.3** Tick **right**, **left**, **left**, from top to bottom. The indicated substituents are **cis** in all three selected structures. Their stereochemical SMILES are given below.

- **4.4** Four drawings are required: **cis-syn**, **trans-syn**, **cis-anti**, and **trans-anti** thymine dimers. **Circle trans-syn and cis-anti**. Including both members of each enantiomeric pair, there are six stereoisomers.

- **4.5** **6: 5 signals; 7: 4 signals; 8: 4 signals.**

- **4.6** One valid assignment is **C = 1,2,6-tribromonorbornadiene**, **D = 1,3,5-tribromonorbornadiene**, and **E = the other 7-configuration of 2,3,7-tribromonorbornadiene**. Precise structures and stereochemical SMILES appear below.

• 4.7

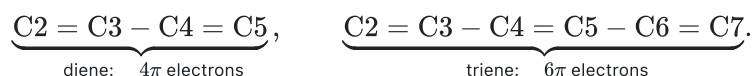
Compound	^{13}C -NMR signals	^1H -NMR signals
12	4	2
13	10	5

Solution

4.1

Number the tropone ring with its carbonyl carbon as C1. The starting material, **3,4-benzotropone (1)**, is $\text{O}=\text{C1C}=\text{C2C}(\text{=CC}=\text{C1})\text{C}=\text{CC}=\text{C2}$.

Its relevant conjugated segments are:

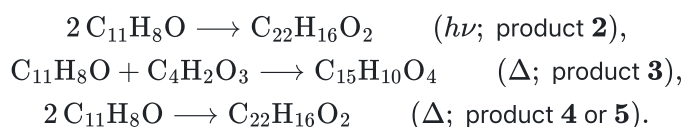


The carbonyl group remains intact in these cycloadditions.

- **Product 2:** Both molecules react through their six-electron triene segments. Consequently, this is a $[6 + 6]$ cycloaddition involving $12 = 4(3)$ electrons, favored photochemically.
- **Product 3:** The four-electron diene segment reacts with the two-electron alkene of **maleic anhydride**, $\text{O}=\text{C1OC}(=\text{O})\text{C}=\text{C1}$. This is a thermal $[4 + 2]$ cycloaddition because $6 = 4(1) + 2$.
- **Products 4 and 5:** Each combines the four-electron diene segment of one molecule with the six-electron triene segment of another. Both are therefore thermal $[6 + 4]$ cycloadducts, involving $10 = 4(2) + 2$ electrons.

The bridging ketone is particularly diagnostic for the six-electron component: closure at C2 and C7 leaves C1, the carbonyl carbon, as a one-carbon bridge between these termini. Products **4** and **5** have different stereochemical arrangements but the same cycloaddition electron count.

The balanced molecular equations for the individual channels are:



Each dimerization equation describes one product channel; forming a mixture does not change the stoichiometry.

4.2

The three possible fusion positions, after accounting for equivalent numbering directions, are 2,3-, 3,4-, and 4,5-. The question identifies 3,4-benzotropone as the unstable isomer, leaving the other two.

For **A, 4,5-benzotropone**, draw the benzene ring fused to the tropone bond opposite the carbonyl group. A symmetry operation exchanges the two sides of the molecule:

- The carbonyl carbon is unique.
- The remaining ten carbons form five equivalent pairs.

Thus,

$$N_{13\text{C}}(\mathbf{A}) = 1 + 5 = \boxed{6}.$$

For **B, 2,3-benzotropone**, draw the benzene ring fused to the bond adjacent to the carbonyl carbon. No symmetry operation exchanges distinct carbon positions while preserving the complete structure, so

$$N_{13\text{C}}(\mathbf{B}) = \boxed{11}.$$

Their names and SMILES are given in the Answers section. Both structures retain a benzenoid aromatic sextet.

4.3

The starting material is **(1E,3Z,5Z,7E)-1,8-dideuterioocta-1,3,5,7-tetraene**, $[\text{2H}]/\text{C}=\text{C}/\text{C}=\text{C}\backslash\text{C}=\text{C}/\text{C}=\text{C}/[\text{2H}]$.

Number its conjugated carbons C1–C8 from left to right. For the pathways depicted in the answer choices:

Row	Reacting segment	Electrons	Required photochemical motion	Selected stereochemistry
Eight-membered ring	C1–C8	8	Disrotatory	The two D atoms are cis: right

Row	Reacting segment	Electrons	Required photochemical motion	Selected stereochemistry
Four-membered ring	C3–C6	4	Disrotatory	The two vinyl substituents are cis: left
Six-membered ring	C1–C6, or the equivalent opposite end	6	Conrotatory	D and the vinyl substituent are cis: left

The terminal double-bond configurations explain these outcomes:

- The full eight-electron segment has **E/E** terminal configurations; disrotation gives **cis** D atoms.
- The middle four-electron segment has **Z/Z** terminal configurations; disrotation gives **cis** vinyl substituents.
- The six-electron segment has **E/Z** terminal configurations; conrotation gives **cis** D and vinyl substituents.

The selected structures are:

Product	Name	Stereochemical SMILES
Eight-membered ring	cis-7,8-Dideuteriocycloocta-1,3,5-triene	[2H] [C@H] 1 / C = C \ C = C / C = C \ [C@H] 1 [2H]
Four-membered ring	cis-3,4-Bis[(E)-2-deuteriovinyl]cyclobut-1-ene	[2H] / C = C / [C@H] 1 C = C [C@H] 1 / C = C / [2H]
Six-membered ring	cis-6-Deuterio-5-[(E)-2-deuteriovinyl]cyclohexa-1,3-diene	[2H] [C@H] 1 C = C C = C [C@H] 1 / C = C / [2H]

Where a product is chiral, the SMILES specifies one member of the enantiomeric pair. Simultaneously reversing all wedges and dashes gives the equally allowed mirror image.

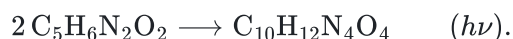
Each electrocyclization forms a terminal σ bond while shifting the remaining π bonds. No atoms are gained or lost:



4.4

Thymine, or **5-methylpyrimidine-2,4(1H,3H)-dione**, has SMILES CC1=CNC(=O)NC1=O.

Only its C5=C6 bond reacts. Two such bonds undergo photochemical $[2 + 2]$ cycloaddition, producing a cyclobutane ring:



There are two ways to connect the two molecules:

- **Syn**: Form C5–C5' and C6–C6' bonds. The methyl-bearing carbons are adjacent in the cyclobutane.
- **Anti**: Form C5–C6' and C6–C5' bonds. The methyl-bearing carbons are opposite in the cyclobutane.

For either connectivity, the two methyl groups can be **cis**, on the same face of the cyclobutane framework, or **trans**, on opposite faces. The original pyrimidine-ring connections are retained.

Dimer name	Stereochemical SMILES	Chirality
cis-syn Thymine cyclobutane dimer	C [C@] 1 2 [C@H] (NC (=O) NC1=O) [C@H] 1 [C@] 2 (C) C (=O) NC (=O) N1	Achiral
trans-syn Thymine cyclobutane dimer	C [C@] 1 2 [C@H] (NC (=O) NC1=O) [C@H] 1 [C@@] 2 (C) C (=O) NC (=O) N1	Chiral—circle
cis-anti Thymine cyclobutane dimer	C [C@] 1 2 [C@H] (NC (=O) NC1=O) [C@@] 1 (C) [C@H] 2 NC (=O) NC1=O	Chiral—circle
trans-anti Thymine cyclobutane dimer	C [C@] 1 2 [C@H] (NC (=O) NC1=O) [C@] 1 (C) [C@H] 2 NC (=O) NC1=O	Achiral

The **cis-syn** arrangement has an internal reflection symmetry exchanging the two thymine units. The **trans-anti** arrangement has an inversion symmetry in an idealized symmetric conformation. Both are achiral.

The **trans-syn** and **cis-anti** arrangements have no improper symmetry operation that superposes them on their mirror images. Each therefore occurs as an enantiomeric pair.

Consequently, the four required drawings represent

$$1 + 2 + 2 + 1 = \boxed{6}$$

individual stereoisomers.

4.5

Use the standard numbering of **norbornadiene, bicyclo[2.2.1]hepta-2,5-diene**, C1=CC2C=CC1C2:

- C1 and C4 are the bridgeheads.
- The double bonds are C2=C3 and C5=C6.
- C7 is the one-carbon bridge.

The given structures can be specified as follows. For **7**, "syn" means that the C7–Br bond points toward the dibrominated alkene bridge.

Compound	Name	Stereochemical SMILES
6	1,7,7-Tribromobicyclo[2.2.1]hepta-2,5-diene	<chem>[C@]12(Br)C=C[C@H](C=C1)C2(Br)Br</chem>
7	7-syn-2,3,7-Tribromobicyclo[2.2.1]hepta-2,5-diene	<chem>[C@H]12C(Br)=C(Br)[C@H](C=C1)[C@H]2Br</chem>
8	1,4,7-Tribromobicyclo[2.2.1]hepta-2,5-diene	<chem>[C@]12(Br)C=C[C@](Br)(C=C1)[C@H]2Br</chem>

Their carbon equivalence classes are:

Compound	Equivalent carbon sets	Number of signals
6	{1}, {4}, {7}, {2, 6}, {3, 5}	5
7	{1, 4}, {2, 3}, {5, 6}, {7}	4
8	{1, 4}, {2, 3}, {5, 6}, {7}	4

In **6**, the mirror plane through C1, C4, and C7 exchanges the two alkene bridges, but the two bridgeheads remain different.

In **7** and **8**, a different mirror plane exchanges the bridgeheads and the two ends of each alkene. C7 remains unique.

4.6

The following assignment of **C**, **D**, and **E** is valid; the letters may be permuted.

Label	Name	Stereochemical SMILES
C	1,2,6-Tribromobicyclo[2.2.1]hepta-2,5-diene	<chem>[C@]12(Br)C(Br)=C[C@H](C=C1Br)C2</chem>
D	1,3,5-Tribromobicyclo[2.2.1]hepta-2,5-diene	<chem>[C@]12(Br)C=C(Br)[C@H](C(Br)=C1)C2</chem>
E	7-anti-2,3,7-Tribromobicyclo[2.2.1]hepta-2,5-diene	<chem>[C@H]12C(Br)=C(Br)[C@H](C=C1)[C@@H]2Br</chem>

To draw these on the supplied frameworks:

- **C**: Put Br on one bridgehead and on both alkene carbons directly bonded to that bridgehead.
- **D**: Put Br on one bridgehead and on both alkene carbons directly bonded to the other bridgehead.
- **E**: Retain the two Br atoms on the same double bond as in **7**, but reverse the C7 substituent orientation. Its C7–Br bond points away from the dibrominated alkene bridge.

Both **C** and **D** retain the mirror plane through C1, C4, and C7, which exchanges the two alkene bridges. **E** retains the plane that exchanges C1 with C4, C2 with C3, and C5 with C6.

These patterns complete the six achiral isomers:

- One with two Br atoms at C7: **6**.
- Two with no Br at C7: **C** and **D**.
- Three with one Br at C7: **7**, **8**, and **E**.

4.7

The averaging illustrated by **10/11** must be included. Movement of a hydrogen nucleus between oxygens is **prototropic tautomerism**, rather than resonance alone; rapid exchange makes symmetry-related positions equivalent on the NMR timescale.

The reference compound **10** is **4,7-dihydroxyphenalen-1-one**, O=C1C=CC2=C(O)C=CC3=C(O)C=CC1=C23.

The following SMILES represent individual keto–enol tautomers of **12** and **13**. Ordinary SMILES cannot encode their time-averaged fractional bond orders or hydrogen occupancies.

Compound	Name of the represented tautomer	SMILES
12	3,4,6,7,9-Pentahydroxyphenalen-1-one	<chem>O=C1C=C(O)C2=C(O)C=C(O)C3=C(O)C=C(O)C1=C23</chem>
13	9-Hydroxy-3,4,6,7-tetrakis(methanesulfonyloxy)phenalen-1-one	<chem>O=C1C=C(OS(=O)(=O)C)C2=C(OS(=O)(=O)C)C=C(OS(=O)(=O)C)C3=C(OS(=O)(=O)C)C=C(O)C1=C23</chem>

For **12**, tautomeric averaging makes all six oxygen-bearing peripheral carbons equivalent. Threefold rotation and reflection give four carbon classes:

Carbon class	Number of carbons in the class
Central carbon shared by the three rings	1
Other ring-junction carbons	3
Oxygen-bearing peripheral carbons	6
Peripheral CH carbons	3

Therefore,

$$N_{13C}(\mathbf{12}) = \boxed{4}.$$

Its protons form two classes:

- Three equivalent ring CH protons.
- Five equivalent, exchanging OH protons.

The five OH protons are distributed over six oxygen positions in the averaged description; the average drawing does not imply six OH protons. Thus,

$$N_{1H}(\mathbf{12}) = \boxed{2}.$$

For **13**, the mesylated oxygens prevent the full threefold equivalence. Exchange between the remaining carbonyl and hydroxyl positions restores a left–right reflection symmetry.

The 13-carbon ring framework contains three individually fixed carbons and five equivalent pairs:

$$N_{\text{ring carbon environments}} = 3 + \frac{13 - 3}{2} = 8.$$

The four mesyl methyl carbons form two equivalent pairs, adding two signals:

$$N_{13C}(\mathbf{13}) = 8 + 2 = \boxed{10}.$$

Its proton classes are:

Proton class	Total integration
Ring CH on the reflection axis	1 H
Other two ring CH positions	2 H
Exchanging OH proton	1 H
First equivalent pair of mesyl methyl groups	6 H
Second equivalent pair of mesyl methyl groups	6 H

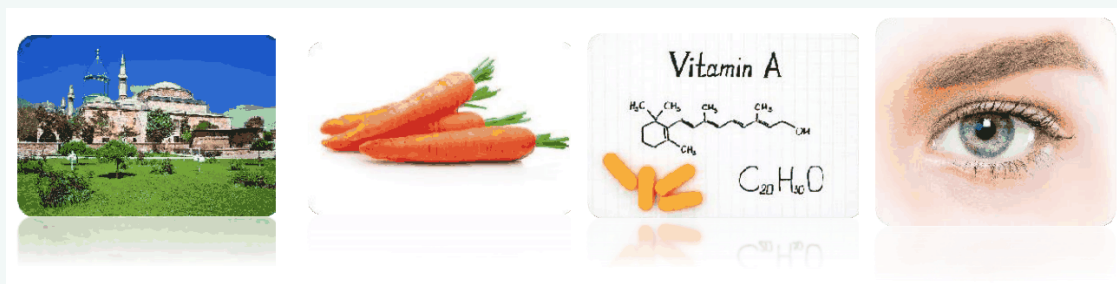
Hence,

$$N_{1H}(\mathbf{13}) = \boxed{5}.$$

These counts include OH resonances and count distinct chemical shifts, rather than individual multiplet lines.

The answers were checked against the official answers published by the organisers.

Problem 5: Konya, Carrot, Beta-Carotene, Vitamin-A, Immune System, Vision



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

Carrot is an important source of β -carotene, which gives the vegetable its orange color. This molecule is a red-orange pigment naturally found in plants and fruits and is a provitamin A carotenoid. It is converted to vitamin A, which is essential for normal growth and development, the immune system, and vision function.

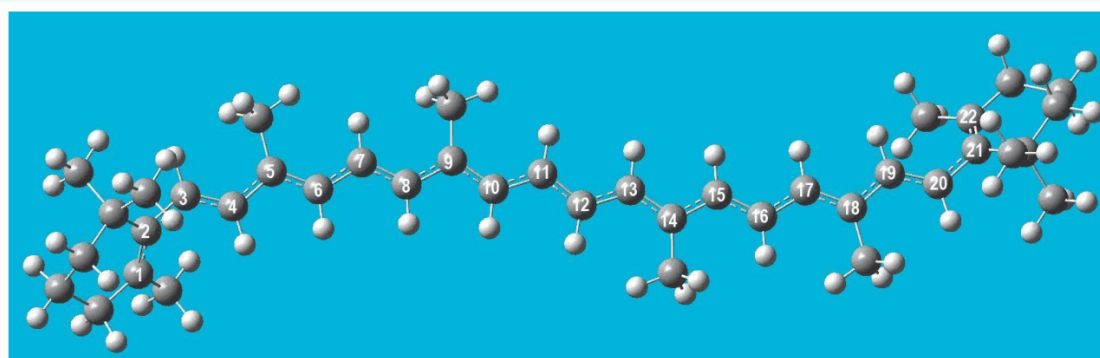


Figure 1. Ball and stick representation of the structure of β -carotene. The gray and white spheres represent the carbon and hydrogen atoms, respectively. The numbered carbon atoms belong to the linear conjugated π -segment of the molecule.

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

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

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

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

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

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

In two dimension system, 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:

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

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 The β -carotene molecule is orange in color because:

- i) It absorbs in the visible region of the electromagnetic spectrum.
- ii) HOMO $\rightarrow$ LUMO transition occurs by absorption of IR photon.
- iii) The spacing between the 22nd and the 23rd energy levels is equal to the energy of the IR photon at the orange wavelength.
- iv) It absorbs green/blue light and it transmits red/yellow color.
- v) It absorbs in the UV-VIS region since the molecule has no net dipole moment.

Choose which pair of the above sentences is correct?

The pairs of sentences are as follows:

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

Although it is highly unrealistic, let us assume that the conjugated segment of the molecule is linear and treated with the particle in a one-dimensional box model as shown in figure 2. In this case, the length of the box can be approximated as $L = 1.40 \times n_C$ (in Å), where n_C is the number of carbon atoms in the conjugated segment.

Use this information to answer the questions 5.2–5.6.

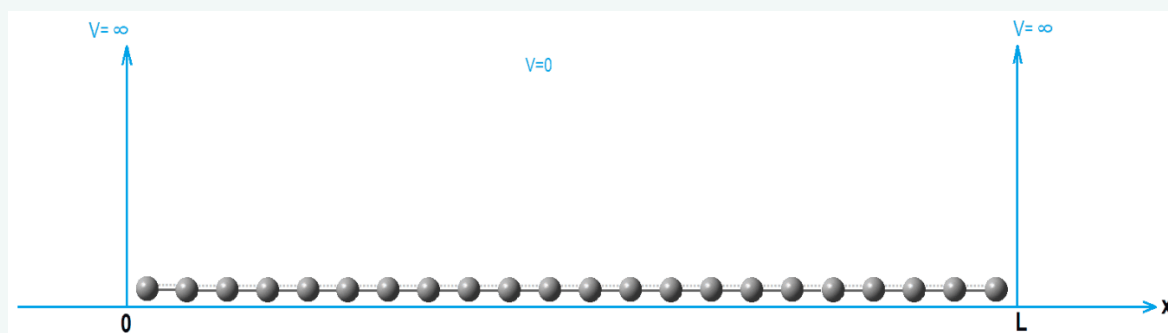


Figure 2. Schematic representation of the conjugated line segment made up of carbon atoms of β -carotene in a one-dimensional box of length L .

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

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

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

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

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

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

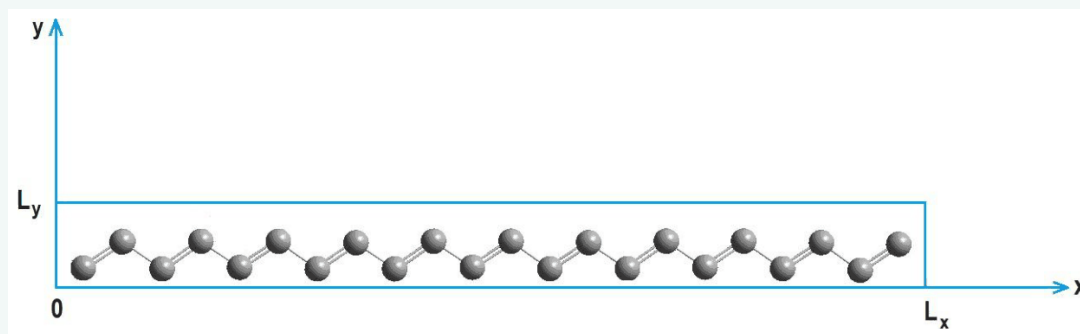


Figure 3. Schematic representation of the conjugated carbon atoms of β -carotene in a two-dimensional box.

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

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

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

Official English text of the problem.

Answers

• **5.1: c) i and iv.**

• **5.2:** $E_1 = 6.35 \times 10^{-21} \text{ J}$; $E_2 = 2.54 \times 10^{-20} \text{ J}$.

• **5.3:** For $0 \leq x \leq L$, with $L = 30.8 \text{ \AA}$,

$$\Psi_1(x) = \sqrt{\frac{2}{L}} \sin \frac{\pi x}{L}, \quad \Psi_2(x) = \sqrt{\frac{2}{L}} \sin \frac{2\pi x}{L}.$$

The first is one positive half-wave; the second has a positive lobe followed by a negative lobe, with an internal node at $x = L/2 = 15.4 \text{ \AA}$.

• **5.4:** Draw horizontal levels at $E/E_1 = 1, 4, 9, 16$, labelled $n = 1, 2, 3, 4$. Successive gaps are in the ratio $3 : 5 : 7$.

• **5.5:** $E_{\pi, \text{total}} = 6.43 \times 10^{-18} \text{ J}$ per molecule.

• **5.6:** HOMO $n = 11$, LUMO $n = 12$; $\lambda = 1.36 \times 10^3 \text{ nm}$.

• **5.7:** HOMO (n_x, n_y) = (11, 1), with $E_H = 1.75 \times 10^{-18} \text{ J}$; LUMO (12, 1), with $E_L = 1.95 \times 10^{-18} \text{ J}$; $\lambda = 969 \text{ nm}$.

• **5.8:** Under the stipulated unchanged quantum numbers, $L_x = 17.8 \text{ \AA}$.

Solution

The molecule is **all-trans- β -carotene**, $\text{C}_{40}\text{H}_{56}$, with SMILES

CC1=C(/C=C/C(C)=C/C=C/C(C)=C/C=C/C(C)=C(C)/C=C/C=C(C)/C=C/C2=C(C)CCCC2(C)C(C)(C)CCC1. This specifies the acyclic double-bond stereochemistry; it does not specify the three-dimensional conformation or the imposed box geometry.

The problem does not print the physical constants. We use

$$h = 6.62607015 \times 10^{-34} \text{ J s}, \quad m_e = 9.1093837 \times 10^{-31} \text{ kg}, \quad c = 2.99792458 \times 10^8 \text{ m s}^{-1}.$$

Each spatial orbital accommodates two electrons with opposite spins. Consequently, the 22 π -electrons occupy the eleven lowest spatial orbitals in the ground state.

5.1 — Origin of the orange color

The measured absorption maximum, 455 nm, lies in the blue part of the visible spectrum. Absorption of blue/green light leaves the transmitted or reflected light enriched in red/yellow wavelengths, giving the orange appearance. Therefore **i** and **iv** are correct, corresponding to **c**.

The other statements are incorrect:

- **ii:** The observed transition involves a visible photon, rather than an infrared photon.
- **iii:** With two electrons per level, the one-dimensional HOMO and LUMO are levels 11 and 12. Moreover, orange light belongs to the visible spectrum, not the infrared.
- **v:** Having no permanent dipole moment does not establish that a molecule absorbs in the UV-visible region. Electronic absorption depends on the transition energy and transition dipole moment.

5.2 — Lowest two one-dimensional energy levels

The prescribed box length is

$$L = (1.40 \text{ Å})(22) = 30.8 \text{ Å} = 3.08 \times 10^{-9} \text{ m}.$$

Thus,

$$E_1 = \frac{h^2}{8m_e L^2} = \frac{(6.62607015 \times 10^{-34} \text{ J s})^2}{8(9.1093837 \times 10^{-31} \text{ kg})(3.08 \times 10^{-9} \text{ m})^2} = \boxed{6.35 \times 10^{-21} \text{ J}}.$$

Since $E_n = n^2 E_1$,

$$E_2 = 4E_1 = \boxed{2.54 \times 10^{-20} \text{ J}}.$$

5.3 — Wavefunction sketches

Let $A = \sqrt{2/L}$. Inside the box,

$$\Psi_1(x) = A \sin \frac{\pi x}{L}, \quad \Psi_2(x) = A \sin \frac{2\pi x}{L}.$$

Both wavefunctions vanish at the walls and outside the box. Label the horizontal axis x , using these positions:

x	0	$L/4$	$L/2$	$3L/4$	L
x , in Å	0	7.70	15.4	23.1	30.8
Ψ_1/A	0	$1/\sqrt{2}$	1	$1/\sqrt{2}$	0
Ψ_2/A	0	1	0	-1	0

For $n = 1$, draw a smooth positive half-sine wave from $x = 0$ to $x = L$, with its maximum $+A$ at $L/2$. It has no internal node.

For $n = 2$, draw one full sine wave: a positive maximum $+A$ at $L/4$, a node at $L/2$, and a negative minimum $-A$ at $3L/4$.

The overall sign of either wavefunction may be reversed without changing its physical meaning.

5.4 — Energy-level diagram

The levels obey $E_n = n^2 E_1$:

n	E_n/E_1	E_n , in J
1	1	6.35×10^{-21}
2	4	2.54×10^{-20}
3	9	5.72×10^{-20}

n	E_n/E_1	E_n , in J
4	16	1.02×10^{-19}

Draw an upward-pointing energy axis with horizontal lines at these heights. The separations increase upwards:

$$E_2 - E_1 = 3E_1, \quad E_3 - E_2 = 5E_1, \quad E_4 - E_3 = 7E_1.$$

Hence the successive gaps have the ratio $\boxed{3 : 5 : 7}$.

5.5 — Total π -electron energy

The 22 electrons fill levels $n = 1, \dots, 11$, two electrons per level. Under the independent-electron approximation,

$$E_{\pi, \text{total}} = 2 \sum_{n=1}^{11} E_n = 2E_1 \sum_{n=1}^{11} n^2.$$

Using

$$\sum_{n=1}^{11} n^2 = \frac{11(12)(23)}{6} = 506,$$

we obtain

$$E_{\pi, \text{total}} = 1012E_1 = 1012(6.3508469 \times 10^{-21} \text{ J}) = \boxed{6.43 \times 10^{-18} \text{ J}}.$$

This is the total energy per molecule relative to the zero potential inside the box.

5.6 — One-dimensional HOMO–LUMO wavelength

The highest occupied level is $n = 11$, and the lowest unoccupied level is $n = 12$. Therefore,

$$\Delta E = E_{12} - E_{11} = (12^2 - 11^2)E_1 = 23E_1 = 1.4606948 \times 10^{-19} \text{ J}.$$

Equating this gap to the photon energy gives

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.62607015 \times 10^{-34} \text{ J s})(2.99792458 \times 10^8 \text{ m s}^{-1})}{1.4606948 \times 10^{-19} \text{ J}}.$$

Thus,

$$\lambda = 1.35993 \times 10^{-6} \text{ m} = \boxed{1.36 \times 10^3 \text{ nm}}.$$

This infrared prediction differs substantially from the experimental 455 nm, reflecting the limitations of the prescribed one-dimensional model.

5.7 — Two-dimensional HOMO, LUMO, and wavelength

Write the energy as

$$E_{n_x, n_y} = A_x n_x^2 + A_y n_y^2,$$

where

$$A_x = \frac{h^2}{8m_e L_x^2} = 8.91223 \times 10^{-21} \text{ J}, \quad A_y = \frac{h^2}{8m_e L_y^2} = 6.69407 \times 10^{-19} \text{ J}.$$

Here $L_x = 2.60 \times 10^{-9} \text{ m}$ and $L_y = 3.0 \times 10^{-10} \text{ m}$.

We must check the ordering of the two-dimensional states. The lowest state with $n_y \geq 2$ is $(1, 2)$:

$$E_{1,2} = A_x + 4A_y = 2.68654 \times 10^{-18} \text{ J}.$$

In comparison,

$$E_{12,1} = 144A_x + A_y = 1.95277 \times 10^{-18} \text{ J} < E_{1,2}.$$

Therefore the first twelve spatial orbitals all have $n_y = 1$, with $n_x = 1, \dots, 12$. Filling eleven orbitals gives

$$\boxed{\text{HOMO} = (11, 1)}, \quad \boxed{\text{LUMO} = (12, 1)}.$$

Their energies are

$$E_H = 121A_x + A_y = 1.7477873 \times 10^{-18} \text{ J} \approx \boxed{1.75 \times 10^{-18} \text{ J}},$$

$$E_L = 144A_x + A_y = 1.9527686 \times 10^{-18} \text{ J} \approx \boxed{1.95 \times 10^{-18} \text{ J}}.$$

The identical y -direction contributions cancel in the gap:

$$\Delta E = E_L - E_H = 23A_x = 2.0498129 \times 10^{-19} \text{ J}.$$

Using this unrounded gap,

$$\lambda = \frac{hc}{\Delta E} = 9.69086 \times 10^{-7} \text{ m} = \boxed{969 \text{ nm}}.$$

5.8 — Length required for absorption at 455 nm

As stipulated, keep the HOMO and LUMO quantum numbers equal to (11, 1) and (12, 1). Their common y -direction energy again cancels:

$$\Delta E = \frac{23h^2}{8m_e L_x^2}.$$

For absorption at $\lambda = 455 \times 10^{-9} \text{ m}$,

$$\frac{hc}{\lambda} = \frac{23h^2}{8m_e L_x^2}.$$

Solving for the positive length,

$$L_x = \sqrt{\frac{23h\lambda}{8m_e c}} = \sqrt{\frac{23(6.62607015 \times 10^{-34} \text{ J s})(455 \times 10^{-9} \text{ m})}{8(9.1093837 \times 10^{-31} \text{ kg})(2.99792458 \times 10^8 \text{ m s}^{-1})}}.$$

Hence,

$$L_x = 1.78155 \times 10^{-9} \text{ m} = \boxed{17.8 \text{ Å}}.$$

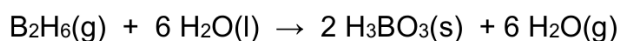
This result uses the question's explicit fixed-quantum-number assumption. If all two-dimensional levels were reordered and refilled at this shorter length, states with $n_y = 2$ would enter the occupied set.

The solution was checked against the official solution.

Problem 6: Thermodynamics through an Interstellar Journey

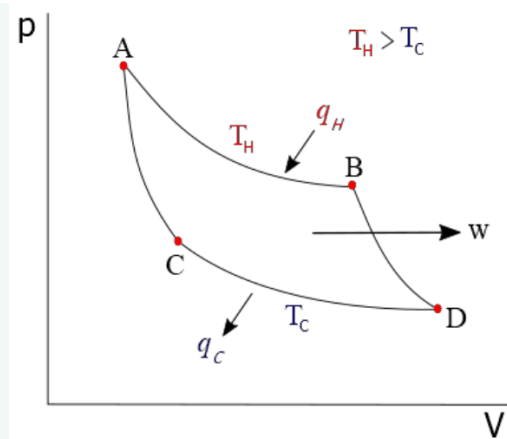
Part 1

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.

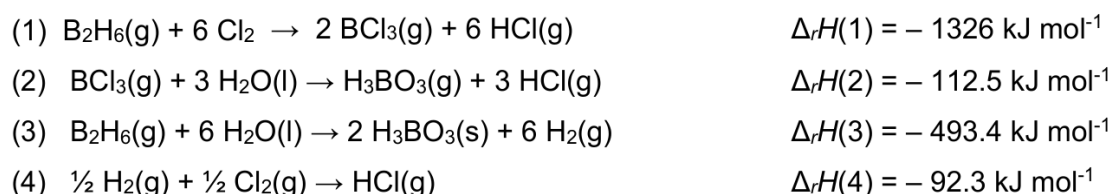


After heat transfers, the remaining energy is released as work (w). Also, q_H and q_C are related to T_C and T_H as follows:

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

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.

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

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

6.4 Calculate the efficiency of the heat engine described above.

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

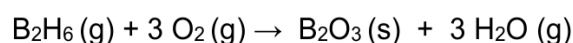
6.6 Calculate the Gibbs energy change (ΔG) in terms of J for $A \rightarrow B$ and $D \rightarrow C$ processes in the heat engine.

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

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

Part 2

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



Combustion of diborane is experimented in a closed container (100 dm^3) at different temperatures and the equilibrium amounts were recorded.

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

Partial pressure of $O_2(g)$ was stabilized to 1 bar and kept constant at all conditions.

Assume that in this hypothetical universe; $\Delta_r S^\circ$ 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 gas species behave as an ideal gas, and all species remain in the same phase, without any further decomposition before or after reaction, at all temperatures then:

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

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

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

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

Temperature	Favored	Unfavored
298 K	☐	☐
8930 K	☐	☐
9005 K	☐	☐
9100 K	☐	☐

6.13 Calculate the $\Delta_f H$ (kJ mol^{-1}) and S° ($\text{kJ mol}^{-1} \text{K}^{-1}$) of $H_2O(g)$ using the values given in the table below. ($\Delta_f H$ = enthalpy of formation, S° = standard entropy)

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

Compound	ΔH_f (298 K)	S° (298 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}	$0.16 \text{ kJ mol}^{-1} \text{K}^{-1}$
$B_2O_3(s)$	$-1273 \text{ kJ mol}^{-1}$	$0.05 \text{ kJ mol}^{-1} \text{K}^{-1}$

Official English text of the problem.

Answers

- 6.1:** Boric acid, H_3BO_3 , SMILES OB(O)O: $\Delta_{\text{sub}} H = +25.0 \text{ kJ mol}^{-1}$.
- 6.2:** $\Delta_r U(2) = -120.0 \text{ kJ mol}^{-1}$; $\Delta_r U(4) = -92.3 \text{ kJ mol}^{-1}$.
- 6.3:** $|w| = 175 \text{ J}$; $|q_C| = 75 \text{ J}$.
- 6.4:** $\eta = 0.700 = 70.0\%$.
- 6.5:** $\Delta S_{A \rightarrow B} = +0.250 \text{ J K}^{-1}$; $\Delta S_{D \rightarrow C} = -0.250 \text{ J K}^{-1}$.
- 6.6:** $\Delta G_{A \rightarrow B} = -250 \text{ J}$; $\Delta G_{D \rightarrow C} = +75 \text{ J}$.
- 6.7:** $p_A/p_B = 1.0305 \approx 1.031$.
- 6.8:** Hydrogen, H_2 , SMILES [H][H]: $n = 2.10 \times 10^{-2} \text{ mol}$.
- 6.9:** $K_p(8930 \text{ K}) = 1.16$; $K_p(9005 \text{ K}) = 0.915$, using dimensionless standard-state-normalized constants.
- 6.10:** $\Delta_r G^\circ(8930 \text{ K}) \approx -11.0 \text{ kJ mol}^{-1}$; $\Delta_r G^\circ(9005 \text{ K}) \approx +6.64 \text{ kJ mol}^{-1}$.
- 6.11:** At 298 K, $\Delta_r G^\circ \approx -2.05 \times 10^3 \text{ kJ mol}^{-1}$, $\Delta_r H^\circ \approx -2.12 \times 10^3 \text{ kJ mol}^{-1}$, and $\Delta_r S^\circ \approx -236 \text{ J mol}^{-1} \text{K}^{-1}$.

- **6.12: Favored:** 298 K and 8930 K. **Unfavored:** 9005 K and 9100 K.

- **6.13:** Water vapor, $\text{H}_2\text{O}(\text{g})$, SMILES o: $\Delta_f H^\circ \approx -269 \text{ kJ mol}^{-1}$, $S^\circ \approx 0.141 \text{ kJ mol}^{-1} \text{ K}^{-1}$.

Solution

Use the gas constant

$$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1} = 0.08314 \text{ bar dm}^3 \text{ mol}^{-1} \text{ K}^{-1}.$$

For the working gas, heat entering is positive, and w denotes work done **on** the gas, so $\Delta U = q + w$. The engine's work output is $|w|$. Extra digits are retained in intermediate calculations.

6.1

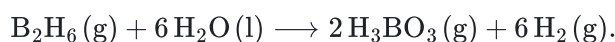
The required sublimation of boric acid is



Combine the supplied reactions as

$$(1) + 2(2) - 12(4).$$

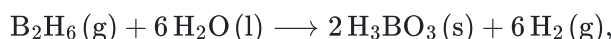
The chlorine, boron trichloride, and hydrogen chloride cancel, giving



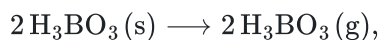
Its reaction enthalpy is

$$\begin{aligned} \Delta_r H_{\text{gas}} &= -1326 + 2(-112.5) - 12(-92.3) \\ &= -443.4 \text{ kJ mol}^{-1}. \end{aligned}$$

Subtract reaction (3),



whose enthalpy is $-493.4 \text{ kJ mol}^{-1}$. The net process is



with enthalpy change

$$-443.4 - (-493.4) = +50.0 \text{ kJ}$$

for subliming two moles. Hence

$$\Delta_{\text{sub}} H(300 \text{ K}) = +25.0 \text{ kJ mol}^{-1}.$$

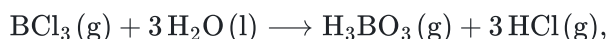
6.2

For ideal gases, neglecting the small pV contributions of condensed phases,

$$\Delta_r H = \Delta_r U + \Delta n_g RT,$$

where Δn_g is gaseous product stoichiometry minus gaseous reactant stoichiometry.

For reaction (2),



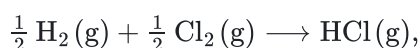
the liquid water does not contribute to Δn_g , so

$$\Delta n_g = (1 + 3) - 1 = 3.$$

Therefore

$$\begin{aligned} \Delta_r U(2) &= -112.5 - \frac{3(8.314)(300)}{1000} \\ &= -119.9826 \text{ kJ mol}^{-1} \\ &\approx -120.0 \text{ kJ mol}^{-1}. \end{aligned}$$

For reaction (4),



$$\Delta n_g = 1 - \frac{1}{2} - \frac{1}{2} = 0.$$

Thus

$$\Delta_r U(4) = \Delta_r H(4) = -92.3 \text{ kJ mol}^{-1}.$$

6.3

The given reversible-engine relation gives

$$|q_C| = |q_H| \frac{T_C}{T_H} = 250 \frac{300}{1000} = \boxed{75 \text{ J}}.$$

The gas returns to its initial state after a cycle, so $\Delta U_{\text{cycle}} = 0$. Its net heat input is

$$q_{\text{net}} = 250 - 75 = 175 \text{ J}.$$

Consequently, $w = -175 \text{ J}$, and the work produced is

$$\boxed{|w| = 175 \text{ J}}.$$

6.4

$$\eta = \frac{|w|}{q_H} = \frac{175}{250} = 1 - \frac{300}{1000} = \boxed{0.700 = 70.0\%}.$$

6.5

For a reversible isothermal process,

$$\Delta S = \frac{q_{\text{rev}}}{T}.$$

During A→B, the gas absorbs heat:

$$\Delta S_{A \rightarrow B} = \frac{250}{1000} = +0.250 \text{ J K}^{-1}.$$

During D→C, it releases heat:

$$\Delta S_{D \rightarrow C} = \frac{-75}{300} = -0.250 \text{ J K}^{-1}.$$

The two reversible adiabatic steps have zero entropy change, so the total entropy change of the working gas over the cycle is zero.

6.6

An ideal gas's enthalpy depends only on temperature. Therefore, for each isothermal step, $\Delta H = 0$, and

$$\Delta G = \Delta H - T\Delta S = -T\Delta S.$$

Thus

$$\boxed{\Delta G_{A \rightarrow B} = -1000(0.250) = -250 \text{ J}},$$

and

$$\boxed{\Delta G_{D \rightarrow C} = -300(-0.250) = +75 \text{ J}}.$$

6.7

For the reversible isothermal expansion of one mole,

$$q_H = nRT_H \ln\left(\frac{V_B}{V_A}\right).$$

Because $p_A V_A = p_B V_B$,

$$\frac{V_B}{V_A} = \frac{p_A}{p_B}.$$

Therefore

$$\ln\left(\frac{p_A}{p_B}\right) = \frac{250}{(1)(8.314)(1000)},$$

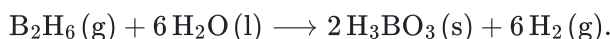
and

$$\frac{p_A}{p_B} = \exp\left(\frac{250}{8314}\right) = 1.030526 \approx 1.031.$$

The standard pressure cancels from this pressure ratio.

6.8

The balanced reaction, consistent with reaction (3), is



All 175 J of work output supplies the sublimation energy. Thus

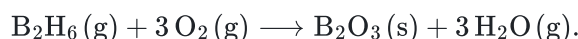
$$n(\text{H}_3\text{BO}_3) = \frac{175 \text{ J}}{25.0 \times 10^3 \text{ J mol}^{-1}} = 7.00 \times 10^{-3} \text{ mol}.$$

The reaction produces six moles of hydrogen for every two moles of boric acid:

$$\begin{aligned} n(\text{H}_2) &= \frac{6}{2} n(\text{H}_3\text{BO}_3) \\ &= 3(7.00 \times 10^{-3}) \\ &= \boxed{2.10 \times 10^{-2} \text{ mol}}. \end{aligned}$$

6.9

The balanced combustion reaction is



Taking the activity of pure solid B_2O_3 as unity,

$$K_p = \frac{(p_{\text{H}_2\text{O}}/p^\circ)^3}{(p_{\text{B}_2\text{H}_6}/p^\circ)(p_{\text{O}_2}/p^\circ)^3}, \quad p^\circ = 1 \text{ bar}.$$

Since $p_{\text{O}_2} = p^\circ$, its factor equals one.

Using $p_i = n_i RT/V$ with $V = 100 \text{ dm}^3$:

Temperature	$p_{\text{B}_2\text{H}_6} / \text{bar}$	$p_{\text{H}_2\text{O}} / \text{bar}$
8930 K	$\frac{0.38(0.08314)(8930)}{100} = 2.82127276$	$\frac{0.20(0.08314)(8930)}{100} = 1.48488040$
9005 K	$\frac{0.49(0.08314)(9005)}{100} = 3.66851093$	$\frac{0.20(0.08314)(9005)}{100} = 1.49735140$

The pressure ratios are dimensionless, giving

$$K_p(8930 \text{ K}) = \frac{(1.48488040)^3}{2.82127276} = 1.16045779 \approx \boxed{1.16},$$

and

$$K_p(9005 \text{ K}) = \frac{(1.49735140)^3}{3.66851093} = 0.91512703 \approx \boxed{0.915}.$$

6.10

The standard reaction Gibbs energy is

$$\Delta_r G^\circ = -RT \ln K_p.$$

At 8930 K,

$$\begin{aligned}\Delta_r G^\circ &= -\frac{(8.314)(8930) \ln(1.16045779)}{1000} \\ &= -11.04859 \text{ kJ mol}^{-1} \\ &\boxed{\approx -11.0 \text{ kJ mol}^{-1}}.\end{aligned}$$

At 9005 K,

$$\begin{aligned}\Delta_r G^\circ &= -\frac{(8.314)(9005) \ln(0.91512703)}{1000} \\ &= +6.64018 \text{ kJ mol}^{-1} \\ &\boxed{\approx +6.64 \text{ kJ mol}^{-1}}.\end{aligned}$$

These are standard reaction Gibbs energies. The actual reaction Gibbs energy at each equilibrium composition is zero.

6.11

By assumption, $\Delta_r H^\circ$ and $\Delta_r S^\circ$ are temperature-independent. Therefore

$$\Delta_r G^\circ(T) = \Delta_r H^\circ - T\Delta_r S^\circ.$$

Subtracting this equation at the two temperatures,

$$\Delta_r S^\circ = -\frac{\Delta_r G^\circ(9005) - \Delta_r G^\circ(8930)}{9005 - 8930}.$$

Using the unrounded values,

$$\begin{aligned}\Delta_r S^\circ &= -\frac{6.640184 - (-11.048592)}{75} \\ &= -0.23585035 \text{ kJ mol}^{-1} \text{ K}^{-1} \\ &= \boxed{-235.85035 \text{ J mol}^{-1} \text{ K}^{-1} \approx -236 \text{ J mol}^{-1} \text{ K}^{-1}}.\end{aligned}$$

Then

$$\begin{aligned}\Delta_r H^\circ &= \Delta_r G^\circ(8930) + 8930\Delta_r S^\circ \\ &= -11.048592 + 8930(-0.23585035) \\ &= -2117.19224 \text{ kJ mol}^{-1} \\ &\boxed{\approx -2.12 \times 10^3 \text{ kJ mol}^{-1}}.\end{aligned}$$

These enthalpy and entropy values also apply at 298 K. Hence

$$\begin{aligned}\Delta_r G^\circ(298) &= -2117.19224 - 298(-0.23585035) \\ &= -2046.90884 \text{ kJ mol}^{-1} \\ &\boxed{\approx -2.05 \times 10^3 \text{ kJ mol}^{-1}}.\end{aligned}$$

As an independent check, the integrated van 't Hoff equation,

$$\ln\left(\frac{K_{p,2}}{K_{p,1}}\right) = -\frac{\Delta_r H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right),$$

gives the same reaction enthalpy.

6.12

Under standard-state conditions, combustion is favored when $\Delta_r G^\circ < 0$.

Here,

$$\Delta_r G^\circ(T) = -2117.19224 + 0.23585035T \text{ kJ mol}^{-1},$$

with T in kelvin. Thus:

Temperature	$\Delta_r G^\circ / \text{kJ mol}^{-1}$	Favored	Unfavored
298 K	-2046.91	✓	
8930 K	-11.05	✓	

Temperature	$\Delta_r G^\circ / \text{kJ mol}^{-1}$	Favored	Unfavored
9005 K	+6.64		✓
9100 K	+29.05		✓

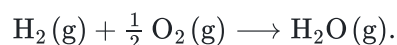
The crossover temperature is

$$T_* = \frac{\Delta_r H^\circ}{\Delta_r S^\circ} = \frac{-2117.19224}{-0.23585035} \approx 8977 \text{ K}.$$

Because both $\Delta_r H^\circ$ and $\Delta_r S^\circ$ are negative, combustion is favored below this temperature.

6.13

The standard formation reaction for water vapor is



Let

$$h = \Delta_f H^\circ(\text{H}_2\text{O}(\text{g})).$$

For the combustion reaction, the sum of product formation enthalpies minus the sum for reactants gives

$$\Delta_r H^\circ = [-1273 + 3h] - [36.40 + 3(0.00)].$$

Therefore

$$-2117.19224 = 3h - 1309.40,$$

so

$$h = \frac{-2117.19224 + 1309.40}{3} = -269.26408 \approx -269 \text{ kJ mol}^{-1}.$$

Similarly, let

$$s = S^\circ(\text{H}_2\text{O}(\text{g}))$$

in $\text{kJ mol}^{-1} \text{K}^{-1}$. Then

$$\begin{aligned} \Delta_r S^\circ &= [0.05 + 3s] - [0.23 + 3(0.16)] \\ &= 3s - 0.66. \end{aligned}$$

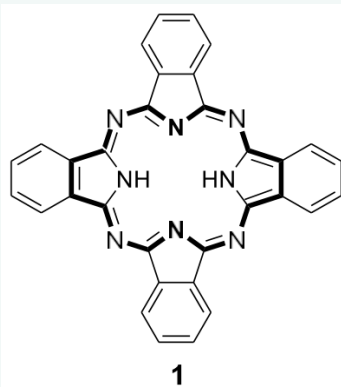
Using $\Delta_r S^\circ = -0.23585035 \text{ kJ mol}^{-1} \text{K}^{-1}$,

$$s = \frac{-0.23585035 + 0.66}{3} = 0.14138322 \approx 0.141 \text{ kJ mol}^{-1} \text{K}^{-1}.$$

These values follow from the stipulated hypothetical-universe data.

The solution was checked against the official solution. Where this solution differs from the official solution, the official solution contains an error or a misprint.

Problem 7: Phthalocyanines



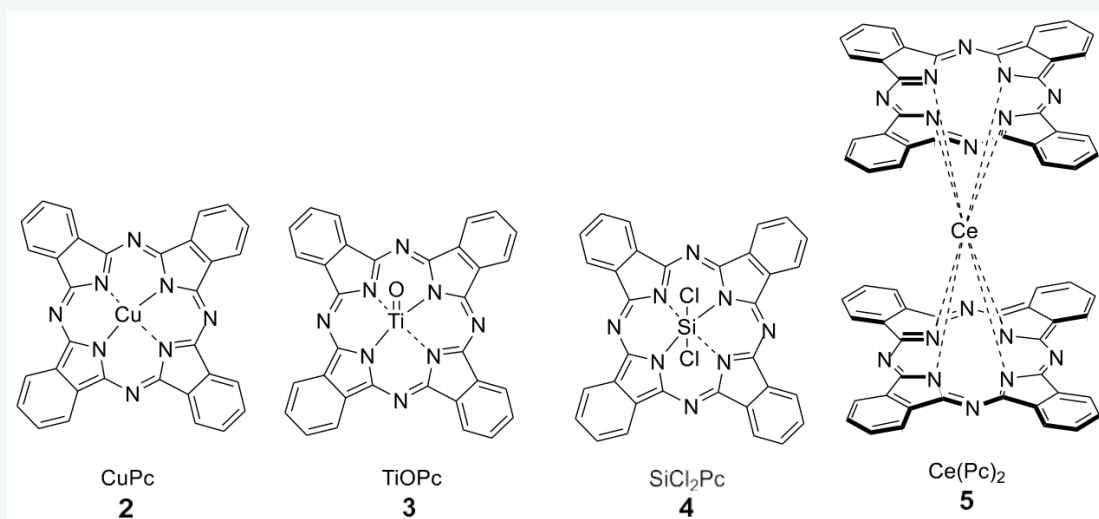


Emeritus Professor Özer Bekaroğlu

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 $(C_8H_4N_2)_4H_2$.

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



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

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

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

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

Metal in compounds	2	3	5
Oxidation number			

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

Geometry	Compound
Octahedral	
Square prism	
Square pyramidal	
Square planar	

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

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

Compound	Magnetic property
2	
3	
4	
5	

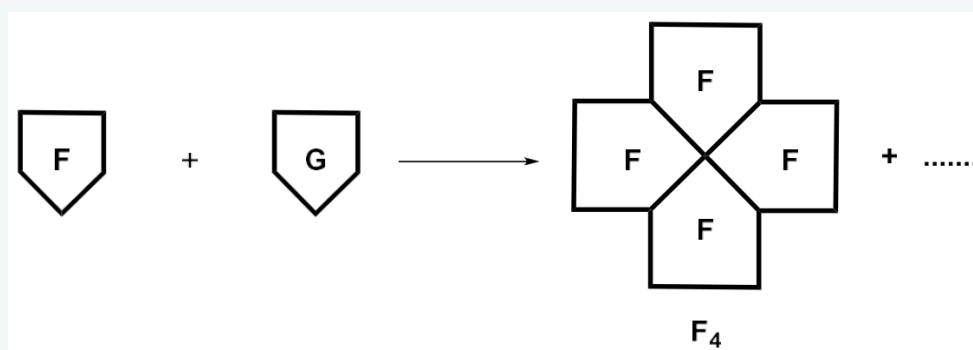
7.6 Write the ground-state electron configuration of the silicon (Si) ion in the compound **4** and find all the quantum numbers for the 2p electrons in its ground state.

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

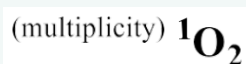
Metal-free phthalocyanine (**1**, H_2Pc) is commonly formed through the cyclotetramerization of phthalonitriles. On the other hand, Pcs having different substituents are called asymmetric, which can be prepared by the statistical cyclization of two different phthalonitriles. This method has no selectivity and the product is a mixture of all possible isomers.

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

- F** and **G** represent two different symmetrical phthalonitriles.
- One of the products is F_4 as given below.
- Draw other products similar to the format of F_4 .



Pcs are used as photosensitizers in the photodynamic therapy (PDT) of cancer due to their strong absorption in the visible spectrum and high molar absorption coefficients. PDT consists of three essential components: **photosensitizer**, light, and oxygen. None of these is individually toxic, but together they initiate a photochemical reaction resulting in the generation of cytotoxic singlet oxygen ($^1O_2$) that can destroy cancer cells.



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

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

- There are no unpaired electrons in that state!

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

Answers

- **7.1:** 18 π -electrons.
- **7.2:** Coordination numbers: copper **4**, titanium **5**, silicon **6**, cerium **8**.
- **7.3:** Oxidation numbers: **2:** +2; **3:** +4; **5:** +4.
- **7.4:** Octahedral: **4**; square prism: **5**; square pyramidal: **3**; square planar: **2**.
- **7.5:** **2:** p; **3:** d; **4:** d; **5:** d.
- **7.6:** Si^{4+} : $1s^2 2s^2 2p^6$. The six quantum-number sets are $(2, 1, -1, \pm \frac{1}{2})$, $(2, 1, 0, \pm \frac{1}{2})$, and $(2, 1, +1, \pm \frac{1}{2})$, taking both signs in each case.
- **7.7:** Six products including the supplied example: F_4 , F_3G , *cis*- F_2G_2 , *trans*- F_2G_2 , FG_3 , and G_4 .
- **7.8:** Pair the two highest occupied electrons in one of the degenerate π^* orbitals; leave the other empty. Bond order: **2**.
- **7.9:** 94.2 kJ mol⁻¹.

Solution

7.1 — Electrons in the highlighted circuit

Compound **1** is metal-free phthalocyanine, H_2Pc , with molecular formula $\text{C}_{32}\text{H}_{18}\text{N}_8$.

SMILES: c12[nH]c(c3ccccc32)nc2nc(c3ccccc32)nc2[nH]c(c3ccccc32)nc2nc(c3ccccc32)n1

The bold conjugated circuit contains nine double bonds. Each contributes two π -electrons:

$$N_{\pi} = 9(2) = \boxed{18}.$$

This also satisfies Hückel's $4n + 2$ count with $n = 4$. The count concerns the highlighted circuit, so the remaining benzenoid bonds are not added.

7.2 — Coordination numbers

Each phthalocyanine ligand coordinates through its four inward-facing nitrogen atoms. Coordination number counts directly attached donor atoms; a multiple bond to one donor atom still contributes only one.

Compound	Donor atoms surrounding the central atom	Coordination number
2 , copper(II) phthalocyanine	Four nitrogen atoms	4
3 , oxotitanium(IV) phthalocyanine	Four nitrogen atoms and one oxygen atom	5
4 , dichloridosilicon(IV) phthalocyanine	Four nitrogen atoms and two chlorine atoms	6
5 , bis(phthalocyaninato)cerium(IV)	Four nitrogen atoms from each of two ligands	8

The following SMILES specify the structures and their coordination connectivity. The arrows $\rightarrow$ denote donor-to-central-atom coordinate bonds. Their spatial geometries are specified in **7.4**.

- **2 — Copper(II) phthalocyanine, CuPc :**
[Cu+2]1234.c56[n-]->1c(c7ccccc75)nc5n->2c(c7ccccc75)nc5[n-]->3c(c7ccccc75)nc5n->4c(c7ccccc75)n6
- **3 — Oxotitanium(IV) phthalocyanine (titanyl phthalocyanine), TiOPc :**
[O-2]->[Ti+4]1234.c56[n-]->1c(c7ccccc75)nc5n->2c(c7ccccc75)nc5[n-]->3c(c7ccccc75)nc5n->4c(c7ccccc75)n6
- **4 — Dichloridosilicon(IV) phthalocyanine, SiCl_2Pc :**
Cl[Si-2]1234(Cl).c56n1c(c7ccccc75)nc5[n+]2c(c7ccccc75)nc5n3c(c7ccccc75)nc5[n+]4c(c7ccccc75)n6

• **5 — Bis(phthalocyaninato)cerium(IV), Ce(Pc)₂:**

```
[Ce+4]12345678.c9%10[n-]->1c(c%11cccc%119)nc9n->2c(c%11cccc%119)nc9[n-]->3c(c%11cccc%119)nc9n->4c(c%11cccc%119)n%10.c9%10[n-]->5c(c%11cccc%119)nc9n->6c(c%11cccc%119)nc9[n-]->7c(c%11cccc%119)nc9n->8c(c%11cccc%119)n%10
```

For **4**, the ordinary-bond SMILES uses formal charge separation to represent six-coordinate silicon. The Si^{-2} and two $[\text{n}^+]$ formal charges are distinct from oxidation numbers; silicon's oxidation number is $+4$. For **3**, the ionic dative representation specifies the terminal oxo connectivity without attempting to express the full titanium–oxygen multiple-bond character.

7.3 — Oxidation numbers

Removal of the two inner N–H protons from metal-free phthalocyanine gives the phthalocyaninate(2–) ligand, Pc^{2-} , with formula $\text{C}_{32}\text{H}_{16}\text{N}_8^{2-}$.

SMILES: c12[n-]c(c3cccc32)nc2nc(c3cccc32)nc2[n-]c(c3cccc32)nc2nc(c3cccc32)n1

The terminal oxygen in **3** is an oxide ligand, O^{2-} , SMILES [O-2]. All three complexes are neutral, so their charges give:

Compound	Charge balance	Central ion and its SMILES	Oxidation number
2	$x - 2 = 0$	Copper(II), Cu^{2+} , <chem>[Cu+2]</chem>	+2
3	$x - 2 - 2 = 0$	Titanium(IV), Ti^{4+} , <chem>[Ti+4]</chem>	+4
5	$x + 2(-2) = 0$	Cerium(IV), Ce^{4+} , <chem>[Ce+4]</chem>	+4

7.4 — Coordination geometries

Geometry	Compound	Description of the required drawing
Octahedral	4	Four nitrogen donors form the equatorial square; the two chloride ligands occupy opposite axial positions.
Square prism	5	The eight nitrogen donors form two parallel, aligned squares, with cerium between the two phthalocyanine ligands.
Square pyramidal	3	Four nitrogen donors form the square base, and the terminal oxygen occupies the apical position.
Square planar	2	Copper and its four nitrogen donors lie in one plane, with the donors surrounding copper approximately at the corners of a square.

The two axial chloride ligands in **4** are therefore *trans*. These spatial arrangements are not specified by the SMILES strings alone.

7.5 — Magnetic properties

A species with an unpaired electron is paramagnetic; a species with all electrons paired is diamagnetic. The phthalocyaninate ligands here are closed-shell dianions.

Compound	Central-ion electron configuration	Number of unpaired electrons	Magnetic property
2	$\text{Cu}^{2+} : [\text{Ar}] 3d^9$	1	p
3	$\text{Ti}^{4+} : [\text{Ar}], 3d^0$	0	d
4	$\text{Si}^{4+} : [\text{Ne}]$	0	d
5	$\text{Ce}^{4+} : [\text{Xe}], 4f^0$	0	d

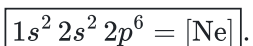
For copper(II), nine electrons distributed among five *d* orbitals necessarily leave one unpaired electron.

7.6 — Silicon electron configuration and quantum numbers

In **4**, the phthalocyaninate ligand has charge -2 , and each chloride ion, Cl^- , SMILES [Cl-], has charge -1 . Therefore,

$$x - 2 - 1 - 1 = 0 \quad \implies \quad x = +4.$$

The central ion is silicon(IV), Si^{4+} , SMILES [Si+4]. Silicon has atomic number 14, so this ion has $14 - 4 = 10$ electrons:



For every $2p$ electron, $n = 2$ and $l = 1$. The three possible orbital magnetic quantum numbers are $m_l = -1, 0, +1$. Each orbital contains two electrons with opposite spins:

Electron	n	l	m_l	m_s
1	2	1	-1	$+\frac{1}{2}$
2	2	1	-1	$-\frac{1}{2}$
3	2	1	0	$+\frac{1}{2}$
4	2	1	0	$-\frac{1}{2}$
5	2	1	+1	$+\frac{1}{2}$
6	2	1	+1	$-\frac{1}{2}$

7.7 — Statistical cyclization products

The four building blocks occupy four successive positions around the macrocycle. Since **F** and **G** are each symmetrical, their individual orientations introduce no additional possibilities.

Draw each product using the four-armed outline in the question, filling its **top, right, bottom, and left** sectors as follows:

Product	Top	Right	Bottom	Left	Description
F_4 , supplied	F	F	F	F	Four F units
F_3G	F	F	F	G	Three F units and one G unit
<i>cis</i> - F_2G_2	F	F	G	G	Identical units occupy adjacent sectors
<i>trans</i> - F_2G_2	F	G	F	G	Identical units occupy opposite sectors
FG_3	F	G	G	G	One F unit and three G units
G_4	G	G	G	G	Four G units

Thus, **five additional products** must be drawn alongside the supplied F_4 .

To establish completeness, classify products by the number of G units:

- Zero or four G units gives one arrangement each.
- One or three G units gives one arrangement each, because rotations identify all placements.
- Two G units gives two arrangements: adjacent or opposite.

Hence,

$$N_{\text{distinct products}} = 1 + 1 + 2 + 1 + 1 = \boxed{6}.$$

The *cis/trans* labels above follow the question's terminology. The actual substituents defining **F** and **G** are unspecified, so these abstract products do not have unique molecular names or chemical SMILES beyond their building-block descriptions.

7.8 — Singlet-oxygen MO diagram and bond order

The molecule is singlet dioxygen, $^1\text{O}_2$, with connectivity SMILES O=O. Ordinary SMILES does not specify its spin multiplicity or orbital occupation; those must be stated separately.

There are 12 valence electrons. Following the question's paired-electron representation, fill the orbitals as shown below. Energy increases upward; the two boxes in each π row denote degenerate orbitals.

MO level, highest first	Occupation
$\sigma^*(2p_z)$	$\uparrow\downarrow$

MO level, highest first	Occupation
$\pi^*(2p)$, two degenerate orbitals	$[\uparrow\downarrow] \quad []$
$\pi(2p)$, two degenerate orbitals	$[\uparrow\downarrow] \quad [\uparrow\downarrow]$
$\sigma(2p_z)$	$[\uparrow\downarrow]$
$\sigma^*(2s)$	$[\uparrow\downarrow]$
$\sigma(2s)$	$[\uparrow\downarrow]$

Either of the degenerate π^* boxes may be shown occupied. The filled core orbitals, $\sigma(1s)^2\sigma^*(1s)^2$, are omitted from the table; their bonding and antibonding contributions cancel.

All electrons are paired in the requested diagram, giving

$$S = 0, \quad 2S + 1 = 1.$$

The valence bonding and antibonding electron counts are

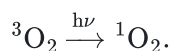
$$N_b = 2 + 2 + 4 = 8, \quad N_{ab} = 2 + 2 = 4.$$

Therefore,

$$\text{Bond order} = \frac{N_b - N_{ab}}{2} = \frac{8 - 4}{2} = 2.$$

7.9 — Energy of the triplet-to-singlet excitation

Triplet dioxygen, $^3\text{O}_2$, has the same connectivity SMILES O=O; its triplet electronic state must be specified separately. The excitation is



For one absorbed photon per molecule,

$$E_{\text{photon}} = \frac{hc}{\lambda}, \quad E_{\text{molar}} = \frac{N_A hc}{\lambda}.$$

Using the standard SI constants

$$\begin{aligned} h &= 6.62607015 \times 10^{-34} \text{ J s}, \\ c &= 2.99792458 \times 10^8 \text{ m s}^{-1}, \\ N_A &= 6.02214076 \times 10^{23} \text{ mol}^{-1}, \end{aligned}$$

and

$$\lambda = 1270 \text{ nm} = 1.270 \times 10^{-6} \text{ m},$$

gives

$$E_{\text{photon}} = \frac{(6.62607015 \times 10^{-34})(2.99792458 \times 10^8)}{1.270 \times 10^{-6}} = 1.56413 \times 10^{-19} \text{ J}.$$

Thus,

$$E_{\text{molar}} = (1.56413 \times 10^{-19})(6.02214076 \times 10^{23}) = 9.41941 \times 10^4 \text{ J mol}^{-1},$$

or

$$E_{\text{molar}} = 94.2 \text{ kJ mol}^{-1}.$$

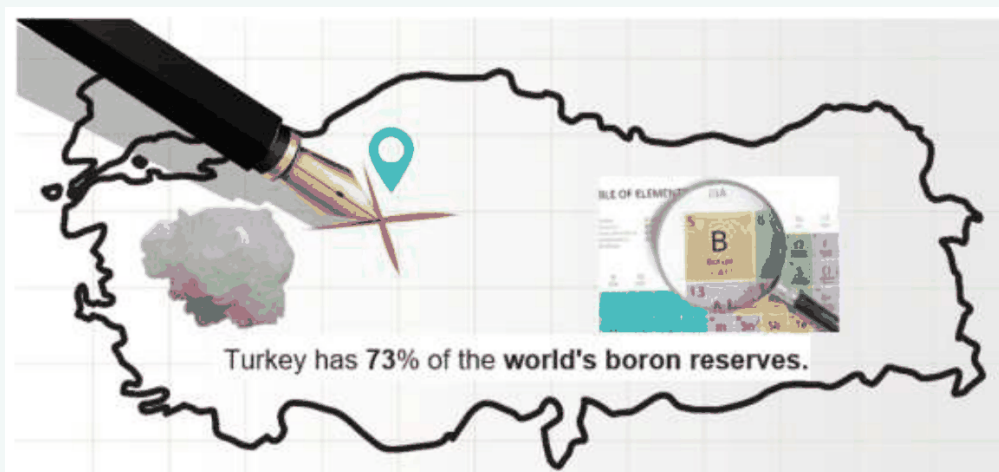
The solution was checked against the official solution.

Problem 8: Boron Compounds and Hydrogen Storage

14% of the total

Question	8.1	8.2	8.3	8.4	8.5	8.6	8.7	8.8	Total
Points	3	3	4	4	4	4	6	3	58
Question	8.9	8.10	8.11	8.12	8.13	8.14	8.15	8.16	
Points	2	3	2	4	4	4	2	2	
Question	8.17								
Points	4								

Problem 8. 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°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°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.

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

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

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

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

8.5. Write the balanced chemical equations for the hydrolysis of NaBH_4 and BNH_6 .

One of the simplest stable borates is diboron trioxide (B_2O_3). Higher borates such as $\text{B}_3\text{O}_6^{3-}$ having cyclic structures containing B–O–bonds can be formed. Since B_2O_3 is an acidic compound, it is easily reacted with water to produce boric acid (H_3BO_3). On the other hand, the high temperature and high-pressure reaction of B_2O_3 with ammonia yields two-dimensional boron nitride, which consists of planar graphite-like sheets of alternating B and N atoms.

8.6. Write the balanced chemical equations for the synthesis of boric acid and boron nitride.

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.

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.

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

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

8.10. Sketch the Lewis dot structure of BH_3-CO molecule by showing the formal charges.

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

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

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

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

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

Catalysts are substances that accelerate the rate of reactions by allowing them to proceed in a lower energy pathway. The catalytic activity of the catalysts is generally determined by the turnover frequency (TOF), which is calculated by dividing the molar amount of the product to the mole of active catalyst and the time ($TOF = \text{mole product}/(\text{mole catalyst} \times \text{time})$). 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 minutes.

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

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

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

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

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

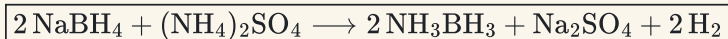
Official English text of the problem.

Answers

- 8.1.



- 8.2.

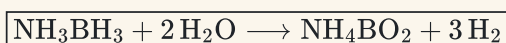
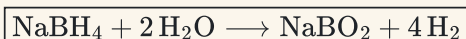


- 8.3. Borohydride ion, $[\text{BH}_4^-]$: **tetrahedral**. Ammonia borane, $[\text{NH}_3^+][\text{BH}_3^-]$: **approximately tetrahedral coordination around both B and N**, with three H atoms on each centre and a single B–N bond.

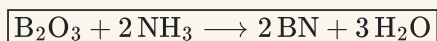
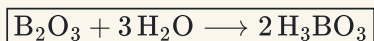
- 8.4.

$$w_{\text{H}}(\text{NaBH}_4) = 10.66\%, \quad w_{\text{H}}(\text{BNH}_6) = 19.59\%$$

- 8.5.

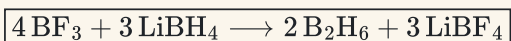


- 8.6.



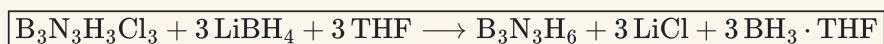
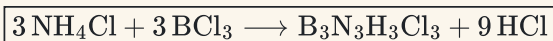
- 8.7. Cyclic trimetaborate ion, $[\text{O}-]\text{B}(\text{O})\text{B}(\text{O}-)\text{O}(\text{O}-)\text{B}(\text{O})\text{O}$: a six-membered alternating B–O ring, with one terminal O^- on each B. Boric acid, $\text{OB}(\text{O})\text{O}$: trigonal-planar $\text{B}(\text{OH})_3$. Hexagonal boron nitride: a planar honeycomb sheet with alternating B and N vertices; a patch of seven fused hexagons contains **12 B and 12 N atoms**. The extended sheet has no finite molecular SMILES.

- 8.8.



- 8.9. Diborane has **four terminal H atoms and two bridging H atoms**, with two three-centre, two-electron B–H–B bonds and no direct B–B bond. Its schematic connectivity string is $[\text{BH}_2]1[\text{H}][\text{BH}_2][\text{H}]1$; the multicentre-bond limitation of this notation is explained below.
- 8.10. Borane carbonyl, $[\text{BH}_3^-]\text{C}\#[\text{O}^+]$: three B–H single bonds, one B–C single bond and a $\text{C}\equiv\text{O}$ triple bond. O has one lone pair. Formal charges: **B = -1, C = 0, O = +1; all H = 0**.
- 8.11. **Third statement**: "No or slight change on it because CO donates its mainly non-bonding electrons to BH_3 ."

- 8.12.



- 8.13. Borazine: a planar alternating B/N six-membered ring, with one H on every atom. A Kekulé contributor has SMILES $[\text{BH}-]1=[\text{NH}+][\text{BH}-]=[\text{NH}+][\text{BH}-]=[\text{NH}+]1$. Its **B,B',B''-trichloro derivative** has Cl on all three B atoms and H on all three N atoms: $[\text{B}-]1(\text{Cl})=[\text{NH}+][\text{B}-](\text{Cl})=[\text{NH}+][\text{B}-](\text{Cl})=[\text{NH}+]1$.

- 8.14.

$$\text{TOF} = 285.5 \text{ min}^{-1} \approx 2.9 \times 10^2 \text{ min}^{-1}$$

- 8.15.

$$x = 75, \quad y = 25$$

Thus the atomic composition is $\text{Cu}_{75}\text{Pt}_{25}$, with simplest atomic ratio Cu_3Pt .

- **8.16.** Draw a cube with **Pt at all eight corners** and **Cu at the centres of all six faces**.
- **8.17.**

$$\rho = 13.0 \text{ g cm}^{-3}$$

Solution

The problem does not include an atomic-mass or constants table. The numerical calculations use the following standard values:

Element	H	B	N	Na	Cu	Pt
Molar atomic mass / g mol^{-1}	1.008	10.81	14.01	22.99	63.55	195.08

$$R = 0.0820574 \text{ L atm mol}^{-1} \text{ K}^{-1}, \quad N_A = 6.02214076 \times 10^{23} \text{ mol}^{-1}.$$

Small molecules appearing below are dihydrogen $[\text{H}][\text{H}]$, water O , ammonia N , hydrogen chloride Cl , and tetrahydrofuran (THF) C1CCOC1 . In salt SMILES, a dot separates ionic components. Extended network solids have no unique finite molecular SMILES; their formulas and structures are specified directly.

8.1. Synthesis of sodium borohydride

The oxygen-containing by-product is sodium metasilicate, Na_2SiO_3 . All four B atoms in one formula unit of anhydrous borax become sodium borohydride, $[\text{Na}^+][\text{BH}_4^-]$.

Let the coefficient of silica, and hence of sodium metasilicate, be s . Oxygen balance gives

$$7 + 2s = 3s \Rightarrow s = 7.$$

Four formula units of NaBH_4 require 16 H atoms, supplied by eight molecules of hydrogen. Sodium balance then requires

$$2 + n_{\text{Na}} = 4 + 2(7) \Rightarrow n_{\text{Na}} = 16.$$

Therefore, at 700 °C under high-pressure hydrogen,

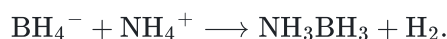


Anhydrous sodium tetraborate, silica and sodium metasilicate are network solids; a finite molecular SMILES would not describe their solid structures.

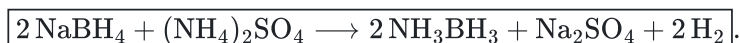
8.2. Synthesis of ammonia borane

One B-bound hydrogen and one hydrogen from an ammonium ion combine to form hydrogen gas. The remaining ammonia and borane units form the Lewis acid–base adduct ammonia borane, $[\text{NH}_3^+][\text{BH}_3^-]$.

The net ionic equation is



The ammonium ion is $[\text{NH}_4^+]$. Since ammonium sulfate contains two ammonium ions,



The reaction is performed in dry THF at 40 °C. The flammable gaseous by-product is dihydrogen.

The salts are ammonium sulfate, $[\text{NH}_4^+][\text{NH}_4^+][\text{O}^-]\text{S}(=\text{O})(=\text{O})[\text{O}^-]$, and sodium sulfate, $[\text{Na}^+][\text{Na}^+][\text{O}^-]\text{S}(=\text{O})(=\text{O})[\text{O}^-]$.

8.3. Geometries of borohydride and ammonia borane

For the **borohydride ion**, $[\text{BH}_4^-]$, B has four bonding electron pairs and no lone pair. VSEPR therefore gives a tetrahedral arrangement:

$$\angle \text{H-B-H} \approx 109.5^\circ.$$

To draw it, place B at the centre, with two B–H bonds in the plane of the page, one solid wedge toward the viewer and one dashed wedge away. Enclose the structure in brackets with an overall negative charge.

For **ammonia borane**, $[\text{NH}_3^+][\text{BH}_3^-]$, nitrogen donates its lone pair to electron-deficient boron. Each centre then has four bonds: three to H and one to the other central atom. Both centres have approximately tetrahedral coordination.

Draw a B—N single bond with three H atoms arranged tetrahedrally around each end. A staggered conformation about this bond is an appropriate drawing. SMILES specifies connectivity and formal charges but does not fix that conformation.

8.4. Hydrogen mass percentages

The hydrogen mass percentage is

$$w_{\text{H}} = \frac{\text{mass of H in one mole of compound}}{\text{molar mass of compound}} \times 100\%.$$

For sodium borohydride,

$$M(\text{NaBH}_4) = 22.99 + 10.81 + 4(1.008) = 37.832 \text{ g mol}^{-1},$$

so

$$w_{\text{H}}(\text{NaBH}_4) = \frac{4(1.008)}{37.832} \times 100\% = 10.66\%.$$

For ammonia borane,

$$M(\text{BNH}_6) = 10.81 + 14.01 + 6(1.008) = 30.868 \text{ g mol}^{-1},$$

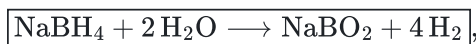
and

$$w_{\text{H}}(\text{BNH}_6) = \frac{6(1.008)}{30.868} \times 100\% = 19.59\%.$$

These are the hydrogen contents of the compounds themselves.

8.5. Hydrolysis reactions

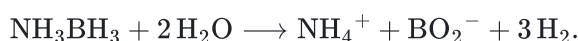
Using the metaborate products specified in the problem,



and



The second equation can equivalently be written

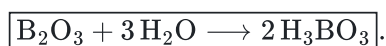


The products are sodium metaborate and ammonium metaborate. A formal monomeric Lewis representation of the **metaborate ion** is $[\text{B}-](=\text{O})=\text{O}$; corresponding formula-unit SMILES are $[\text{Na}+].[\text{B}-](=\text{O})=\text{O}$ and $[\text{NH}_4+].[\text{B}-](=\text{O})=\text{O}$. These formula-unit representations do not describe hydration or condensed borate structures.

Both equations conserve every element and give the stated four and three equivalents of hydrogen. Water supplies part of the hydrogen released as gas, so the gas yield is not simply the original hydrogen mass content calculated in 8.4.

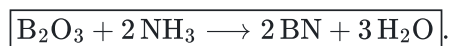
8.6. Formation of boric acid and boron nitride

Hydration of the acidic oxide gives **boric acid**, $\text{OB}(\text{O})\text{O}$:



Its structural formula is $\text{B}(\text{OH})_3$.

At high temperature and pressure, reaction with ammonia gives boron nitride and water:



Both B atoms become part of the nitride, while the three O atoms leave in three water molecules.

8.7. Structures of the borate ion, boric acid and boron nitride

For the **cyclic trimetaborate ion**, $\text{B}_3\text{O}_6^{3-}$, SMILES $[\text{O}-]\text{B1OB}([\text{O}-])\text{OB}([\text{O}-])\text{O1}$:

- Draw a six-membered ring with the sequence B—O—B—O—B—O.
- Attach one additional, terminal O atom to each B.
- Give each terminal O a formal charge of -1 ; the three bridging O atoms are neutral.
- Each B is bonded to three O atoms and has approximately trigonal-planar coordination.

This gives three B atoms, six O atoms and total charge -3 .

For **boric acid**, OB(O)O , draw a central B bonded to three hydroxyl groups:



The B atom and its three directly attached O atoms lie in one plane, with O—B—O angles approximately 120° . Each O bears one H.

For a **hexagonal boron nitride sheet**, draw a planar honeycomb of fused hexagons. Label successive vertices alternately B and N, so every bond joins unlike atoms. Each B has three N neighbours, and each N has three B neighbours.

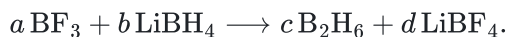
A precise patch satisfying the requested size is obtained by drawing one central hexagon and fusing one hexagon to each of its six sides. The resulting seven-hexagon patch has **24 vertices: 12 B and 12 N atoms**. Indicate continuation of the lattice at its perimeter. An infinite sheet cannot be encoded by a finite molecular SMILES.

8.8. Synthesis of diborane

The reactants are **boron trifluoride**, FB(F)F , and **lithium borohydride**, $[\text{Li}^+].[\text{BH}_4^-]$.

The hint identifies the lithium-containing product as **lithium tetrafluoroborate**, $[\text{Li}^+].[\text{B}^-](\text{F})(\text{F})(\text{F})\text{F}$, rather than a boron-free product.

Write

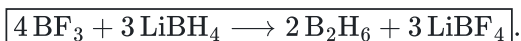


Lithium, fluorine and hydrogen balances give

$$b = d, \quad 3a = 4d, \quad 4b = 6c.$$

The smallest integer coefficients are $a = 4$, $b = d = 3$, $c = 2$. Boron balance is also satisfied: $4 + 3 = 2(2) + 3$.

Thus,



8.9. Geometry and bonding of diborane

Diborane, B_2H_6 , contains four terminal H atoms and two bridging H atoms.

To draw it precisely:

1. Place the two B atoms horizontally apart.
2. Attach two terminal H atoms to each B. Both B atoms and all four terminal H atoms lie in one plane.
3. Place one bridging H above this plane and the other below it, symmetrically between the B atoms.
4. Connect each bridging H to both B atoms to indicate a three-centre bridge. Do not draw a direct B—B bond.

The plane containing both B atoms and both bridging H atoms is perpendicular to the plane containing the four terminal H atoms. The idealized molecule has D_{2h} symmetry.

Its 12 valence electrons are distributed as follows:

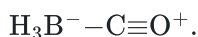
$$4 \text{ terminal two-centre bonds} \times 2e^- + 2 \text{ three-centre bridges} \times 2e^- = 12e^-.$$

A schematic connectivity string is $[\text{BH}_2]1[\text{H}][\text{BH}_2][\text{H}]1$. **This is not a faithful ordinary, valence-valid SMILES representation of the bonding:** standard SMILES cannot directly express a three-centre, two-electron bond. In particular, each bridging H must not be interpreted as making two independent ordinary covalent bonds.

8.10. Lewis structure of borane carbonyl

The reactants are **borane**, $[\text{BH}_3]$, and **carbon monoxide**, $[\text{C}-]\#[\text{O}+]$. The carbon-centred lone pair of carbon monoxide forms the bond to B.

The product is **borane carbonyl**, $[\text{BH}_3-]\text{C}\#[\text{O}+]$, with connectivity



Draw three B–H single bonds, one B–C single bond, a C≡O triple bond, and **one lone pair on O**. There are no lone pairs on B or C in this Lewis structure.

Using

$$\text{FC} = (\text{valence electrons}) - (\text{nonbonding electrons}) - \frac{1}{2}(\text{bonding electrons}),$$

the formal charges are

$$\text{FC}(\text{B}) = 3 - 0 - 4 = -1,$$

$$\text{FC}(\text{C}) = 4 - 0 - 4 = 0,$$

$$\text{FC}(\text{O}) = 6 - 2 - 3 = +1,$$

$$\text{FC}(\text{H}) = 1 - 0 - 1 = 0.$$

The total charge is zero. B is approximately tetrahedral, and the B–C–O arrangement is approximately linear.

8.11. Effect on the carbon–oxygen bond

The correct choice is:

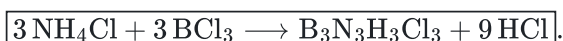
No or slight change on it because CO donates its mainly non-bonding electrons to BH_3 .

The donation comes from the mainly carbon-centred, approximately nonbonding σ orbital of carbon monoxide. It therefore produces only a small change in the C–O bond. Electron-deficient borane does not provide the substantial π -back donation invoked by the first option.

8.12. Two-step synthesis of borazine

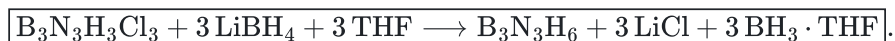
The starting materials are **ammonium chloride**, $[\text{NH}_4+]\cdot[\text{Cl}-]$, and **boron trichloride**, $\text{Cl}_3\text{B}(\text{Cl})\text{Cl}$.

In the first step, three B atoms and three N atoms form the six-membered ring. Each B retains one Cl, and each N retains one H. The remaining H and Cl atoms form hydrogen chloride:



There are 12 H atoms and 12 Cl atoms on each side.

In the second step, the three B-bound Cl atoms are replaced by H. Each borohydride supplies one hydride for this substitution and leaves a borane unit, which is trapped by THF:



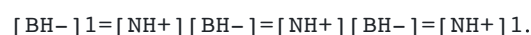
The by-products are **lithium chloride**, $[\text{Li}+]\cdot[\text{Cl}-]$, and the **borane–tetrahydrofuran adduct**, $[\text{BH}_3-][\text{O}+]\text{1CCCC1}$.

In the latter, an oxygen lone pair from THF forms the bond to B. This is the Lewis acid–base stabilization identified by the hint.

8.13. Structures of borazine and its chlorine derivative

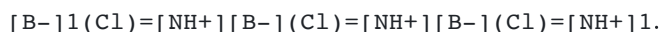
Borazine, $\text{B}_3\text{N}_3\text{H}_6$, has a planar six-membered ring with alternating B and N atoms. Draw alternating single and double bonds around the ring and attach one H to every ring atom.

One Kekulé Lewis contributor is encoded by



Each B and N is approximately trigonal planar. The actual ring bonding is delocalized; the SMILES selects one localized Lewis contributor.

For **B,B',B''-trichloroborazine**, $B_3N_3H_3Cl_3$, retain the same ring and replace the H attached to each B with Cl. All three N atoms retain their H atoms:



The negative B and positive N charges in these strings are the formal charges of the chosen alternating-double-bond contributors. They follow because each such B and N has a total bond order of four.

The chlorine substituents occupy the B positions because the first synthesis step retains B–Cl bonds, and the second step reduces those bonds to B–H.

8.14. Turnover frequency

The hydrogen amount follows from the ideal-gas equation:

$$n_{H_2} = \frac{PV}{RT} = \frac{(1.000 \text{ atm})(0.06725 \text{ L})}{(0.0820574 \text{ L atm mol}^{-1} \text{ K}^{-1})(273.15 \text{ K})} = 3.00036 \times 10^{-3} \text{ mol}.$$

The mass of Pt in the catalyst is

$$m_{Pt} = (5.0 \times 10^{-3} \text{ g})(0.082) = 4.10 \times 10^{-4} \text{ g}.$$

Hence

$$n_{Pt} = \frac{4.10 \times 10^{-4} \text{ g}}{195.08 \text{ g mol}^{-1}} = 2.10170 \times 10^{-6} \text{ mol}.$$

The stated definition uses moles of hydrogen product and moles of Pt atoms:

$$\text{TOF} = \frac{n_{H_2}}{n_{Pt} t} = \frac{3.00036 \times 10^{-3}}{(2.10170 \times 10^{-6})(5)} = 285.5 \text{ min}^{-1}.$$

Thus, to the precision of the catalyst mass and Pt percentage,

$$\boxed{\text{TOF} \approx 2.9 \times 10^2 \text{ min}^{-1}}.$$

As a consistency check, the starting ammonia borane amount is

$$(0.1000 \text{ mol L}^{-1})(0.0100 \text{ L}) = 1.00 \times 10^{-3} \text{ mol}.$$

Complete hydrolysis gives approximately 3.00×10^{-3} mol of hydrogen, matching the measured volume.

8.15. Alloy composition

An atom at a cube corner contributes $1/8$ to the unit cell; an atom at a face centre contributes $1/2$.

With Pt at the corners,

$$N_{Pt} = 8 \left(\frac{1}{8} \right) = 1.$$

With Cu at the face centres,

$$N_{Cu} = 6 \left(\frac{1}{2} \right) = 3.$$

The total is four atoms per cell, so the atomic percentages are

$$x = \frac{3}{4}(100) = 75, \quad y = \frac{1}{4}(100) = 25.$$

Therefore,

$$\boxed{\text{Cu}_{75}\text{Pt}_{25}, \quad x = 75, \quad y = 25}.$$

Its simplest atomic ratio is Cu_3Pt .

8.16. Unit-cell drawing

Draw a cube with:

- **Eight Pt atoms:** one at each corner.

- **Six Cu atoms:** one at the centre of each face.

In fractional coordinates, the Pt atoms occupy all corners (i, j, k) , where $i, j, k \in \{0, 1\}$. The Cu atoms occupy

$$\begin{aligned} & \left(\frac{1}{2}, \frac{1}{2}, 0\right), \quad \left(\frac{1}{2}, \frac{1}{2}, 1\right), \\ & \left(\frac{1}{2}, 0, \frac{1}{2}\right), \quad \left(\frac{1}{2}, 1, \frac{1}{2}\right), \\ & \left(0, \frac{1}{2}, \frac{1}{2}\right), \quad \left(1, \frac{1}{2}, \frac{1}{2}\right). \end{aligned}$$

The cube has no body-centre atom. The drawing shows 14 atomic positions on the boundary, whose sharing gives the effective content of three Cu and one Pt per cell.

8.17. Density of the randomly occupied alloy

An fcc conventional unit cell contains four atomic sites. For composition Cu_2Pt_1 , the mean site occupancies are $2/3$ Cu and $1/3$ Pt. Thus the average numbers per cell are

$$N_{\text{Cu}} = \frac{8}{3}, \quad N_{\text{Pt}} = \frac{4}{3}.$$

These fractional values are averages over many randomly occupied cells.

The mean molar mass per mole of atomic sites is

$$\overline{M} = \frac{2M_{\text{Cu}} + M_{\text{Pt}}}{3} = \frac{2(63.55) + 195.08}{3} = 107.3933 \text{ g mol}^{-1}.$$

The unit-cell mass is therefore

$$m_{\text{cell}} = \frac{4\overline{M}}{N_A} = \frac{4(107.3933)}{6.02214076 \times 10^{23}} = 7.13323 \times 10^{-22} \text{ g}.$$

Convert the edge length to centimetres:

$$a = 380 \text{ pm} = 3.80 \times 10^{-8} \text{ cm}.$$

Then

$$V_{\text{cell}} = a^3 = (3.80 \times 10^{-8})^3 = 5.4872 \times 10^{-23} \text{ cm}^3.$$

Finally,

$$\rho = \frac{m_{\text{cell}}}{V_{\text{cell}}} = \frac{7.13323 \times 10^{-22}}{5.4872 \times 10^{-23}} = 13.0 \text{ g cm}^{-3}.$$

The solution was checked against the official solution. Where this solution differs from the official solution, the official solution contains an error or a misprint.

Problem 9: Quantification of Heavy Metal Ions

| 12% of the total | Points | 5 | 5 | 8 | 16 | 5 | 6 | 25 | 30 | 100 |

Problem 9. Quantification of Heavy Metal Ions

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

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

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

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

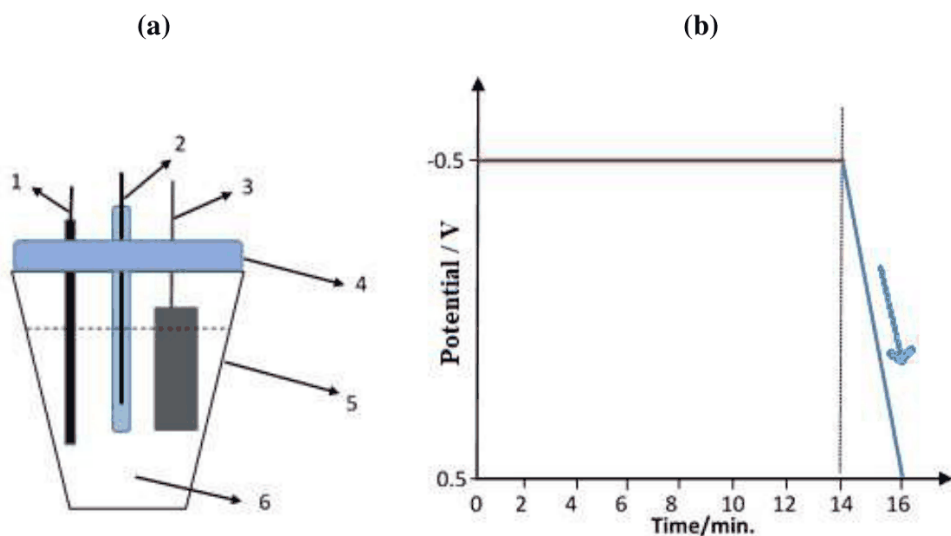


Figure 1. a) Electrochemical cell design; 1) Working electrode (Pt wire), 2) reference electrode (Ag/AgCl, 3M KCl), 3) counter electrode (Pt foil), 4) cell tap, 5) electrochemical cell, 6) 10-mL of sample solution. **b)** Potential change of working electrode as a function of time. y-axis: potential/V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

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

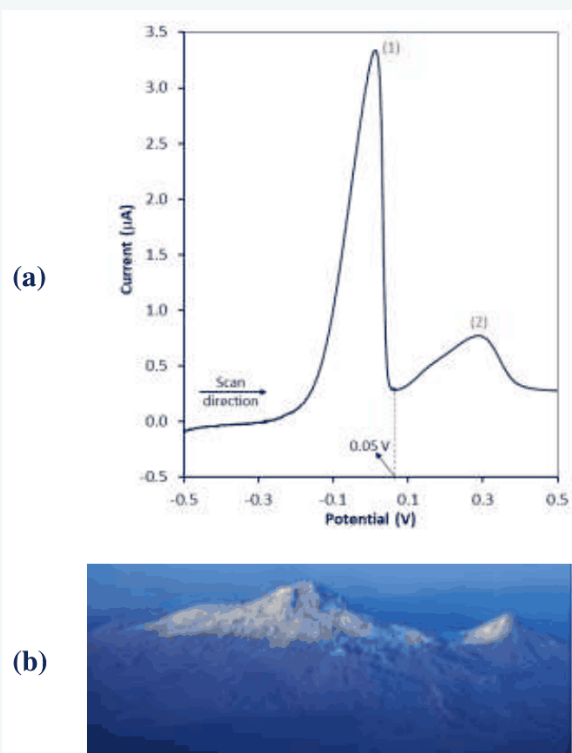


Figure 2. a) Potential scan of the working electrode as a function of current in 0.1 M H_2SO_4 solution after keeping it constant at a potential of -0.50 V in 10-mL of wastewater sample as seen in Figure 1b (horizontal line). y-axis: current/ μA , x-axis: potential/V vs Ag/AgCl, **b)** A view of *Great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

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

assumed that 14 min. is sufficient to complete the expected electrochemical reactions.

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

Step 7) 5-mL of ethylenediaminetetraacetic acid (EDTA, 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 EDTA solution is equivalent to 3.85 mg/mL $BaCO_3$. Then, pH of the solution was adjusted to 10.0. Excess EDTA was titrated with standard 0.0010 M $Ni(NO_3)_2$ solution and it was observed that 95.60 mL of $Ni(NO_3)_2$ solution was consumed up to the endpoint.

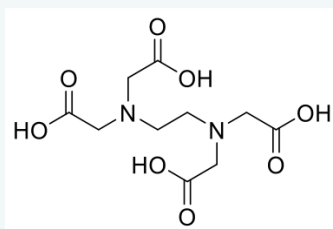


Figure 3. Chemical structure of EDTA (H_4Y).

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

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

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

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

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

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



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

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

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

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

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

Official English text of the problem.

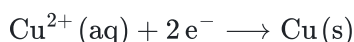
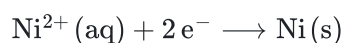
Answers

- **9.1. Fourth box:** peak 1 is nickel oxidation; peak 2 is copper oxidation.
- **9.2. Fifth box:** hydrogen evolution, H_2 , SMILES `[H][H]`.
- **9.3.** $v = +8.33 \text{ mV s}^{-1}$.
- **9.4.** $E_{\text{AgCl/Ag}}^\circ = +0.222 \text{ V}$, relative to the standard hydrogen electrode.
- **9.5. Fifth box:** selective electrochemical stripping of nickel from the copper–nickel deposit into solution.
- **9.6.** Complexation: $\text{Ni}^{2+} + \text{H}_4\text{Y} \longrightarrow [\text{NiY}]^{2-} + 4\text{H}^+$. Back titration, using fully deprotonated EDTA notation: $\text{Ni}^{2+} + \text{Y}^{4-} \longrightarrow [\text{NiY}]^{2-}$. Species names and SMILES are given below.
- **9.7.** $c_{\text{mass}}(\text{Ni}^{2+}) \approx 11.4 \text{ mg L}^{-1}$, or approximately *11 mg L⁻¹* to two significant figures.
- **9.8.** $\text{pH}_{\text{min}} \approx 3.11$.

Solution

9.1. Identification of the stripping peaks

During the deposition step, nickel(II) ions, Ni^{2+} , SMILES `[Ni+2]`, and copper(II) ions, Cu^{2+} , SMILES `[Cu+2]`, are reduced onto the working electrode:

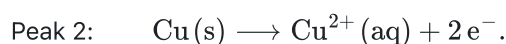


The subsequent scan goes from -0.50 to $+0.50 \text{ V}$: it moves toward **more positive potential**, despite the downward appearance of the line in Figure 1b. The deposited metals are therefore oxidized and stripped into solution.

Nickel has the lower standard reduction potential:

$$E_{\text{Ni}^{2+}/\text{Ni}}^\circ = -0.24 \text{ V} < E_{\text{Cu}^{2+}/\text{Cu}}^\circ = +0.34 \text{ V}.$$

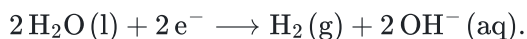
Nickel is consequently oxidized at the earlier, less positive stripping peak, followed by copper:



Thus, **tick the fourth box**.

9.2. Effect of applying -1.2 V

The much more negative working-electrode potential promotes reduction of water and hydrogen evolution:



The species are water, SMILES O; hydrogen, SMILES [H][H]; and hydroxide ion, SMILES [OH-].

Thus, **tick the fifth box: hydrogen evolution.**

9.3. Scan rate

The potential changes by 1.00 V in 2 min = 120 s:

$$v = \frac{\Delta E}{\Delta t} = \frac{(+0.50) - (-0.50)}{120} = 8.333 \times 10^{-3} \text{ V s}^{-1}.$$

Therefore,

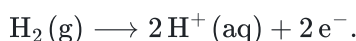
$$v = +8.33 \text{ mV s}^{-1}.$$

The positive sign indicates increasing potential.

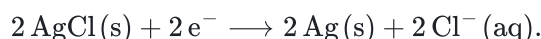
9.4. Standard potential of the silver/silver chloride electrode

Hydrochloric acid supplies hydrogen ions, H^+ , SMILES [H+], and chloride ions, Cl^- , SMILES [Cl-]. Silver(I) chloride has the ionic-component SMILES [Ag+] . [Cl-]; this specifies its constituents, not its crystal lattice.

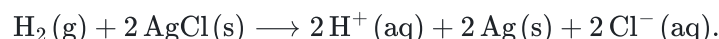
The left-hand electrode undergoes oxidation:



The right-hand electrode undergoes reduction:



The overall cell reaction is therefore



Two electrons are transferred, and the reaction quotient is

$$Q = \frac{a_{\text{H}^+}^2 a_{\text{Cl}^-}^2}{p_{\text{H}_2}/p^\circ}.$$

Taking solution activities as concentrations divided by the standard concentration, and neglecting the small chloride contribution from dissolved silver chloride,

$$a_{\text{H}^+} = a_{\text{Cl}^-} = 1.50 \times 10^{-2}, \quad \frac{p_{\text{H}_2}}{p^\circ} = 0.92.$$

Thus,

$$Q = \frac{(1.50 \times 10^{-2})^4}{0.92} = 5.5027 \times 10^{-8}.$$

Since the standard hydrogen electrode has $E^\circ = 0$,

$$E_{\text{cell}}^\circ = E_{\text{AgCl/Ag}}^\circ.$$

The Nernst equation gives

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{RT}{2F} \ln Q,$$

so, using $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ and $F = 96485 \text{ C mol}^{-1}$,

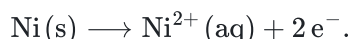
$$\begin{aligned} E_{\text{AgCl/Ag}}^\circ &= 0.437 + \frac{(8.314)(298)}{2(96485)} \ln(5.5027 \times 10^{-8}) \\ &= 0.437 - 0.2146 \\ &= 0.2224 \text{ V}. \end{aligned}$$

Therefore,

$$E_{\text{AgCl/Ag}}^\circ = +0.222 \text{ V vs SHE}.$$

9.5. Purpose of step 5

In Figure 2a, +0.05 V lies after the nickel stripping peak and before the copper stripping peak. Holding the electrode at this potential selectively oxidizes deposited nickel:



Under the problem's stated assumption of complete reaction, nickel is transferred into the fresh acid solution while copper remains on the electrode. This separates nickel for its subsequent determination.

Thus, **tick the fifth box**.

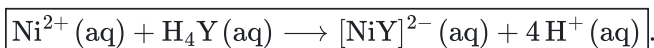
9.6. Complexation and back-titration equations

The ligand and complex are:

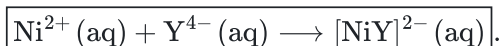
- **Ethylenediaminetetraacetic acid**, H_4Y : O=C(O)CN(CC(=O)O)CCN(CC(=O)O)CC(=O)O
- **Ethylenediaminetetraacetate ion**, Y^{4-} : O=C([O-])CN(CC(=O)[O-])CCN(CC(=O)[O-])CC(=O)[O-]
- **Nickel(II)-EDTA complex**, $[\text{NiY}]^{2-}$, using dative-bond SMILES: [Ni+2]12345<-N(CC(=O)[O-]->1)(CC(=O)[O-]->2)CCN->3(CC(=O)[O-]->4)CC(=O)[O-]->5

EDTA coordinates through its two amine nitrogen atoms and one oxygen atom from each of its four carboxylate groups. This gives an approximately octahedral nickel coordination environment. The SMILES specifies donor connectivity; no particular coordination stereoisomer or conformation is selected.

For complexation of the sample nickel, written with the acid specified in the problem,



For back titration of the excess EDTA, written using the fully deprotonated ligand,



These are alternative protonation conventions for the same underlying complex formation. The second equation does not require all uncomplexed EDTA to exist as Y^{4-} at pH 10; protonation equilibria accompany complexation.

Crucially, **one mole of nickel(II) consumes one mole of EDTA** in both stages.

9.7. Nickel concentration in the wastewater

Interpret the EDTA standardization as 3.85 mg of barium carbonate equivalent per millilitre of EDTA solution.

Barium carbonate, BaCO_3 , has ionic-component SMILES [Ba+2].[O-]C(=O)[O-]. Each mole contains one mole of barium(II) ion, [Ba+2], corresponding to one mole of EDTA in a 1:1 metal-EDTA complex.

Using

$$M(\text{BaCO}_3) = 197.34 \text{ g mol}^{-1}, \quad M(\text{Ni}) = 58.69 \text{ g mol}^{-1},$$

the EDTA concentration is

$$c_{\text{EDTA}} = \frac{3.85 \times 10^{-3} \text{ g} / (197.34 \text{ g mol}^{-1})}{1.00 \times 10^{-3} \text{ L}} = 0.0195095 \text{ mol L}^{-1}.$$

The amount added in 5 mL is

$$n_{\text{EDTA,added}} = (0.005 \text{ L})(0.0195095 \text{ mol L}^{-1}) = 9.75474 \times 10^{-5} \text{ mol}.$$

The back titration measures the unconsumed EDTA:

$$\begin{aligned} n_{\text{EDTA,excess}} &= n_{\text{Ni,titrant}} \\ &= (0.09560 \text{ L})(0.0010 \text{ mol L}^{-1}) \\ &= 9.560 \times 10^{-5} \text{ mol}. \end{aligned}$$

Keeping guard digits in the subtraction, the nickel recovered from the wastewater aliquot is

$$\begin{aligned}
 n_{\text{Ni, sample}} &= n_{\text{EDTA, added}} - n_{\text{EDTA, excess}} \\
 &= 9.75474 \times 10^{-5} - 9.560 \times 10^{-5} \\
 &= 1.9474 \times 10^{-6} \text{ mol.}
 \end{aligned}$$

This nickel came from 10 mL = 0.010 L of wastewater. Hence,

$$\begin{aligned}
 c_{\text{mass}}(\text{Ni}^{2+}) &= \frac{(1.9474 \times 10^{-6} \text{ mol})(58.69 \text{ g mol}^{-1})(10^3 \text{ mg g}^{-1})}{0.010 \text{ L}} \\
 &= 11.429 \text{ mg L}^{-1}.
 \end{aligned}$$

Thus the nominal calculated result is

$$c_{\text{mass}}(\text{Ni}^{2+}) \approx 11.4 \text{ mg L}^{-1},$$

or approximately 11 mg L⁻¹ to two significant figures.

The 100-mL beaker does **not** introduce a dilution factor: five 10-mL portions were mixed, with no instruction to dilute them to 100 mL. The result represents the pooled wastewater sample.

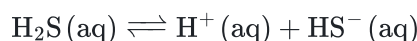
9.8. Minimum pH for nickel sulfide precipitation

The nickel recovered in step 5 is contained in 10 mL, so its concentration before precipitation is

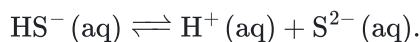
$$[\text{Ni}^{2+}] = \frac{1.9474 \times 10^{-6} \text{ mol}}{0.010 \text{ L}} = 1.9474 \times 10^{-4} \text{ mol L}^{-1}.$$

The sulfur species are hydrogen sulfide, H₂S, SMILES s; hydrosulfide ion, HS⁻, SMILES [SH-]; and sulfide ion, S²⁻, SMILES [S-2].

Their acid-dissociation equilibria are



and



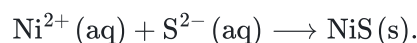
Multiplying the two equilibrium expressions gives

$$K_{a1}K_{a2} = \frac{[\text{H}^+]^2[\text{S}^{2-}]}{[\text{H}_2\text{S}]}.$$

Therefore,

$$[\text{S}^{2-}] = \frac{K_{a1}K_{a2}[\text{H}_2\text{S}]}{[\text{H}^+]^2}.$$

Nickel(II) sulfide, NiS, has ionic-component SMILES [Ni+2].[S-2]; its precipitation reaction is



At the onset of precipitation,

$$[\text{Ni}^{2+}][\text{S}^{2-}] = K_{\text{sp}}.$$

Thus the required sulfide concentration is

$$[\text{S}^{2-}]_{\text{crit}} = \frac{4.0 \times 10^{-20}}{1.9474 \times 10^{-4}} = 2.0540 \times 10^{-16} \text{ mol L}^{-1}.$$

Using the specified saturated concentration [H₂S] = 0.1 M,

$$\begin{aligned}
 &= \sqrt{\frac{K_{a1}K_{a2}[\text{H}_2\text{S}]}{[\text{S}^{2-}]_{\text{crit}}}} \\
 &= \sqrt{\frac{(9.6 \times 10^{-8})(1.3 \times 10^{-14})(0.1)}{2.0540 \times 10^{-16}}} \\
 &= 7.7948 \times 10^{-4} \text{ mol L}^{-1}.
 \end{aligned}$$

Consequently,

$$\text{pH}_{\min} = -\log_{10}(7.7948 \times 10^{-4}) = 3.108 \approx 3.11.$$

Increasing the pH increases the sulfide concentration, so precipitation becomes favorable above this threshold. The copper sulfide solubility product is unnecessary because step 5 selectively transfers nickel into the solution.

The solution was checked against the official solution. Where this solution differs from the official solution, the official solution contains an error or a misprint.