

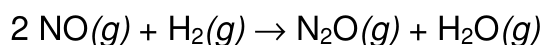
IChO 2011

Theory problems and solutions · Ankara, Turkey · 8 theory problems with complete solutions

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Problem 1: Kinetics of the reaction of nitric oxide with hydrogen

Nitrogen oxides, common pollutants in the ambient air, are primarily nitric oxide, NO, and nitrogen dioxide, NO₂. Atmospheric nitric oxide is produced mainly during thunderstorms and in the internal combustion engines. At high temperatures NO reacts with H₂ to produce nitrous oxide, N₂O, a greenhouse gas.



To study the kinetics of this reaction at 820 °C, initial rates for the formation of N₂O were measured using various initial partial pressures of NO and H₂.

Exp.	Initial pressure, torr: <i>p</i> _{NO}	Initial pressure, torr: <i>p</i> _{H₂}	Initial rate of production of N ₂ O, torr s ⁻¹
1	120.0	60.0	8.66 · 10 ⁻²
2	60.0	60.0	2.17 · 10 ⁻²
3	60.0	180.0	6.62 · 10 ⁻²

Throughout this problem do not use concentrations. Use units of pressure (torr) and time in seconds.

1.1 Determine the experimental rate law and calculate the rate constant.

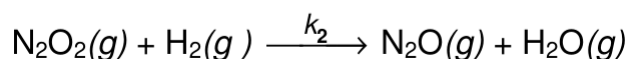
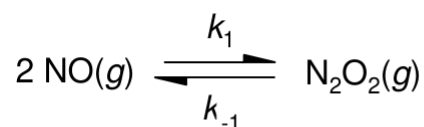
1.2 Calculate the initial rate of disappearance of NO, if NO with a pressure of 2.00 · 10² torr and H₂ with 1.00 · 10² torr are mixed at 820 °C.

(If you have been unable to calculate the value for the rate constant, you can use the value of 2 · 10⁻⁷ in appropriate unit.)

1.3 Calculate the time elapsed to reduce the partial pressure of H₂ to the half of its initial value, if NO with a pressure of 8.00 · 10² torr and H₂ with 1.0 torr are mixed at 820 °C.

(If you have been unable to calculate the value for the rate constant, you can use the value of 2 · 10⁻⁷ in appropriate unit.)

A proposed mechanism for the reaction between NO and H₂ is given below:



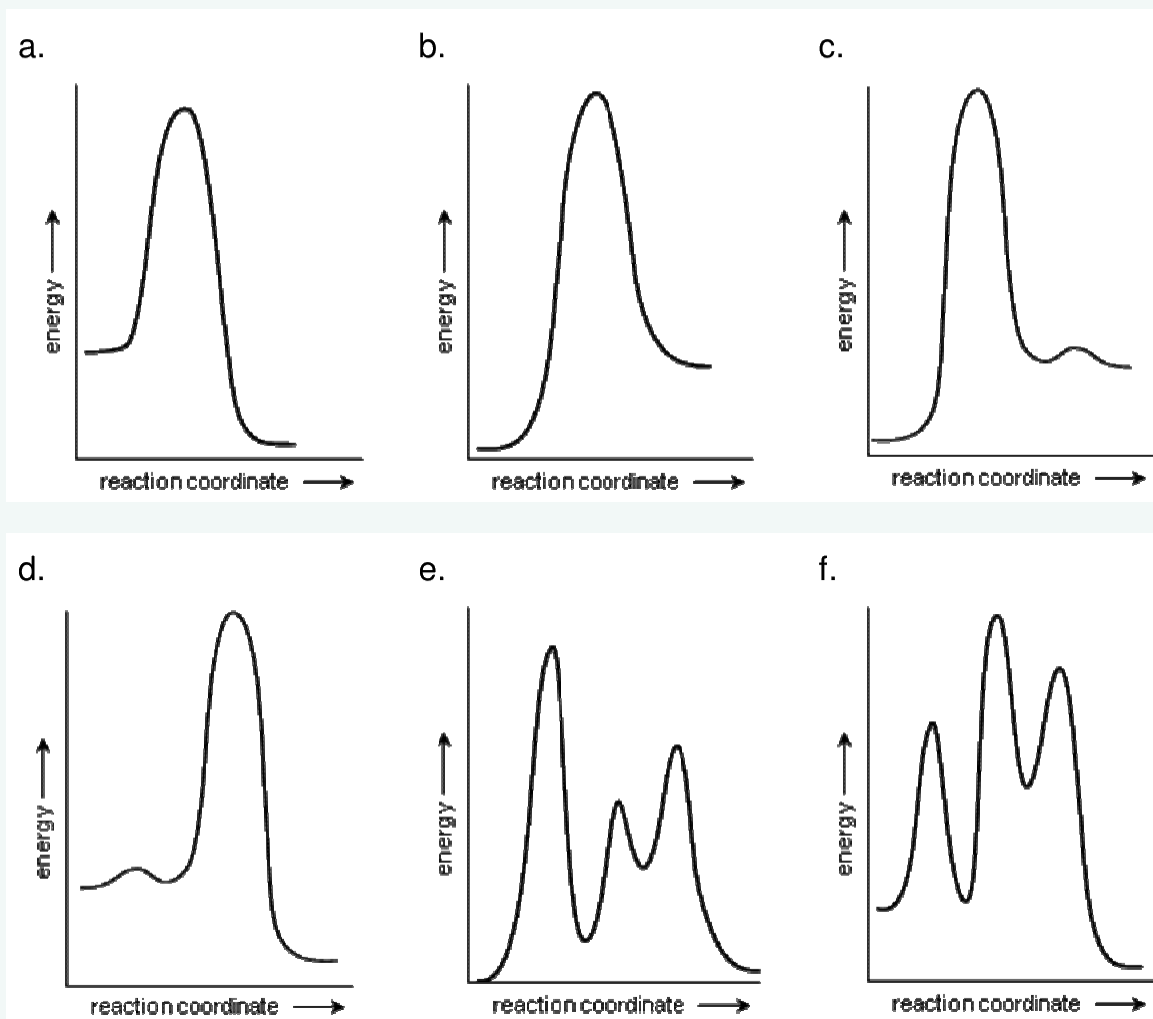
1.4 Derive the rate law for the formation of N_2O from the proposed mechanism using the steady-state approximation for the intermediate.

1.5 Under what condition does this rate law reduce to the experimentally determined rate law found in Part 1.1? Tick the relevant answer.

- ☐ If $k_{-1} \ll k_2 p_{\text{H}_2}$
- ☐ If $k_{-1} \gg k_2 p_{\text{H}_2}$
- ☐ If $k_{-1} > k_2$
- ☐ If $k_1 > k_{-1}$

1.6 Express the experimentally determined rate constant k in terms of k_1 , k_{-1} and k_2 .

1.7 Select the schematic energy diagram that is consistent with the proposed reaction mechanism and experimental rate law.



Answers

- 1.1

$$r = \frac{dp_{\text{N}_2\text{O}}}{dt} = kp_{\text{NO}}^2 p_{\text{H}_2}, \quad k \approx 1.0 \times 10^{-7} \text{ torr}^{-2} \text{ s}^{-1}.$$

Second order in NO, first order in H₂, third order overall.

- 1.2

$$-\left. \frac{dp_{\text{NO}}}{dt} \right|_0 \approx 0.80 \text{ torr s}^{-1}.$$

- 1.3

$$t_{1/2} \approx 11 \text{ s}$$

(10.8 s using the large-excess approximation).

- 1.4

$$\frac{dp_{\text{N}_2\text{O}}}{dt} = \frac{k_1 k_2 p_{\text{NO}}^2 p_{\text{H}_2}}{k_{-1} + k_2 p_{\text{H}_2}}.$$

- 1.5 Tick the **second option**:

$$k_{-1} \gg k_2 p_{\text{H}_2}.$$

- 1.6

$$k = \frac{k_1 k_2}{k_{-1}}.$$

- 1.7 Diagram d.

Solution

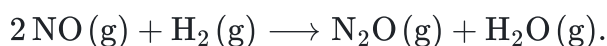
The molecular names and SMILES used here are:

Formula	Name	SMILES
NO	Nitric oxide	[N]=O
NO ₂	Nitrogen dioxide	O=[N+][O-]
H ₂	Hydrogen	[H][H]
N ₂ O	Nitrous oxide	N#[N+][O-]
H ₂ O	Water	O
N ₂ O ₂	Dinitrogen dioxide, the nitric oxide dimer	O=NN=O

The dimer SMILES represents its connectivity; the problem does not specify its conformation.

1.1

The balanced overall reaction is



Using partial pressures at constant temperature and volume, define

$$r = \frac{dp_{\text{N}_2\text{O}}}{dt} = -\frac{dp_{\text{H}_2}}{dt} = -\frac{1}{2} \frac{dp_{\text{NO}}}{dt}.$$

Assume an experimental rate law

$$r = kp_{\text{NO}}^m p_{\text{H}_2}^n.$$

Experiments 1 and 2 have the same hydrogen pressure. Therefore,

$$\frac{r_1}{r_2} = \frac{8.66 \times 10^{-2}}{2.17 \times 10^{-2}} = 3.99 = \left(\frac{120.0}{60.0} \right)^m.$$

Thus $m \approx 2$.

Experiments 2 and 3 have the same nitric oxide pressure:

$$\frac{r_3}{r_2} = \frac{6.62 \times 10^{-2}}{2.17 \times 10^{-2}} = 3.05 = \left(\frac{180.0}{60.0} \right)^n.$$

Thus $n \approx 1$. The integer-order law supported by the data is consequently

$$r = kp_{\text{NO}}^2 p_{\text{H}_2}.$$

Using experiment 1,

$$k = \frac{8.66 \times 10^{-2} \text{ torr s}^{-1}}{(120.0 \text{ torr})^2 (60.0 \text{ torr})} = 1.0023 \times 10^{-7} \text{ torr}^{-2} \text{ s}^{-1}.$$

Experiments 2 and 3 give 1.0046×10^{-7} and $1.0216 \times 10^{-7} \text{ torr}^{-2} \text{ s}^{-1}$, respectively. Allowing for the small scatter,

$$k \approx 1.0 \times 10^{-7} \text{ torr}^{-2} \text{ s}^{-1}.$$

The following numerical calculations use $k = 1.00 \times 10^{-7} \text{ torr}^{-2} \text{ s}^{-1}$.

1.2

Two molecules of nitric oxide disappear for every molecule of nitrous oxide produced. Hence,

$$-\frac{dp_{\text{NO}}}{dt} \Big|_0 = 2kp_{\text{NO},0}^2 p_{\text{H}_2,0}.$$

Substitution gives

$$\begin{aligned} -\frac{dp_{\text{NO}}}{dt} \Big|_0 &= 2(1.00 \times 10^{-7} \text{ torr}^{-2} \text{ s}^{-1})(2.00 \times 10^2 \text{ torr})^2 (1.00 \times 10^2 \text{ torr}) \\ &= \boxed{0.80 \text{ torr s}^{-1}}. \end{aligned}$$

1.3

Hydrogen initially has a pressure of 1.0 torr, whereas nitric oxide has 800 torr. When the hydrogen pressure falls to 0.50 torr, the nitric oxide pressure decreases by only

$$2(1.0 - 0.50) = 1.0 \text{ torr}.$$

Thus p_{NO} changes from 800 to 799 torr, so treating it as constant is an excellent approximation.

The hydrogen disappearance law becomes

$$-\frac{dp_{\text{H}_2}}{dt} = kp_{\text{NO}}^2 p_{\text{H}_2} \approx k_{\text{obs}} p_{\text{H}_2},$$

where

$$k_{\text{obs}} = (1.00 \times 10^{-7})(800)^2 \text{ s}^{-1} = 0.0640 \text{ s}^{-1}.$$

Integration gives

$$\ln\left(\frac{p_{\text{H}_2,0}}{p_{\text{H}_2}}\right) = k_{\text{obs}} t.$$

At half the initial hydrogen pressure,

$$t_{1/2} = \frac{\ln 2}{0.0640 \text{ s}^{-1}} = 10.8 \text{ s} \approx \boxed{11 \text{ s}}.$$

As a check, retaining the small nitric oxide depletion gives

$$p_{\text{NO}} = 798.0 \text{ torr} + 2p_{\text{H}_2},$$

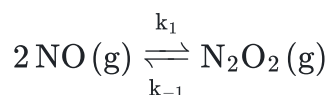
and therefore

$$t_{1/2} = \frac{1}{k} \int_{0.50 \text{ torr}}^{1.0 \text{ torr}} \frac{dp}{p(798.0 \text{ torr} + 2p)^2} = 10.85 \text{ s}.$$

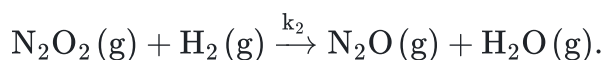
This differs from the large-excess approximation by only 0.14%.

1.4

The two elementary steps are



and



The intermediate is dinitrogen dioxide. Its pressure changes according to

$$\frac{dp_{\text{N}_2\text{O}_2}}{dt} = k_1 p_{\text{NO}}^2 - k_{-1} p_{\text{N}_2\text{O}_2} - k_2 p_{\text{N}_2\text{O}_2} p_{\text{H}_2}.$$

Under the steady-state approximation, its formation and consumption rates approximately balance:

$$0 \approx k_1 p_{\text{NO}}^2 - (k_{-1} + k_2 p_{\text{H}_2}) p_{\text{N}_2\text{O}_2}.$$

Consequently,

$$p_{\text{N}_2\text{O}_2} \approx \frac{k_1 p_{\text{NO}}^2}{k_{-1} + k_2 p_{\text{H}_2}}.$$

Nitrous oxide is formed in the second step, giving

$$\frac{dp_{\text{N}_2\text{O}}}{dt} = k_2 p_{\text{N}_2\text{O}_2} p_{\text{H}_2} = \boxed{\frac{k_1 k_2 p_{\text{NO}}^2 p_{\text{H}_2}}{k_{-1} + k_2 p_{\text{H}_2}}}.$$

1.5

To recover a first-order dependence on hydrogen, the denominator must be approximately independent of its pressure. This requires

$$k_{-1} \gg k_2 p_{\text{H}_2}.$$

Then

$$r \approx \frac{k_1 k_2}{k_{-1}} p_{\text{NO}}^2 p_{\text{H}_2},$$

which matches the experimental law. Thus the **second checkbox** should be ticked.

Physically, the intermediate dissociates back into nitric oxide much faster than it reacts with hydrogen. Under the opposite limiting condition, the hydrogen pressure would cancel from the rate law, giving $r \approx k_1 p_{\text{NO}}^2$, contrary to experiment.

1.6

Comparing

$$r \approx \frac{k_1 k_2}{k_{-1}} p_{\text{NO}}^2 p_{\text{H}_2}$$

with the experimental expression gives

$$k = \frac{k_1 k_2}{k_{-1}}.$$

Here k_1 and k_2 have units $\text{torr}^{-1} \text{s}^{-1}$, while k_{-1} has units s^{-1} . Their combination therefore has the required units $\text{torr}^{-2} \text{s}^{-1}$.

1.7

The correct choice is **diagram d**.

Two elementary steps require two transition-state maxima separated by an intermediate minimum. Among the proposed diagrams, c and d have this form.

In diagram d, the barrier from the intermediate back to the reactants is small, while the barrier from the intermediate toward products is much larger. This is consistent with

$$k_{-1} \gg k_2 p_{\text{H}_2},$$

and hence with the observed rate law.

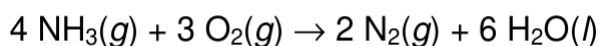
Precisely, diagram d starts at the reactant energy, rises over a small first maximum, falls into a shallow intermediate minimum, rises to a much higher second maximum, and finally falls to products below the reactants.

The solution was checked against the official solution.

Problem 2: Combustion of ammonia

Anhydrous ammonia is an ultra-clean, energy-dense alternative liquid fuel. It produces no greenhouse gases on combustion.

In an experiment, gaseous NH_3 is burned with O_2 in a container of fixed volume according to the equation given below.



The initial and final states are at 298 K. After combustion with 14.40 g of O_2 , some of NH_3 remains unreacted.

2.1 Calculate the heat released during the process.

$$\Delta_f H^\circ(\text{NH}_3(g)) = -46.11 \text{ kJ mol}^{-1} \quad \text{and} \quad \Delta_f H^\circ(\text{H}_2\text{O}(l)) = -285.83 \text{ kJ mol}^{-1}$$

To determine the amount of NH_3 gas dissolved in water, produced during the combustion process, a 10.00 cm^3 sample of the aqueous solution was withdrawn from the reaction vessel and added to 15.0 cm^3 of a H_2SO_4 solution ($c = 0.0100 \text{ mol dm}^{-3}$). The resulting solution was titrated with a standard NaOH solution ($c = 0.0200 \text{ mol dm}^{-3}$) and the equivalence point was reached at 10.64 cm^3 .

$$(K_b(\text{NH}_3) = 1.8 \cdot 10^{-5}; \quad K_a(\text{HSO}_4^-) = 1.1 \cdot 10^{-2})$$

2.2 Calculate pH of the solution in the container after combustion.

2.3 At the end point of titration, NH_4^+ and SO_4^{2-} ions are present in the solution. Write the equations for the relevant equilibria to show how the presence of these two ions affects the pH and calculate their equilibrium constant(s).

2.4 Tick the correct statement for the pH of the solution at the equivalence point.

☐ $\text{pH} > 7$ ☐ $\text{pH} = 7$ ☐ $\text{pH} < 7$

Official English text of the problem.

Answers

- 2.1:** Heat released: 227.7 kJ . Thus $q_V = -227.7 \text{ kJ}$ for the reacting system.
- 2.2:** $\text{pH} = 10.59 \approx 10.6$. The usual weak-base approximation gives 10.60.
- 2.3:** Ammonium ion, $[\text{NH}_4^+]$, undergoes acidic hydrolysis with $K_a = 5.6 \times 10^{-10}$. Sulfate ion, $[\text{O}^-]\text{S}(=\text{O})(=\text{O})[\text{O}^-]$, undergoes basic hydrolysis with $K_b = 9.1 \times 10^{-13}$. The balanced equilibria are given below.
- 2.4:** Tick $\text{pH} < 7$.

Solution

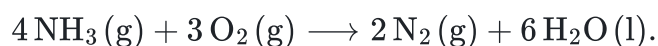
The chemical species used below have the following names and SMILES. Physical states are indicated in the equations; SMILES do not specify physical state.

Formula	Name	SMILES
NH_3	Ammonia	N
O_2	Dioxygen	O=O

Formula	Name	SMILES
N ₂	Dinitrogen	N#N
H ₂ O	Water	O
H ₂ SO ₄	Sulfuric acid	OS(=O)(=O)O
NaOH	Sodium hydroxide	[Na+] . [OH-]
NH ₄ ⁺	Ammonium ion	[NH4+]
SO ₄ ²⁻	Sulfate ion	[O-]S(=O)(=O)[O-]
HSO ₄ ⁻	Hydrogen sulfate ion	OS(=O)(=O)[O-]
H ₃ O ⁺	Hydronium ion	[OH3+]
OH ⁻	Hydroxide ion	[OH-]

2.1 — Heat released at constant volume

The balanced combustion equation is



Since ammonia remains unreacted, oxygen is the limiting reagent and is completely consumed:

$$n(\text{O}_2) = \frac{14.40 \text{ g}}{32.00 \text{ g mol}^{-1}} = 0.4500 \text{ mol}.$$

The reaction extent is therefore

$$\xi = \frac{0.4500}{3} = 0.1500 \text{ mol}.$$

The standard formation enthalpies of elemental N₂(g) and O₂(g) are zero. Thus, per mole of reaction as written,

$$\begin{aligned} \Delta_r H^\circ &= 6\Delta_f H^\circ(\text{H}_2\text{O}(\text{l})) - 4\Delta_f H^\circ(\text{NH}_3(\text{g})) \\ &= 6(-285.83) - 4(-46.11) \\ &= -1530.54 \text{ kJ mol}^{-1}. \end{aligned}$$

At constant volume, with only pressure–volume work, the heat equals the internal-energy change. Using ideal-gas behavior and neglecting the liquid's pV contribution,

$$\Delta_r U^\circ = \Delta_r H^\circ - \Delta \nu_g RT.$$

Water is liquid, so the change in gaseous stoichiometric coefficients is

$$\Delta \nu_g = 2 - (4 + 3) = -5.$$

Consequently,

$$\begin{aligned} \Delta_r U^\circ &= -1530.54 - (-5)(8.314 \times 10^{-3})(298) \\ &= -1518.15 \text{ kJ mol}^{-1}, \end{aligned}$$

and

$$q_V = \xi \Delta_r U^\circ = (0.1500)(-1518.15) = -227.7 \text{ kJ}.$$

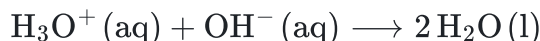
Therefore, the **heat released is 227.7 kJ**.

2.2 — pH of the solution after combustion

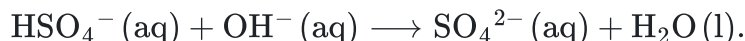
Sulfuric acid supplies two acid equivalents per mole. Ammonia consumes one acid equivalent per mole; the overall neutralization is



The excess acid is then neutralized by hydroxide during the back titration, through reactions including



and



The initial amount of sulfuric acid is

$$n(\text{H}_2\text{SO}_4) = (0.0100)(15.0 \times 10^{-3}) = 1.50 \times 10^{-4} \text{ mol}.$$

The amount of hydroxide used is

$$n(\text{OH}^-) = (0.0200)(10.64 \times 10^{-3}) = 2.128 \times 10^{-4} \text{ mol}.$$

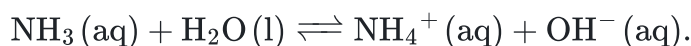
Hence the total amount of dissolved ammonia in the aliquot is

$$\begin{aligned} n_{\text{ammonia}} &= 2n(\text{H}_2\text{SO}_4) - n(\text{OH}^-) \\ &= 3.00 \times 10^{-4} - 2.128 \times 10^{-4} \\ &= 8.72 \times 10^{-5} \text{ mol}. \end{aligned}$$

Its analytical concentration in the original solution is

$$C = \frac{8.72 \times 10^{-5}}{10.00 \times 10^{-3}} = 8.72 \times 10^{-3} \text{ mol dm}^{-3}.$$

Ammonia establishes the equilibrium



Neglecting water's small contribution to the hydroxide concentration, let

$$x = [\text{OH}^-] = [\text{NH}_4^+], \quad [\text{NH}_3] = C - x.$$

Then

$$K_b = \frac{x^2}{C - x} = 1.8 \times 10^{-5},$$

so

$$x = \frac{-K_b + \sqrt{K_b^2 + 4K_bC}}{2} = 3.8728 \times 10^{-4} \text{ mol dm}^{-3}.$$

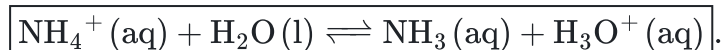
Using $K_w = 1.0 \times 10^{-14}$ at 298 K,

$$\text{pOH} = 3.412, \quad \boxed{\text{pH} = 14.00 - 3.412 = 10.59}.$$

The approximation $x \approx \sqrt{K_b C}$ gives $\text{pH} = 10.60$, consistent with reporting the result as approximately 10.6.

2.3 — Hydrolysis equilibria and their constants

Ammonium is the conjugate acid of ammonia. It produces hydronium ions and therefore lowers the pH:



Its acid-dissociation constant is

$$\boxed{K_a(\text{NH}_4^+) = \frac{K_w}{K_b(\text{NH}_3)} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}}.$$

Sulfate is the conjugate base of hydrogen sulfate. It produces hydroxide ions and therefore raises the pH:



Its base-dissociation constant is

$$\boxed{K_b(\text{SO}_4^{2-}) = \frac{K_w}{K_a(\text{HSO}_4^-)} = \frac{1.0 \times 10^{-14}}{1.1 \times 10^{-2}} = 9.1 \times 10^{-13}}.$$

2.4 — pH at the equivalence point

The acidic hydrolysis constant of ammonium is approximately

$$\frac{K_a(\text{NH}_4^+)}{K_b(\text{SO}_4^{2-})} \approx 6.1 \times 10^2$$

times the basic hydrolysis constant of sulfate.

Their analytical amounts are comparable: the sulfate-to-ammonium ratio is only

$$\frac{1.50 \times 10^{-4}}{8.72 \times 10^{-5}} = 1.72.$$

Thus ammonium's acidic effect dominates sulfate's basic effect. Tick the **third box**:

$$\boxed{\text{pH} < 7}.$$

The solution was checked against the official solution.

Problem 3: Isotope effects in diatomic molecules

At a temperature of 0 K, the total energy of a gaseous diatomic molecule AB is approximately given by:

$$E = E_o + E_{\text{vib}}$$

where E_o is the electronic energy of the ground state, and E_{vib} is the vibrational energy.

Allowed values of the vibrational energies are given by the expression:

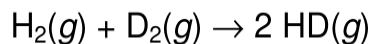
$$E_{\text{vib}} = \left(\nu + \frac{1}{2}\right)\varepsilon \quad \nu = 0, 1, 2, \dots \quad \varepsilon = \frac{h}{2\pi} \sqrt{\frac{k}{\mu}} \quad \mu(\text{AB}) = \frac{m_A m_B}{m_A + m_B}$$

where h is the Planck's constant, ν is the vibrational quantum number, k is the force constant, and μ is the reduced mass of the molecule. At 0 K, it may be safely assumed that ν is zero, and E_o and k are independent of isotopic substitution in the molecule.

Deuterium, D, is an isotope of hydrogen atom with mass number 2. For the H_2 molecule, k is 575.11 N m^{-1} , and the isotopic molar masses of H and D are 1.0078 and $2.0141 \text{ g mol}^{-1}$, respectively.

At a temperature of 0 K: $\varepsilon_{\text{H}_2} = 1.1546 \varepsilon_{\text{HD}}$ and $\varepsilon_{\text{D}_2} = 0.8167 \varepsilon_{\text{HD}}$.

3.1 Calculate the enthalpy change, ΔH , in $\text{kJ} \cdot \text{mol}^{-1}$ for the following reaction at 0 K:



3.2 Calculate the frequency in s^{-1} of infrared photons that can be absorbed by HD molecule.

(If you have been unable to calculate the value for ε_{HD} then use $8.000 \cdot 10^{-20} \text{ J}$ for the calculation.)

The allowed electronic energies of H atom are given by the expression:

$$E = -\frac{R_H}{n^2}, \quad n = 1, 2, \dots \quad \text{where } R_H = 13.5984 \text{ eV, and } 1 \text{ eV} = 1.602 \cdot 10^{-19} \text{ J}$$

The total energy of H_2 molecule in its ground state is -31.675 eV , relative to the same reference as that of hydrogen atom.

3.3 Calculate the dissociation energy, DE, in eV of a hydrogen molecule in its ground state such that both H atoms are produced in their ground states.

3.4 A molecule H_2 in the ground state dissociates into its atoms after absorbing a photon of wavelength 77.0 nm . Determine all possibilities for the electronic states of hydrogen atoms produced. For each case calculate the total kinetic energy, KE, in eV of the dissociated hydrogen atoms.

3.5 Calculate the electron affinity, EA, of H_2^+ ion in eV if its dissociation energy is 2.650 eV . If you have been unable to calculate the value for the dissociation energy of H_2 then use 4.500 eV for the calculation.)

Official English text of the problem.

Answers

- **3.1:** For $\text{H}_2(\text{g}) + \text{D}_2(\text{g}) \rightarrow 2 \text{HD}(\text{g})$, $\Delta H = +0.6544 \text{ kJ mol}^{-1}$.
- **3.2:** $f = 1.143 \times 10^{14} \text{ s}^{-1}$.
- **3.3:** $\text{DE} = 4.478 \text{ eV}$.
- **3.4:** The possible principal quantum numbers are $(n_A, n_B) = (1, 1)$, with total $\text{KE} \approx 11.63 \text{ eV}$, and $(1, 2)$ or $(2, 1)$, with total $\text{KE} \approx 1.43 \text{ eV}$.
- **3.5:** $\text{EA}(\text{H}_2^+) = 15.427 \text{ eV}$, the energy released in $\text{H}_2^+ + \text{e}^- \rightarrow \text{H}_2$.

Solution

The numerical values of h , N_A , and c are not printed in the supplied excerpt. We use their standard SI values:

$h = 6.62607015 \times 10^{-34} \text{ J s}$, $N_A = 6.02214076 \times 10^{23} \text{ mol}^{-1}$, $c = 299792458 \text{ m s}^{-1}$, together with the supplied conversion $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$.

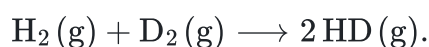
The species used below have the following names and SMILES:

Species	Name	SMILES
H_2	Dihydrogen, containing two protium atoms	[1H][1H]
D_2	Dideuterium	[2H][2H]
HD	Hydrogen deuteride	[1H][2H]
H_2^+	Dihydrogen radical cation	[H][H+]
H	Hydrogen atom	[H]
H^+	Hydrogen ion, a proton	[H+]

These SMILES do not specify vibrational or atomic electronic states. For H_2^+ , the SMILES gives a formal connectivity and charge representation; its actual bond contains one delocalized electron and has bond order $1/2$.

3.1

The balanced isotope-exchange reaction is



First calculate the reduced mass of one HD molecule:

$$\begin{aligned} \mu_{\text{HD}} &= \frac{M_{\text{H}} M_{\text{D}}}{M_{\text{H}} + M_{\text{D}}} \frac{1}{N_A} \\ &= \frac{(1.0078)(2.0141)}{1.0078 + 2.0141} \frac{10^{-3} \text{ kg mol}^{-1}}{6.02214076 \times 10^{23} \text{ mol}^{-1}} \\ &= 1.11538 \times 10^{-27} \text{ kg}. \end{aligned}$$

Since the force constant is independent of isotopic substitution,

$$\begin{aligned} \varepsilon_{\text{HD}} &= \frac{h}{2\pi} \sqrt{\frac{k}{\mu_{\text{HD}}}} \\ &= \frac{6.62607015 \times 10^{-34} \text{ J s}}{2\pi} \sqrt{\frac{575.11 \text{ N m}^{-1}}{1.11538 \times 10^{-27} \text{ kg}}} \\ &= 7.57250 \times 10^{-20} \text{ J}. \end{aligned}$$

At 0 K, each molecule has vibrational energy $\varepsilon/2$. The electronic contributions cancel because all three isotopic molecules have the same E_0 . Also, $\Delta H = \Delta U$: the ideal-gas correction $\Delta n_g RT$ vanishes.

Thus, per mole of reaction as written,

$$\begin{aligned}
\Delta H &= \frac{N_A}{2}(2\varepsilon_{\text{HD}} - \varepsilon_{\text{H}_2} - \varepsilon_{\text{D}_2}) \\
&= \frac{N_A \varepsilon_{\text{HD}}}{2}(2 - 1.1546 - 0.8167) \\
&= (6.02214076 \times 10^{23})(7.57250 \times 10^{-20})(0.01435) \text{ J mol}^{-1} \\
&= \boxed{+0.6544 \text{ kJ mol}^{-1}}.
\end{aligned}$$

The reaction is endothermic because the products have the higher combined zero-point vibrational energy.

3.2

For the harmonic oscillator, the fundamental absorption takes the molecule from $\nu = 0$ to $\nu = 1$. Its energy is

$$\Delta E = \left(\frac{3}{2} - \frac{1}{2} \right) \varepsilon_{\text{HD}} = \varepsilon_{\text{HD}}.$$

Writing the photon frequency as f , to distinguish it from the vibrational quantum number ν ,

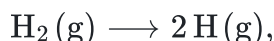
$$hf = \varepsilon_{\text{HD}}.$$

Therefore,

$$f = \frac{7.57250 \times 10^{-20} \text{ J}}{6.62607015 \times 10^{-34} \text{ J s}} = \boxed{1.143 \times 10^{14} \text{ s}^{-1}}.$$

3.3

The dissociation reaction is



with both product atoms in $n = 1$. Each ground-state atom has energy

$$E_1 = -R_H = -13.5984 \text{ eV}.$$

The quoted molecular energy already includes its ground-state vibrational contribution. Hence

$$\begin{aligned}
\text{DE} &= 2E_1 - E(\text{H}_2) \\
&= 2(-13.5984) - (-31.675) \\
&= 4.4782 \text{ eV} \\
&\approx \boxed{4.478 \text{ eV}}.
\end{aligned}$$

3.4

The photodissociation reaction is



The absorbed photon has energy

$$\begin{aligned}
E_\gamma &= \frac{hc}{\lambda} \\
&= \frac{(6.62607015 \times 10^{-34})(299792458)}{77.0 \times 10^{-9}} \text{ J} \\
&= 16.1036 \text{ eV}.
\end{aligned}$$

After dissociation into two ground-state atoms, the available excess energy would be

$$Q = E_\gamma - DE = 16.1036 - 4.4782 = 11.6254 \text{ eV}.$$

Exciting an atom from $n = 1$ to n requires

$$E_{\text{exc}}(n) = R_H \left(1 - \frac{1}{n^2} \right).$$

Thus, for product states n_A, n_B ,

$$\text{KE} = Q - R_H \left(1 - \frac{1}{n_A^2} \right) - R_H \left(1 - \frac{1}{n_B^2} \right) \geq 0.$$

The first two excitation energies are

$$E_{\text{exc}}(2) = 13.5984 \left(1 - \frac{1}{4} \right) = 10.1988 \text{ eV},$$

$$E_{\text{exc}}(3) = 13.5984 \left(1 - \frac{1}{9} \right) = 12.0875 \text{ eV}.$$

One atom can therefore reach $n = 2$, but $n = 3$ or higher is inaccessible. Exciting both atoms requires at least

$$2E_{\text{exc}}(2) = 20.3976 \text{ eV} > Q,$$

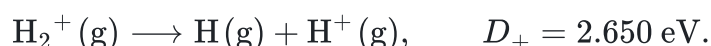
so at least one atom must remain in its ground state.

Product states (n_A, n_B)	Total atomic electronic energy	Total kinetic energy
(1, 1)	-27.1968 eV	11.6254 eV $\approx$ 11.63 eV
(1, 2) or (2, 1)	-16.9980 eV	11.6254 - 10.1988 = 1.4266 eV $\approx$ 1.43 eV

Interchanging the two identical hydrogen atoms does not create a distinct physical outcome. The supplied energy model identifies electronic states by their principal quantum number n .

3.5

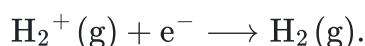
The molecular ion dissociates according to



Take a separated proton and free electron as the zero of electronic energy, consistently with the supplied hydrogen-atom energy formula. Then

$$\begin{aligned} E(\text{H}_2^+) &= E(\text{H}) + E(\text{H}^+) - D_+ \\ &= -13.5984 + 0 - 2.650 \\ &= -16.2484 \text{ eV}. \end{aligned}$$

Electron attachment is



Electron affinity is the positive energy released in this process:

$$\begin{aligned} \text{EA} &= E(\text{H}_2^+) + E(\text{e}^-) - E(\text{H}_2) \\ &= -16.2484 + 0 - (-31.675) \\ &= 15.4266 \text{ eV} \\ &\approx \boxed{15.427 \text{ eV}}. \end{aligned}$$

Equivalently, the thermochemical cycle gives

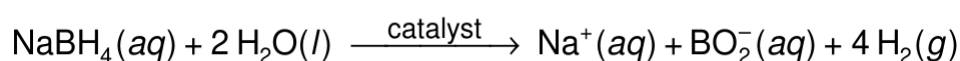
$$EA = R_H + DE(H_2) - DE(H_2^+) = 13.5984 + 4.4782 - 2.650.$$

The energy change for electron attachment is therefore -15.427 eV.

The solution was checked against the official solution.

Problem 4: Hydrogen storage in sodium borohydride

For sustainable energy, hydrogen appears to be the best energy carrier. The most efficient way of using hydrogen is generation of electrical energy in a fuel cell. However, storing hydrogen in large quantities is a challenge in fuel cell applications. Among the chemical hydrides considered as solid hydrogen storage materials, sodium borohydride (NaBH_4), being non-toxic, stable and environmentally benign, appears to be the most promising one. The hydrolysis of sodium borohydride that releases H_2 gas is a slow reaction at ambient temperature and, therefore, needs to be catalyzed.



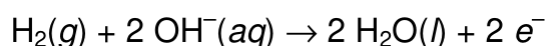
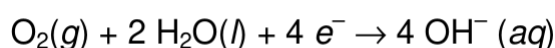
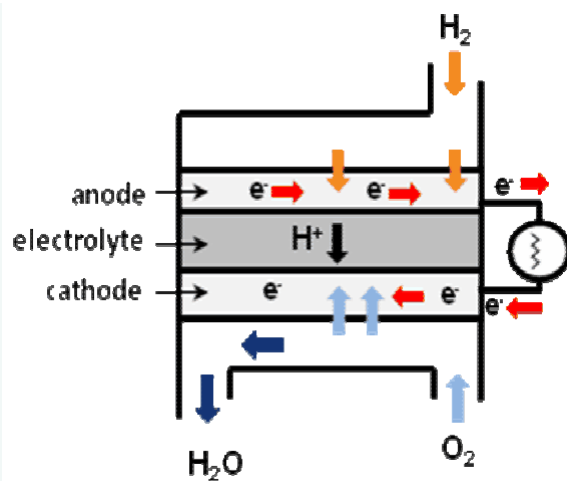
Colloidal ruthenium(0) nanoclusters are the most active catalysts in this hydrolysis even at room temperature and lead to a complete H_2 release from sodium borohydride. Kinetic studies show that the catalytic hydrolysis of NaBH_4 is a first order reaction with respect to the catalyst, but a zero order with respect to the substrate. The rate of hydrogen production per mole of ruthenium is $92 \text{ mol H}_2 \cdot (\text{mol Ru})^{-1} \cdot \text{min}^{-1}$ at 25°C .

4.1 Calculate the amount of ruthenium catalyst (in mg) which must be added to 0.100 dm^3 of NaBH_4 solution with a concentration of 1.0 mol dm^{-3} to supply the hydrogen gas at a rate of $0.100 \text{ dm}^3 \text{ min}^{-1}$ at 25°C and 1.0 atm , that is required for a portable fuel cell.

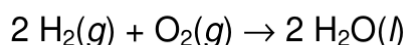
4.2 For how many minutes will this system supply hydrogen gas at this rate?

4.3 The Arrhenius activation energy for this catalytic hydrolysis of sodium borohydride is $E_a = 42.0 \text{ kJ mol}^{-1}$. Calculate the temperature required to achieve the same rate of hydrogen evolution by using a half of the amount of ruthenium catalyst used at 25.0°C .

4.4 A fuel cell (see figure) is made up of three segments sandwiched together: the anode, the electrolyte, and the cathode. Hydrogen is used as fuel and oxygen as oxidant. Two chemical reactions occur at the interfaces of the three different segments:



The net result of the two reactions is



The hydrogen for the fuel cell is supplied from the hydrolysis of sodium borohydride. Calculate the standard potential for the cathode half reaction if the standard reduction potential for the anode half reaction is -0.83 V and $\Delta_f G^\circ(\text{H}_2\text{O}(l))$ is -237 kJ mol^{-1} .

4.5 Calculate the volume of air at a temperature of 25°C and a pressure of 1.0 atm needed to generate a constant current of 2.5 A for 3.0 hours in this fuel cell. Assume that air contains 20% by volume $\text{O}_2(g)$.

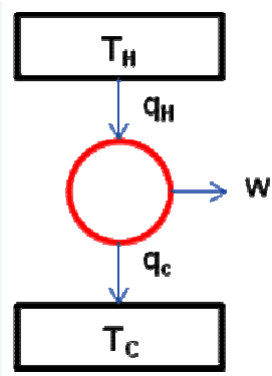
4.6 The efficiency of a fuel cell is given by the ratio of the work produced to the heat dissipated by the cell reaction. Thus, the maximum efficiency for a fuel cell is given by:

$$\eta_{\text{fuel cell}} = \frac{\text{work}}{\text{heat}}$$

Calculate the maximum efficiency for the fuel cell using the data given below at 25°C and a standard pressure.

	$S^\circ (\text{J mol}^{-1} \text{K}^{-1})$
$\text{H}_2(g)$	130.7
$\text{O}_2(g)$	205.2
$\text{H}_2\text{O}(l)$	70.0

The second law of thermodynamics states that it is impossible to convert all of the heat, q_H , from a high-temperature reservoir at T_H into work. At least, some of the energy, q_C , must be transferred to a low-temperature reservoir at T_C . Thus, a heat engine with 100% efficiency is thermodynamically impossible. When the heat engine is working reversibly, as in a Carnot cycle, the efficiency will be a maximum.



For a heat engine working reversibly between two reservoirs the following relations are applied:

$$q_H = w + q_C$$

and

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

4.7 What should be the temperature of the hot reservoir, T_H , of a Carnot heat engine to maintain the efficiency of the fuel cell calculated in part 4.6, if the temperature of cold reservoir T_C is 40°C ?

(If you have been unable to calculate the value for the efficiency then use the value 0.80 for the calculation.)

Official English text of the problem.

Answers

- **4.1:** $m(\text{Ru}) = 4.5 \text{ mg}$.
- **4.2:** 98 min .
- **4.3:** $T = 310.9 \text{ K} = 37.7^\circ\text{C}$.
- **4.4:** $E_{\text{cathode}}^\circ = +0.40 \text{ V}$, as a reduction potential.
- **4.5:** 8.6 dm^3 of air at 25°C and 1.0 atm .
- **4.6:** $\eta_{\text{max}} = 0.830 = 83.0\%$.
- **4.7:** $T_H = 1.84 \times 10^3 \text{ K}$, approximately $1.56 \times 10^3^\circ\text{C}$.

Solution

The molecular and ionic species used in the solution have the following names and SMILES:

Species	Name	SMILES
NaBH_4	Sodium borohydride	<chem>[Na+] . [BH4-]</chem>
H_2	Hydrogen	<chem>[H] [H]</chem>
H_2O	Water	<chem>O</chem>
Na^+	Sodium ion	<chem>[Na+]</chem>

Species	Name	SMILES
BO_2^-	Metaborate ion	[O-]B=O
O_2	Oxygen	O=O
OH^-	Hydroxide ion	[OH-]

The metaborate SMILES is a formal monomeric representation of the formula used in the problem. These SMILES do not specify phases, solvation, or the structure of the ruthenium nanoclusters.

Use the standard constants

$$R = 0.082057 \text{ dm}^3 \text{ atm mol}^{-1} \text{ K}^{-1} = 8.314 \text{ J mol}^{-1} \text{ K}^{-1},$$

$$F = 96485 \text{ C mol}^{-1}, \quad M(\text{Ru}) = 101.07 \text{ g mol}^{-1}.$$

4.1

The balanced hydrolysis reaction is



At $25^\circ\text{C} = 298.15 \text{ K}$, the required molar hydrogen-production rate follows from the ideal-gas equation:

$$\dot{n}_{\text{H}_2} = \frac{P\dot{V}}{RT} = \frac{(1.0 \text{ atm})(0.100 \text{ dm}^3 \text{ min}^{-1})}{(0.082057 \text{ dm}^3 \text{ atm mol}^{-1} \text{ K}^{-1})(298.15 \text{ K})} = 4.0874 \times 10^{-3} \text{ mol min}^{-1}.$$

Each mole of ruthenium produces 92 moles of hydrogen per minute, so

$$n_{\text{Ru}} = \frac{4.0874 \times 10^{-3} \text{ mol min}^{-1}}{92 \text{ min}^{-1}} = 4.4429 \times 10^{-5} \text{ mol}.$$

Therefore,

$$m_{\text{Ru}} = (4.4429 \times 10^{-5} \text{ mol})(101.07 \text{ g mol}^{-1}) = 4.4904 \times 10^{-3} \text{ g} = \boxed{4.5 \text{ mg}}.$$

4.2

The initial amount of sodium borohydride is

$$n_{\text{NaBH}_4} = cV = (1.0 \text{ mol dm}^{-3})(0.100 \text{ dm}^3) = 0.100 \text{ mol}.$$

The hydrolysis produces four moles of hydrogen per mole of sodium borohydride:

$$n_{\text{H}_2, \text{total}} = 4(0.100) = 0.400 \text{ mol}.$$

Because the reaction is zero order in the substrate, the stated model gives a constant production rate until the substrate is exhausted. Thus,

$$t = \frac{n_{\text{H}_2, \text{total}}}{\dot{n}_{\text{H}_2}} = \frac{0.400 \text{ mol}}{4.0874 \times 10^{-3} \text{ mol min}^{-1}} = 97.86 \text{ min} \approx \boxed{98 \text{ min}}.$$

4.3

The hydrogen-production rate is proportional to the amount of catalyst:

$$\dot{n}_{\text{H}_2} = k(T)n_{\text{Ru}}.$$

To maintain the same molar production rate with half the catalyst,

$$k(T_2) \frac{n_{\text{Ru}}}{2} = k(T_1) n_{\text{Ru}}, \quad \frac{k(T_2)}{k(T_1)} = 2.$$

The Arrhenius equation gives

$$\ln \frac{k(T_2)}{k(T_1)} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right).$$

Consequently,

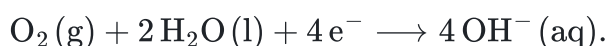
$$T_2 = \left[\frac{1}{298.15 \text{ K}} - \frac{(8.314 \text{ J mol}^{-1} \text{ K}^{-1}) \ln 2}{42000 \text{ J mol}^{-1}} \right]^{-1} = 310.867 \text{ K}.$$

Hence,

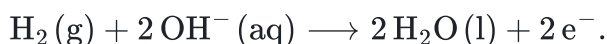
$$\boxed{T_2 = 310.9 \text{ K} = 37.7^\circ \text{C}}.$$

4.4

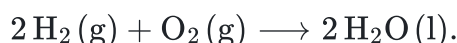
Oxygen is reduced at the cathode because it accepts electrons:



Hydrogen is oxidized at the anode because it releases electrons:



Multiplying the anode reaction by two and adding it to the cathode reaction gives



Four moles of electrons are transferred per mole of this overall reaction. The standard Gibbs energies of formation of elemental hydrogen and oxygen in their standard states are zero, so

$$\Delta_r G^\circ = 2 \Delta_f G^\circ(\text{H}_2\text{O}(\text{l})) = 2(-237) = -474 \text{ kJ mol}^{-1}.$$

Using $\Delta_r G^\circ = -nFE_{\text{cell}}^\circ$,

$$E_{\text{cell}}^\circ = \frac{474000 \text{ J mol}^{-1}}{4(96485 \text{ C mol}^{-1})} = 1.22817 \text{ V}.$$

Both electrode potentials in

$$E_{\text{cell}}^\circ = E_{\text{cathode,red}}^\circ - E_{\text{anode,red}}^\circ$$

are reduction potentials. Therefore,

$$E_{\text{cathode,red}}^\circ = 1.22817 + (-0.83) = 0.39817 \text{ V} \approx \boxed{+0.40 \text{ V}}.$$

4.5

The total charge delivered is

$$Q = It = (2.5 \text{ A})(3.0 \times 3600 \text{ s}) = 27000 \text{ C}.$$

The cathode reaction consumes one mole of oxygen per four moles of electrons:

$$n_{\text{O}_2} = \frac{Q}{4F} = \frac{27000}{4(96485)} = 0.069959 \text{ mol}.$$

For ideal gases at the same temperature and pressure, volume fraction equals mole fraction. Air containing 20% oxygen therefore has the required total amount

$$n_{\text{air}} = \frac{n_{\text{O}_2}}{0.20} = 0.349795 \text{ mol.}$$

Its volume is

$$V_{\text{air}} = \frac{n_{\text{air}} RT}{P} = \frac{(0.349795)(0.082057)(298.15)}{1.0} \text{ dm}^3 = 8.5578 \text{ dm}^3.$$

Thus,

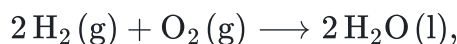
$$\boxed{V_{\text{air}} = 8.6 \text{ dm}^3}.$$

4.6

At constant temperature and pressure, the maximum electrical work obtainable is $-\Delta_r G^\circ$. Using the total reaction enthalpy release as the available chemical-energy input,

$$\eta_{\text{max}} = \frac{-\Delta_r G^\circ}{-\Delta_r H^\circ}.$$

For



the standard entropy change is

$$\begin{aligned} \Delta_r S^\circ &= 2S^\circ(\text{H}_2\text{O}(\text{l})) - 2S^\circ(\text{H}_2(\text{g})) - S^\circ(\text{O}_2(\text{g})) \\ &= 2(70.0) - 2(130.7) - 205.2 \\ &= -326.6 \text{ J mol}^{-1} \text{ K}^{-1}. \end{aligned}$$

Since

$$\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ,$$

we obtain

$$\begin{aligned} \Delta_r H^\circ &= \Delta_r G^\circ + T\Delta_r S^\circ \\ &= -474 + (298.15)(-0.3266) \\ &= -571.3758 \text{ kJ mol}^{-1}. \end{aligned}$$

Therefore,

$$\eta_{\text{max}} = \frac{474}{571.3758} = 0.8295766 \approx \boxed{0.830 = 83.0\%}.$$

4.7

For the reversible heat engine,

$$\eta = \frac{w}{q_{\text{H}}} = \frac{q_{\text{H}} - q_{\text{C}}}{q_{\text{H}}} = 1 - \frac{q_{\text{C}}}{q_{\text{H}}}.$$

The reversible relation $q_{\text{H}}/T_{\text{H}} = q_{\text{C}}/T_{\text{C}}$ gives

$$\eta = 1 - \frac{T_{\text{C}}}{T_{\text{H}}}.$$

Using absolute temperatures,

$$T_{\text{C}} = 40 + 273.15 = 313.15 \text{ K.}$$

With the unrounded efficiency from part 4.6,

$$T_{\text{H}} = \frac{T_{\text{C}}}{1 - \eta} = \frac{313.15}{1 - 0.8295766} = 1837.48 \text{ K.}$$

Thus,

$$T_H \approx 1.84 \times 10^3 \text{ K} \approx 1.56 \times 10^3 \text{ }^\circ\text{C}.$$

The solution was checked against the official solution.

Problem 5: Polynitrogen compounds

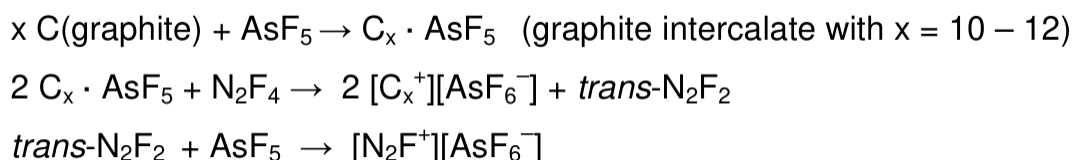
Polynitrogen compounds have great potential for being used as high energy density materials. They are thermodynamically unstable. Huge amount of energy is released from their decomposition or reactions leading to more stable products. The only known polynitrogen species are N_2 , N_3^- and N_5^+ , isolated in 1772, 1890 and 1999, respectively, and recently reported cyclic anion, N_5^- .

5.1 Write the Lewis structure for N_5^+ with three energetically favourable resonance forms. Indicate the lone pairs and formal charges. Draw the molecular geometry of N_5^+ .

5.2 Write the Lewis structures for cyclic N_5^- with five energetically favourable resonance forms. Indicate the lone pairs and formal charges. Draw the molecular geometry of cyclic N_5^- .

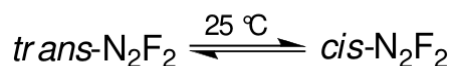
5.3 The synthesis of $[\text{N}_5^+][\text{AsF}_6^-]$, a white ionic solid, was achieved by reacting $[\text{N}_2\text{F}^+][\text{AsF}_6^-]$ with hydrazoic acid, HN_3 , in liquid HF at -78°C . Write the balanced chemical equation for this reaction.

The preparation of $[\text{N}_2\text{F}^+][\text{AsF}_6^-]$ requires the reaction of N_2F_2 with strong Lewis acid AsF_5 as follows:



In the synthesis of N_2F_2 , the *trans* isomer is formed which is thermodynamically less stable than *cis*- N_2F_2 . However, conversion of *trans*- N_2F_2 to *cis*- N_2F_2 requires surmounting a high energy barrier of 251 kJ mol^{-1} , so that equilibration between the *cis* and the *trans* isomers does not significantly take place without a suitable catalyst.

When *trans*- N_2F_2 is maintained in a closed container for six days at room temperature in the presence of a small amount of SbF_5 as a catalyst, *cis-trans* thermal equilibrium is established.



The standard enthalpies of formation of *trans*- and *cis*- N_2F_2 are 67.31 and $62.03 \text{ kJ mol}^{-1}$, respectively, and their standard entropies at 25°C are 262.10 and $266.50 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively.

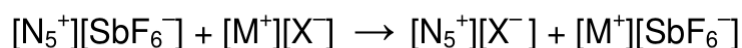
5.4 Find the ratio of the number of *cis*- N_2F_2 molecules over that of the *trans*- N_2F_2 molecules in an equilibrium mixture at 25°C .

5.5 Write the Lewis structures showing the geometry of N_2F^+ ion and those of *trans*- and *cis*-isomers of N_2F_2 . Include all lone pairs and formal charges. Suggest an appropriate hybridization for each nitrogen atom in N_2F_2 and N_2F^+ .

Solid $[\text{N}_5^+][\text{AsF}_6^-]$ is marginally stable at room temperature but reacts explosively with water to produce arsenic pentafluoride, hydrogen fluoride, molecular nitrogen and oxygen.

5.6 Write a balanced equation for the reaction between $[\text{N}_5^+][\text{AsF}_6^-]$ and water.

Conversion of $[\text{N}_5^+][\text{SbF}_6^-]$ into other N_5^+ salts can be achieved by a metathesis reaction:



where $\text{M}^+ = \text{Na}^+, \text{K}^+, \text{Cs}^+$, and $\text{X}^- =$ large anion such as SnF_6^{2-} and $\text{B}(\text{CF}_3)_4^-$.

Since $[\text{Cs}^+][\text{SbF}_6^-]$ has a low solubility in anhydrous HF, and $[\text{K}^+][\text{SbF}_6^-]$ has a low solubility in SO_2 , these two solvents were used extensively to carry out metathesis reactions at -78°C and -64°C , respectively.

5.7 Write the balanced equation for the preparation of $[\text{N}_5^+]_2[\text{SnF}_6^{2-}]$ and $[\text{N}_5^+][\text{B}(\text{CF}_3)_4^-]$ in solution starting with $[\text{Cs}^+]_2[\text{SnF}_6^{2-}]$ and $[\text{K}^+][\text{B}(\text{CF}_3)_4^-]$, respectively. Indicate the appropriate solvent.

When $[\text{N}_5^+]_2[\text{SnF}_6^{2-}]$ decomposes under carefully controlled conditions at $25\text{--}30^\circ\text{C}$, $[\text{N}_5^+][\text{SnF}_5^-]$ and N_5F are formed. The $[\text{N}_5^+][\text{SnF}_5^-]$ salt is a white solid and has a thermal stability comparable to that of $[\text{N}_5^+][\text{SbF}_6^-]$ ($50\text{--}60^\circ\text{C}$). The solution ^{119}Sn NMR spectrum has shown that the SnF_5^- anion in this compound is, in fact, a mixture of dimeric and tetrameric polyanions. In both of these polyanions the coordination number of Sn atom is 6 and there are bridging fluorine atoms.

5.8 Draw the structures of dimeric and tetrameric polyanions.

Official English text of the problem.

Answers

The complete lone-pair assignments and SMILES are given in the corresponding solution parts.

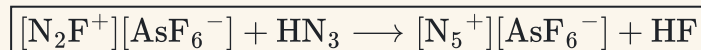
1. **5.1:** Pentazenium, N_5^+ , has the three favourable resonance forms



Its geometry is an open, planar, V-shaped chain.

2. **5.2:** Cyclopentazolate, N_5^- , has five equivalent resonance forms, each containing two double bonds and one negatively charged nitrogen. It is a planar pentagonal ring.

3. **5.3:**



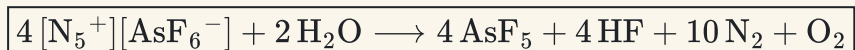
in liquid HF at -78°C .

4. 5.4:

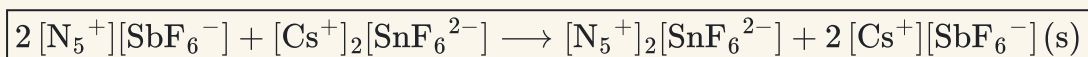
$$\frac{N_{\text{cis}}}{N_{\text{trans}}} = 14.3$$

5. **5.5:** Fluorodiazonium is linear, $\text{F}-\text{N}^+\equiv\text{N}$, with both nitrogen atoms sp -hybridized. Both difluorodiazene isomers have planar $\text{F}-\text{N}=\text{N}-\text{F}$ skeletons and sp^2 -hybridized nitrogen atoms; their fluorines lie on opposite sides for *trans* and the same side for *cis*.

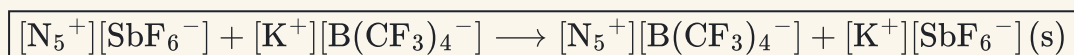
6. 5.6:



7. 5.7:



Solvent: anhydrous HF , at -78°C .



Solvent: liquid SO_2 , at -64°C .

8. **5.8:** The dimer is $\text{Sn}_2\text{F}_{10}^{2-}$, comprising two edge-sharing coordination octahedra with two fluoride bridges. The tetramer is cyclic $\text{Sn}_4\text{F}_{20}^{4-}$, comprising four corner-sharing coordination octahedra with four fluoride bridges. Every tin has four terminal and two bridging fluorines.

Solution

SMILES specify connectivity and, where indicated, double-bond stereochemistry. Lone pairs and spatial geometry are described separately. For ionic salts, the constituent-ion SMILES are supplied; joining these with . in the required stoichiometric ratio gives a formula-unit SMILES.

5.1 — Pentazenium: resonance forms and geometry

The pentazenium cation, N_5^+ , contains

$$5(5) - 1 = 24$$

valence electrons.

For an open chain with an octet on every nitrogen, let B be the sum of its four bond orders. Counting the electrons needed for five octets gives

$$40 - 2B = 24, \quad B = 8.$$

For an octet-satisfying nitrogen whose total bond order is s ,

$$\text{number of lone pairs} = 4 - s, \quad \text{formal charge} = s - 3.$$

Number the nitrogen atoms 1–5 along the chain. The three favourable forms are:

Form	Bond orders: 1–2, 2–3, 3–4, 4–5	Formal charges: atoms 1–5	Lone-pair counts: atoms 1–5	SMILES
A	3, 1, 1, 3	0, +1, –1, +1, 0	1, 0, 2, 0, 1	$\text{N}\#[\text{N}^+][\text{N}^-][\text{N}^+]\# \text{N}$

Form	Bond orders: 1–2, 2–3, 3–4, 4–5	Formal charges: atoms 1–5	Lone-pair counts: atoms 1–5	SMILES
B	2, 2, 1, 3	−1, +1, 0, +1, 0	2, 0, 1, 0, 1	[N−]= [N+]=N[N+]#N
C	3, 1, 2, 2	0, +1, 0, +1, −1	1, 0, 1, 0, 2	N#[N+]N=[N+]= [N−]

Each form has eight bonding pairs, four lone pairs, and total charge +1. These forms avoid the greater charge separation or doubly negative nitrogen found in other octet-satisfying chain structures.

To describe the molecular drawing, place atom 3 at the vertex of a **V**, with the sequences 3–2–1 and 3–4–5 forming its two approximately straight arms. All five nitrogen atoms lie in a plane.

In the symmetric Lewis form A, the central nitrogen has two bonds and two lone pairs, giving a bent arrangement. Atoms 2 and 4 each have two bonding domains and no lone pairs, giving approximately linear arrangements.

5.2 — Cyclopentazolate: five resonance forms and geometry

The cyclopentazolate anion, N_5^- , has

$$5(5) + 1 = 26$$

valence electrons.

Its five-membered ring contains two double bonds and three single bonds in each favourable Lewis form. The nitrogen joined to both neighbours by single bonds carries charge −1 and **two lone pairs**. Each of the other four nitrogens has **one lone pair** and zero formal charge.

Number the ring atoms consecutively 1–5, with a closing bond between 5 and 1:

Negatively charged atom	Double-bond edges	SMILES of the resonance form
1	2=3 and 4=5	[N−]1N=NN=N1
2	3=4 and 5=1	N1[N−]N=NN=1
3	4=5 and 1=2	N1=N[N−]N=N1
4	5=1 and 2=3	N1N=N[N−]N=1
5	1=2 and 3=4	N1=NN=N[N−]1

These are resonance contributors of the same ion. The negative charge is delocalized around the ring.

The two double bonds supply four π electrons; one lone pair on the formally negative nitrogen supplies another two. Thus the ring has

$$6 \pi \text{ electrons,}$$

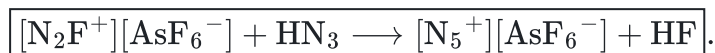
satisfying the $4n + 2$ aromaticity criterion with $n = 1$.

Draw a **planar regular pentagon**, with nitrogen at every vertex and equivalent bonds of intermediate single/double character. The ideal internal angles are 108° . Each nitrogen has an in-plane lone pair; the additional electron pair participates in the delocalized π system.

5.3 — Formation of pentazenium hexafluoroarsenate

The two nitrogen atoms of fluorodiazonium and the three nitrogen atoms of hydrazoic acid supply the five-nitrogen cation. The hydrogen from the acid combines with the fluorine from fluorodiazonium to produce hydrogen fluoride. Hexafluoroarsenate is the counterion on both sides.

Therefore,



All coefficients are 1. The reaction is conducted in liquid HF at -78°C .

The additional species are:

Species	Name	SMILES
N_2F^+	Fluorodiazonium ion	<chem>N#[N+]F</chem>
HN_3	Hydrazoic acid, or hydrogen azide	<chem>[H]N=[N+]=[N-]</chem>
HF	Hydrogen fluoride	<chem>[H]F</chem>
AsF_6^-	Hexafluoroarsenate(V) ion	<chem>F[As-](F)(F)(F)(F)F</chem>

The reactant salt is fluorodiazonium hexafluoroarsenate(V), and the product is pentazenium hexafluoroarsenate(V). The hexafluoroarsenate ion has octahedral coordination around arsenic.

5.4 — Equilibrium cis/trans ratio

Take the forward reaction as conversion of the *trans* isomer to the *cis* isomer.

The standard reaction enthalpy is

$$\begin{aligned}\Delta_r H^\circ &= \Delta_f H_{\text{cis}}^\circ - \Delta_f H_{\text{trans}}^\circ \\ &= 62.03 - 67.31 \\ &= -5.28 \text{ kJ mol}^{-1}.\end{aligned}$$

The standard reaction entropy is

$$\begin{aligned}\Delta_r S^\circ &= 266.50 - 262.10 \\ &= +4.40 \text{ J K}^{-1} \text{ mol}^{-1}.\end{aligned}$$

At $T = 298.15 \text{ K}$,

$$\begin{aligned}\Delta_r G^\circ &= \Delta_r H^\circ - T\Delta_r S^\circ \\ &= -5280 - (298.15)(4.40) \\ &= -6591.86 \text{ J mol}^{-1} \\ &\approx -6.59 \text{ kJ mol}^{-1}.\end{aligned}$$

Using $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$,

$$\ln K = -\frac{\Delta_r G^\circ}{RT} = \frac{6591.86}{(8.314)(298.15)} \approx 2.659.$$

Hence,

$$K = e^{2.659} \approx 14.3.$$

For the gaseous isomers under the ideal-gas approximation,

$$K = \frac{p_{\text{cis}}}{p_{\text{trans}}} = \frac{n_{\text{cis}}}{n_{\text{trans}}} = \frac{N_{\text{cis}}}{N_{\text{trans}}},$$

so

$$\frac{N_{\text{cis}}}{N_{\text{trans}}} = 14.3.$$

Both the lower enthalpy and the higher entropy favour the *cis* isomer. The activation barrier affects the rate of equilibration, not this equilibrium ratio; the catalyst allows equilibrium to be reached more rapidly.

5.5 — Fluorodiazonium and the difluorodiazene isomers

For fluorodiazonium, N_2F^+ , the valence-electron count is

$$2(5) + 7 - 1 = 16.$$

Its Lewis structure is



with SMILES F[N+]#N.

The complete lone-pair and charge inventory is:

Atom	Bonds	Lone pairs	Formal charge
Fluorine	One single bond	3	0
Nitrogen bonded to fluorine	One single and one triple bond	0	+1
Terminal nitrogen	One triple bond	1	0

Both nitrogens have two electron domains and are appropriately described as *sp*-hybridized. The three atoms lie on a straight line, with an ideal bond angle of 180° .

For difluorodiazene, N_2F_2 , the electron count is

$$2(5) + 2(7) = 24.$$

Both stereoisomers have the Lewis connectivity



Each nitrogen has **one lone pair**, and each fluorine has **three lone pairs**. Every formal charge is zero.

Isomer	Name and stereochemical SMILES	Geometrical description
<i>trans</i>	(<i>E</i>)-Difluorodiazene, <chem>F/N=N/F</chem>	The fluorines lie on opposite sides of the double bond.
<i>cis</i>	(<i>Z</i>)-Difluorodiazene, <chem>F/N=N\F</chem>	The fluorines lie on the same side of the double bond.

At each nitrogen there are three electron domains: the nitrogen–nitrogen double bond, the nitrogen–fluorine single bond, and one lone pair. Thus **both nitrogens are *sp*²-hybridized** in both isomers. Their unhybridized *p* orbitals form the π bond. Draw all four atoms in one plane, with bent arrangements at the nitrogen atoms.

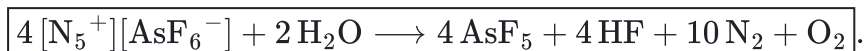
5.6 — Reaction with water

Start with four formula units of pentazenium hexafluoroarsenate(V).

- Four arsenic atoms require four molecules of arsenic pentafluoride.
- Of the 24 fluorine atoms, 20 enter arsenic pentafluoride, leaving four for hydrogen fluoride.
- Four hydrogen atoms require two water molecules.

- Twenty nitrogen atoms produce ten nitrogen molecules.
- The two oxygen atoms produce one oxygen molecule.

Therefore,



The additional molecular species are:

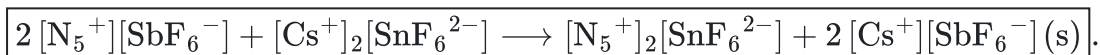
Species	Name	SMILES
H ₂ O	Water	O
AsF ₅	Arsenic pentafluoride	F[As](F)(F)(F)F
N ₂	Dinitrogen	N#N
O ₂	Dioxygen	O=O

Arsenic pentafluoride has trigonal-bipyramidal molecular geometry. The dioxygen SMILES records its connectivity; it does not specify its triplet ground state.

5.7 — Metathesis reactions and solvents

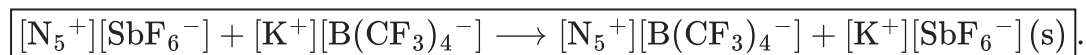
The hexafluorostannate(IV) ion carries charge 2−, so it requires **two pentazenium cations**.

Consequently,



Use **anhydrous hydrogen fluoride at** −78 °C. Precipitation of poorly soluble cesium hexafluoroantimonate(V) favours formation of bis(pentazenium) hexafluorostannate(IV).

The tetrakis(trifluoromethyl)borate ion is singly charged, so the second reaction has a 1:1 stoichiometry:



Use **liquid sulfur dioxide at** −64 °C. Precipitation of poorly soluble potassium hexafluoroantimonate(V) favours formation of pentazenium tetrakis(trifluoromethyl)borate.

The additional ions and solvent are:

Species	Name	SMILES
SbF ₆ [−]	Hexafluoroantimonate(V) ion	F[Sb-](F)(F)(F)(F)F
SnF ₆ ^{2−}	Hexafluorostannate(IV) ion	F[Sn-2](F)(F)(F)(F)F
B(CF ₃) ₄ [−]	Tetrakis(trifluoromethyl)borate ion	[B-](C(F)(F)F)(C(F)(F)F)(C(F)(F)F)C(F)(F)F
Cs ⁺	Caesium ion	[Cs+]
K ⁺	Potassium ion	[K+]
SO ₂	Sulfur dioxide	O=S=O

The two hexafluorometallate ions are octahedral. The boron atom has tetrahedral coordination by four carbon atoms. Sulfur dioxide is bent.

5.8 — Dimeric and tetrameric fluorostannate anions

For an oligomer with n tin atoms, the composition is $\text{Sn}_n\text{F}_{5n}^{n-}$. Let t be the number of terminal fluorines and b the number of fluorines bridging two tin centres.

Counting fluorine atoms gives

$$t + b = 5n.$$

Since every tin has coordination number 6, counting tin–fluorine contacts gives

$$t + 2b = 6n.$$

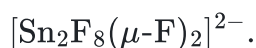
Subtracting,

$$\boxed{b = n, \quad t = 4n}.$$

Thus the dimer requires two bridges and eight terminal fluorines; the tetramer requires four bridges and sixteen terminal fluorines.

Dimer: $\text{Sn}_2\text{F}_{10}^{2-}$.

The dimeric pentafluorostannate(IV) anion has connectivity



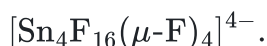
SMILES: F[Sn-2]1(F)(F)(F)[F+][Sn-2](F)(F)(F)(F)[F+]1

Draw two tin centres linked through **two shared fluorine atoms**, producing an alternating four-membered ring. Attach four additional, terminal fluorines to each tin. Each tin therefore has six fluorine neighbours in a distorted octahedral arrangement.

The two shared fluorines form a common **edge of the coordination octahedra**; this does not imply a fluorine–fluorine bond. The two bridging positions at each tin are cis.

Tetramer: $\text{Sn}_4\text{F}_{20}^{4-}$.

The tetrameric pentafluorostannate(IV) anion has connectivity



SMILES: F[Sn-2]1(F)(F)(F)[F+][Sn-2](F)(F)(F)(F)[F+][Sn-2](F)(F)(F)(F)[F+][Sn-2](F)(F)(F)(F)[F+]1

Draw four tin centres arranged cyclically, with **one bridging fluorine between each neighbouring pair**. This gives an alternating eight-membered ring containing four tin and four fluorine atoms. Attach four terminal fluorines to every tin.

The structure therefore contains four **corner-sharing coordination octahedra** in a closed ring. Each tin has two cis bridging fluorines and four terminal fluorines. A square arrangement is a convenient connectivity sketch; the SMILES does not prescribe ring puckering or exact bond angles.

In these two SMILES, every tin–fluorine contact is represented as an ordinary single bond. This assigns formal charges of -2 to each six-bonded tin and $+1$ to each two-bonded bridging fluorine, giving the correct overall charges:

$$2(-2) + 2(+1) = -2, \quad 4(-2) + 4(+1) = -4.$$

These formal charges are distinct from oxidation states: tin is $+IV$, and fluorine is $-I$.

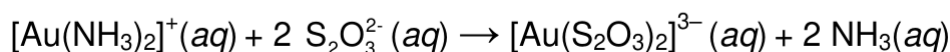
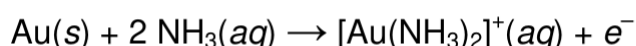
The solution was checked against the official solution. Where this solution differs from the official solution, the official solution contains an error or a misprint.

Problem 6: Thiosulfate leaching of gold

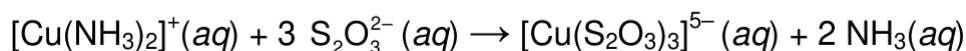
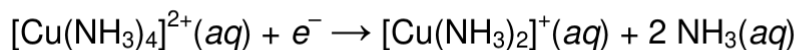
Extraction of gold using sodium cyanide, a very poisonous chemical, causes environmental problems and gives rise to serious public concern about the use of this so called "cyanide process". Thiosulfate leaching of gold has been considered as an alternative. In this process, the main reagent is ammonium thiosulfate, $(\text{NH}_4)_2\text{S}_2\text{O}_3$, which is relatively non-toxic. Although this process appears to be environmentally benign, the chemistry involved is very complex and needs to be studied thoroughly. The solution used for leaching gold contains $\text{S}_2\text{O}_3^{2-}$, Cu^{2+} , NH_3 , and dissolved O_2 . The solution must have a pH greater than 8.5 to allow free ammonia to be present.

According to the proposed mechanism, a local voltaic micro-cell is formed on the surface of gold particles during the leaching process and operates as follows:

Anode:



Cathode:



6.1 Write the overall cell reaction for this voltaic cell.

6.2 In the presence of ammonia $[\text{Cu}(\text{S}_2\text{O}_3)_3]^{5-}$ is oxidized by O_2 back to $[\text{Cu}(\text{NH}_3)_4]^{2+}$. Write a balanced equation for this oxidation-reduction reaction in basic solution.

6.3 In this leaching process, the $[\text{Cu}(\text{NH}_3)_4]^{2+}$ complex ion functions as catalyst and speeds up the dissolution of gold. Write the net overall oxidation-reduction reaction for dissolution of the gold metal, which is catalyzed by $[\text{Cu}(\text{NH}_3)_4]^{2+}$ complex ion.

6.4 Draw the coordination geometries of the metal in $[\text{Au}(\text{NH}_3)_2]^+$ and $[\text{Au}(\text{S}_2\text{O}_3)_2]^{3-}$ complex ions, indicating the coordinating atoms.

The formation constants, K_f , of $[\text{Au}(\text{NH}_3)_2]^+$ and $[\text{Au}(\text{S}_2\text{O}_3)_2]^{3-}$ complexes are $1.00 \cdot 10^{26}$ and $1.00 \cdot 10^{28}$, respectively. Consider a leaching solution in which the equilibrium concentrations of the species are as follows:

$[\text{S}_2\text{O}_3^{2-}] = 0.100$; $[\text{NH}_3] = 0.100$ and the total concentration of gold(I) species = $5.50 \cdot 10^{-5} \text{ mol dm}^{-3}$.

6.5 Calculate the percentage of gold(I) ion that exists in the form of thiosulfate complex.

When the concentration of O_2 is not high enough and $pH > 10$, $S_2O_3^{2-}$ reduces $[Cu(NH_3)_4]^{2+}$ to $[Cu(S_2O_3)_3]^{5-}$ with the formation of tetrathionate ion $S_4O_6^{2-}$:



In basic solution tetrathionate disproportionates to trithionate, $S_3O_6^{2-}$, and thiosulfate.

6.6 Write a balanced equation for this disproportionation reaction.

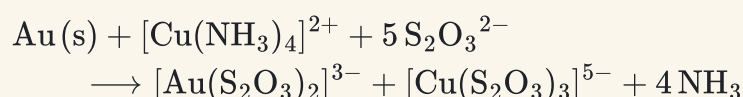
6.7 When the O_2 concentration is too high, $S_2O_3^{2-}$ is oxidized by oxygen to yield trithionate and sulfate ions. Write a balanced equation for this reaction.

Official English text of the problem.

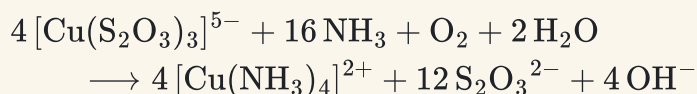
Answers

Names and SMILES for the species used here are collected at the end of the Solution.

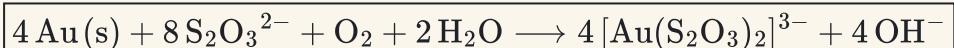
• **6.1**



• **6.2**



• **6.3**

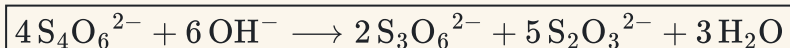


- **6.4** Both gold(I) complexes are **linear**, with coordination number 2 and a donor–gold–donor angle of 180° . In $[Au(NH_3)_2]^+$, the donors are **nitrogen atoms**; in $[Au(S_2O_3)_2]^{3-}$, they are the **terminal sulfur atoms** of the thiosulfate ligands.

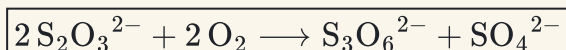
• **6.5**

99.0%

• **6.6**



• **6.7**

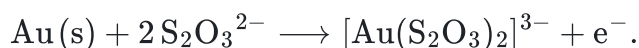


Solution

All dissolved ions and ammonia in the following equations are aqueous; the oxygen is dissolved oxygen.

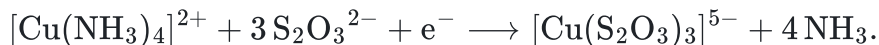
6.1 — Overall cell reaction

Adding the two given anode steps cancels the diamminegold(I) intermediate and ammonia:

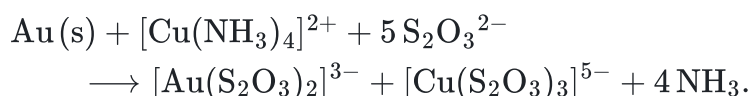


Gold is oxidized from oxidation state 0 to +1.

Adding the two cathode steps cancels the diamminecopper(I) intermediate:



Copper is reduced from +2 to +1. Adding these net half-reactions cancels one electron:



The total charge is -8 on each side.

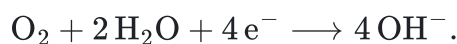
6.2 — Regeneration of the copper(II) complex

In $[\text{Cu}(\text{S}_2\text{O}_3)_3]^{5-}$, the three thiosulfate ligands contribute charge -6 , so copper has oxidation state $+1$. In $[\text{Cu}(\text{NH}_3)_4]^{2+}$, ammonia is neutral, so copper has oxidation state $+2$.

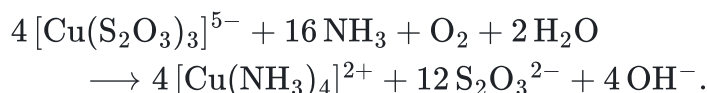
The oxidation half-reaction, including ligand exchange, is therefore



The oxygen reduction half-reaction in basic solution is



Multiplying the copper half-reaction by four and adding gives



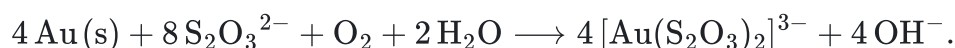
Both sides have total charge -20 .

6.3 — Net dissolution of gold

Multiply the reaction in 6.1 by four and add the regeneration reaction in 6.2. The following cancel:

- Four tetraamminecopper(II) ions and four tris(thiosulfato)cuprate(I) ions.
- Sixteen ammonia molecules.
- Twelve of the twenty thiosulfate ions initially appearing on the reactant side.

The result is



Thus, four gold atoms each lose one electron, and one oxygen molecule accepts the four electrons. The copper complex is regenerated, explaining its catalytic role.

6.4 — Coordination geometries

Both complexes contain gold(I), which has a $5d^{10}$ configuration and characteristically forms linear complexes with two donor atoms.

For **diamminegold(I)**, $[\text{Au}(\text{NH}_3)_2]^+$, each ammonia ligand donates its nitrogen lone pair.

- Draw gold at the center of a straight **N–Au–N** arrangement.

- Attach three hydrogen atoms to each nitrogen.
- Mark the N–Au–N angle as 180° , and enclose the complex in brackets with overall charge $+1$.

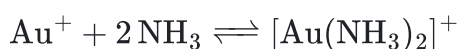
For **bis(thiosulfato)aurate(I)**, $[\text{Au}(\text{S}_2\text{O}_3)_2]^{3-}$, each thiosulfate ligand binds through its terminal sulfur atom: the sulfur atom that is not bonded to oxygen. This sulfur donor is favored by the soft gold(I) ion.

- Draw a straight **S–Au–S** arrangement with angle 180° .
- Each coordinating sulfur is bonded to a second sulfur bearing three oxygen atoms.
- Enclose the complete complex in brackets with overall charge $3-$.

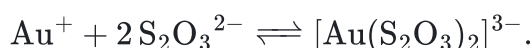
The linear geometry concerns the two donor atoms and gold; it does not require all atoms of the ligands to lie on that line.

6.5 — Percentage present as the thiosulfate complex

The formation equilibria are



and



Their formation constants give

$$K_{f,N} = \frac{[\text{Au}(\text{NH}_3)_2]^+}{[\text{Au}^+][\text{NH}_3]^2}, \quad K_{f,T} = \frac{[\text{Au}(\text{S}_2\text{O}_3)_2]^{3-}}{[\text{Au}^+][\text{S}_2\text{O}_3^{2-}]^2}.$$

Dividing eliminates the free gold(I) concentration:

$$\frac{[\text{Au}(\text{S}_2\text{O}_3)_2]^{3-}}{[\text{Au}(\text{NH}_3)_2]^+} = \frac{1.00 \times 10^{28}}{1.00 \times 10^{26}} \left(\frac{0.100}{0.100} \right)^2 = 100.$$

To check the contribution of uncomplexed gold(I), use the gold mass balance:

$$C_{\text{Au}} = [\text{Au}^+] + [\text{Au}(\text{NH}_3)_2]^+ + [\text{Au}(\text{S}_2\text{O}_3)_2]^{3-}.$$

Using numerical concentrations in mol dm^{-3} ,

$$C_{\text{Au}} = [\text{Au}^+] (1 + 10^{26}(0.100)^2 + 10^{28}(0.100)^2) = [\text{Au}^+] (1 + 10^{24} + 10^{26}).$$

Therefore,

$$[\text{Au}^+] = \frac{5.50 \times 10^{-5}}{1 + 10^{24} + 10^{26}} = 5.45 \times 10^{-31} \text{ mol dm}^{-3}.$$

The free-ion contribution is negligible. The complex concentrations are

$$\begin{aligned} [\text{Au}(\text{NH}_3)_2]^+ &= 5.45 \times 10^{-7} \text{ mol dm}^{-3}, \\ [\text{Au}(\text{S}_2\text{O}_3)_2]^{3-} &= 5.45 \times 10^{-5} \text{ mol dm}^{-3}. \end{aligned}$$

Using the unrounded values, the required percentage is

$$\frac{10^{26}}{1 + 10^{24} + 10^{26}} \times 100\% = 99.0099 \dots \% = \boxed{99.0\%}.$$

6.6 — Disproportionation of tetrathionate

The sums of the sulfur oxidation numbers in tetrathionate, trithionate, and thiosulfate are respectively

Ion	Sum for sulfur	Average for sulfur
$\text{S}_4\text{O}_6^{2-}$	+10	+2.5
$\text{S}_3\text{O}_6^{2-}$	+10	+10/3
$\text{S}_2\text{O}_3^{2-}$	+4	+2

Formation of trithionate increases the average sulfur oxidation state, while formation of thiosulfate decreases it, consistent with disproportionation.

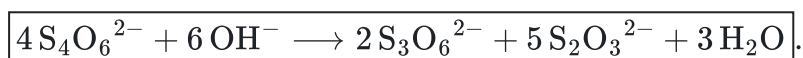
Let a tetrathionate ions produce b trithionate ions and c thiosulfate ions. Sulfur conservation and electron balance require

$$4a = 3b + 2c, \quad 10a = 10b + 4c.$$

These give the smallest integer ratio

$$a : b : c = 4 : 2 : 5.$$

Balancing oxygen, hydrogen, and charge with hydroxide and water gives



There are 16 sulfur atoms, 30 oxygen atoms, and 6 hydrogen atoms on each side; both sides have charge -14 .

6.7 — Oxidation of thiosulfate by excess oxygen

Balancing sulfur and charge gives two thiosulfate ions for one trithionate ion and one sulfate ion.

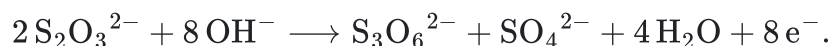
The sulfur oxidation-number sum increases from

$$2(+4) = +8$$

to

$$(+10) + (+6) = +16.$$

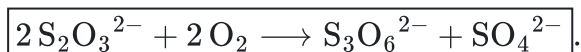
Thus, eight electrons are released. The corresponding oxidation half-reaction in basic solution is



Two oxygen molecules accept these electrons:



Adding and cancelling electrons, hydroxide, and water gives



Both sides contain four sulfur atoms and ten oxygen atoms and have charge -4 .

Species names and SMILES

The coordination complexes below use dative-bond SMILES: arrows point from donor atoms toward the metal. These encode connectivity, but the linear gold coordination geometries must be specified separately as in 6.4. The sulfur oxyanions are represented by one localized bonding and charge description.

Species and name	SMILES
Au, gold atom	[Au]
Au^+ , gold(I) ion	[Au+]

Species and name	SMILES
NH ₃ , ammonia	N
O ₂ , dioxygen	O=O
H ₂ O, water	O
OH ⁻ , hydroxide ion	[OH-]
S ₂ O ₃ ²⁻ , thiosulfate ion	[O-]S(=O)(=O)[S-]
[Au(NH ₃) ₂] ⁺ , diamminegold(I) ion	[NH3]->[Au+]<-[NH3]
[Au(S ₂ O ₃) ₂] ³⁻ , bis(thiosulfato)aurate(I) ion	[Au+](<-[S-]S(=O)(=O)[O-])<-[S-]S(=O)(=O)[O-]
[Cu(NH ₃) ₄] ²⁺ , tetraamminecopper(II) ion	[Cu+2](<-[NH3])(<-[NH3])(<-[NH3])<-[NH3]
[Cu(NH ₃) ₂] ⁺ , diamminecopper(I) ion	[NH3]->[Cu+]<-[NH3]
[Cu(S ₂ O ₃) ₃] ⁵⁻ , tris(thiosulfato)cuprate(I) ion	[Cu+](<-[S-]S(=O)(=O)[O-])(<-[S-]S(=O)(=O)[O-])<-[S-]S(=O)(=O)[O-]
S ₄ O ₆ ²⁻ , tetrathionate ion	[O-]S(=O)(=O)SSS(=O)(=O)[O-]
S ₃ O ₆ ²⁻ , trithionate ion	[O-]S(=O)(=O)SS(=O)(=O)[O-]
SO ₄ ²⁻ , sulfate ion	[O-]S(=O)(=O)[O-]

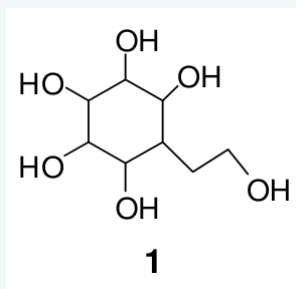
The gold-atom SMILES does not represent the extended metallic lattice of solid gold.

The solution was checked against the official solution.

Problem 7: Synthesis of a carbasugar

Carbohydrates are essential components of living cells and a source of energy for animals. They include simple sugars with small molecules as well as macromolecular substances. When the ring oxygen (endocyclic oxygen) in sugars is replaced by a methylene group, the compounds formed are called as *pseudosugars* or *carbasugars*. Since carbasugars are hydrolytically stable towards acids and enzymes, several carbasugars have found application in the field of glycosidase inhibition.

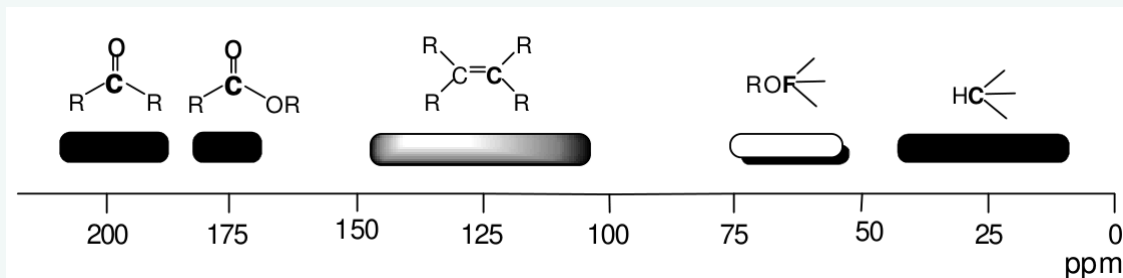
The total syntheses of two isomeric carbasugars having skeleton **1** are described below.



The total synthesis of **1** starts with a reduction of benzene by sodium in liquid ammonia to give **A**. The C-13 NMR spectrum of **A** consists of two signals at 124.0 and 26.0 ppm.

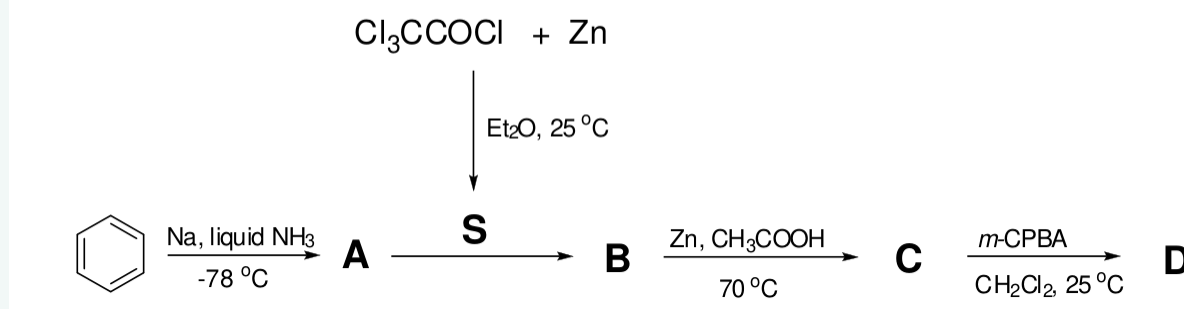
Trichloroacetyl chloride in the presence of Zn gives a reactive species **S** (see the Scheme 7.1). One equivalent of **S** undergoes [2+2]cycloaddition with **A** to form a racemic product **B**. The reaction of **B** with Zn in acetic acid gives **C**. Compound **C** contains only carbon, hydrogen and oxygen. The C-13 NMR spectrum of **C** exhibits three sp^2 carbon signals at 210.0, 126.5 and 125.3 ppm.

The reaction of **C** with one equivalent *m*-chloroperbenzoic acid (*m*-CPBA) in methylene chloride gives **D** as a major product. The C-13 NMR spectrum of **D** exhibits also three signals in the sp^2 region at 177.0, 125.8, 124.0 ppm.



^{13}C -NMR chemical shift ranges of typical functional groups

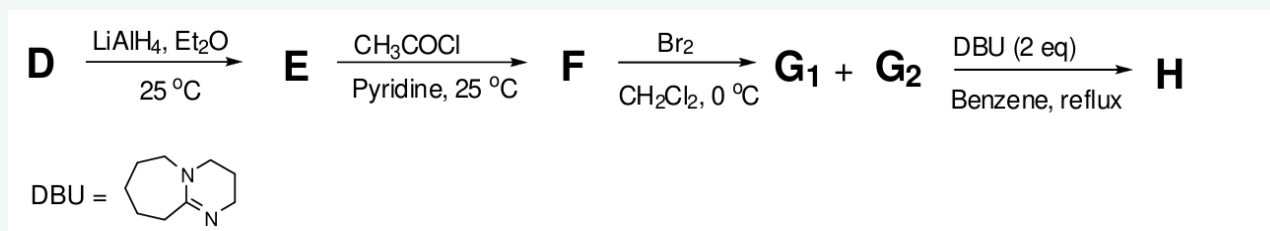
Scheme 7.1:



Scheme 7.1:

7.1 Draw the structures of **A**, **B**, **C**, **D**, and the intermediate **S**.

Reduction of **D** with LiAlH_4 yields **E** which reacts with an excess of acetyl chloride in pyridine to give **F** (Scheme 7.2).



Scheme 7.2:

7.2 Draw the structures (use one enantiomer) of **E** and **F** using dashed-wedged line notation. Assign the configurations (*R* or *S*) at the asymmetric carbon atoms in **E**.

The compound **F** (use the drawn enantiomer) reacts with bromine to give the stereoisomers **G₁** and **G₂**.

7.3 Draw the structures of **G₁** and **G₂** using dashed-wedged line notation.

A mixture of **G**₁ and **G**₂ reacts with two equivalents of 1,8-diazabicyclo- [5.4.0]undec-7-ene (DBU), which is a strong amine base, to afford **H**.

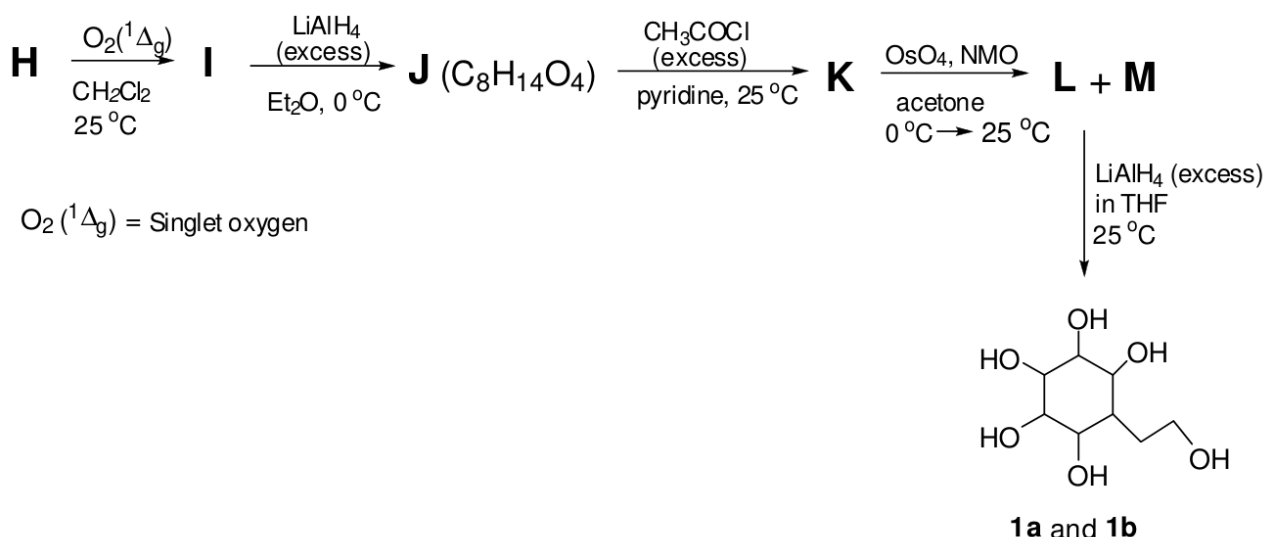
7.4 Draw the structure of **H** using dashed-wedged line notation.

Reaction of **H** with singlet oxygen (in situ generated) affords **I**. Although two isomers are theoretically possible, **I** is formed as the single isomer due to steric hindrance and electronic repulsion.

The reaction of **I** with excess of LiAlH_4 results in the formation of **J** (see the Scheme 7.3). The C-13 NMR spectrum of **J** shows 8 signals, two in the sp^2 region.

Reaction of **J** with excess acetyl chloride in the presence of pyridine yields **K**. Subsequent reaction of **K** with OsO_4 in the presence of 4-methylmorpholine 4-oxide (NMO) gives stereoisomers **L** and **M**. Upon reduction with excess LiAlH_4 , **L** and **M** give the stereoisomers **1a** and **1b**, respectively.

Scheme 7.3:



Scheme 7.3:

7.5 Draw the structures of **I**, **J**, **K**, **L**, **M**, **1a**, and **1b** using dashed-wedged line notation.

Official English text of the problem.

Answers

Drawing convention. Use a flat hexagon numbered clockwise: C_1 at the lower right, C_2 at the bottom, C_3 at the lower left, C_4 at the upper left, C_5 at the top, and C_6 at the upper right. These fixed labels track atoms throughout the synthesis; they are independent of systematic-name locants.

A **+** denotes a solid wedge toward the reader; a **–** denotes a dashed wedge away. Write **OAc** for $-\text{O}-\text{C}(=\text{O})-\text{CH}_3$. From **E** onward, the bond from C_1 to the hydroxyethyl or acetoxyethyl side chain is always **+**.

The SMILES for **B–D** show one member of each racemic pair. All subsequent structures follow that chosen enantiomer. The labels **G₁/G₂**, and **L/M** together with **1a/1b**, may be interchanged consistently.

- 7.1

A — cyclohexa-1,4-diene: C1=CCC=CC1

S — dichloroketene: O=C=C(Cl)Cl

B — racemic cis-8,8-dichlorobicyclo[4.2.0]oct-3-en-7-one:

O=C1C(Cl)(Cl)[C@H]2[C@@H]1CC=CC2

C — racemic cis-bicyclo[4.2.0]oct-3-en-7-one:

O=C1C[C@H]2[C@@H]1CC=CC2

D — racemic cis-7-oxabicyclo[4.3.0]non-3-en-8-one:

O=C1C[C@H]2[C@@H](O1)CC=CC2

In **B** and **C**, a cyclobutanone is cis-fused to the cyclohexene. In **D**, oxygen is inserted between the carbonyl carbon and the adjacent bridgehead, giving a cis-fused five-membered lactone.

- 7.2

E — (1S,6S)-6-(2-hydroxyethyl)cyclohex-3-en-1-ol:

OCC[C@H]1[C@@H](O)CC=CC1

F — 2-[(1S,6S)-6-acetoxycyclohex-3-en-1-yl]ethyl acetate:

CC(=O)OCC[C@H]1[C@@H](OC(C)=O)CC=CC1

Both have $C_4 = C_5$. In **E**, the C_1 -hydroxyethyl group and C_2 -OH are **+**, hence cis. Both asymmetric carbons are *S*. In **F**, replace both alcohol hydrogens by acetyl groups without changing either configuration.

- 7.3

Both products are stereoisomers of **2-(2-acetoxy-4,5-dibromocyclohexyl)ethyl acetate**.

G₁:

CC(=O)OCC[C@H]1[C@@H](OC(C)=O)C[C@@H](Br)[C@H](Br)C1

Draw C_4 -Br **+** and C_5 -Br **–**.

G₂:

CC(=O)OCC[C@H]1[C@@H](OC(C)=O)C[C@H](Br)[C@@H](Br)C1

Draw C_4 -Br **–** and C_5 -Br **+**.

The original C_1 side chain and C_2 -OAc remain **+** in both products.

- 7.4

H — 2-(6-acetoxycyclohexa-2,4-dien-1-yl)ethyl acetate:

CC(=O)OCC[C@H]1[C@@H](OC(C)=O)C=CC=C1

Draw the conjugated diene $C_3 = C_4 - C_5 = C_6$, retaining + bonds to the C_1 side chain and C_2 -OAc.

• 7.5

I — 2-(8-acetoxy-2,3-dioxabicyclo[2.2.2]oct-5-en-7-yl)ethyl acetate, the endoperoxide:

CC(=O)OCC[C@H]1[C@@H](OC(C)=O)[C@H]2C=C[C@@H]1OO2

Draw an $-O-O^-$ bridge between C_3 and C_6 , with both carbon-oxygen bonds $-$. The remaining double bond is $C_4 = C_5$.

J — 3-(2-hydroxyethyl)cyclohex-5-ene-1,2,4-triol:

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

Draw C_2 -OH +, C_3 -OH $-$, and C_6 -OH $-$, with $C_4 = C_5$.

K — 2-(2,5,6-triacetoxycyclohex-3-en-1-yl)ethyl acetate:

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

This is the tetraacetate of J, retaining every configuration.

L — 2-(2,3,6-triacetoxy-4,5-dihydroxycyclohexyl)ethyl acetate, diastereomer L:

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

M — 2-(2,3,6-triacetoxy-4,5-dihydroxycyclohexyl)ethyl acetate, diastereomer M:

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

1a — 6-(2-hydroxyethyl)cyclohexane-1,2,3,4,5-pentol, stereoisomer 1a:

OCC[C@H]1[C@@H](O)[C@H](O)[C@@H](O)[C@@H](O)[C@@H]1O

1b — 6-(2-hydroxyethyl)cyclohexane-1,2,3,4,5-pentol, stereoisomer 1b:

OCC[C@H]1[C@@H](O)[C@H](O)[C@H](O)[C@H](O)[C@@H]1O

Their precise wedge-dash drawings are:

Compound	C_2 substituent	C_3 substituent	C_4 substituent	C_5 substituent	C_6 substituent
L	OAc +	OAc $-$	OH +	OH +	OAc $-$
M	OAc +	OAc $-$	OH $-$	OH $-$	OAc $-$
1a	OH +	OH $-$	OH +	OH +	OH $-$
1b	OH +	OH $-$	OH $-$	OH $-$	OH $-$

Solution

For reductions, the equations below use formal reducing-hydrogen equivalents: $2 [H]$ represents $2 H^+ + 2 e^-$ in a balanced organic reduction half-equation. The stated reductant and work-up supply these equivalents.

7.1 — Identification of A, S, B, C, and D

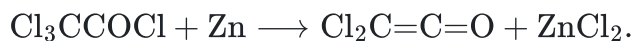
Benzene, c1ccccc1, undergoes reduction to the nonconjugated diene A:



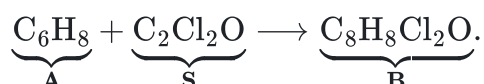
Cyclohexa-1,4-diene has four equivalent alkene carbons and two equivalent methylene carbons. It therefore gives precisely the two observed carbon environments:

$$\delta_{\text{alkene}} = 124.0 \text{ ppm}, \quad \delta_{\text{methylene}} = 26.0 \text{ ppm}.$$

Trichloroacetyl chloride, $\text{O}=\text{C}(\text{Cl})\text{C}(\text{Cl})(\text{Cl})\text{Cl}$, undergoes zinc-mediated dechlorination to **dichloroketene S**:

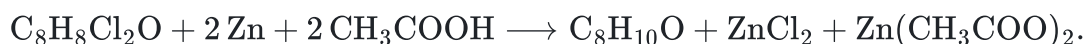


The ketene's central carbon is approximately linear. Its carbon-carbon double bond undergoes [2+2] cycloaddition with one double bond of **A**, producing the four-membered ketone ring of **B**:



The alkene's relative configuration is retained, giving a **cis-fused** product. Attack on either face of the achiral diene produces the two enantiomers in equal amounts.

Zinc in acetic acid, $\text{CC}(=\text{O})\text{O}$, replaces both chlorines by hydrogen:



Thus **C** is the corresponding chlorine-free bicyclic cyclobutanone. Its three sp^2 signals are assigned as follows:

Chemical shift	Assignment
210.0 ppm	Ketone carbonyl carbon
126.5, 125.3 ppm	The two inequivalent alkene carbons

The next reagent is **3-chloroperoxybenzoic acid**, $\text{O}=\text{C}(\text{OO})\text{c}1\text{cccc}(\text{Cl})\text{c}1$. The shift from a ketone carbonyl at 210.0 ppm to an ester carbonyl at 177.0 ppm, together with retention of two alkene signals, identifies a **Baeyer–Villiger oxidation**.

The more substituted bridgehead carbon migrates preferentially over the methylene carbon. Oxygen is therefore inserted between the bridgehead and the carbonyl carbon, expanding the cyclobutanone to the five-membered lactone **D**. Migration retains configuration.

The balanced oxidation is

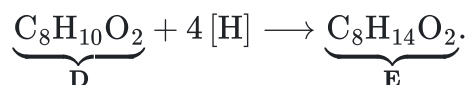


where the acid by-product is **3-chlorobenzoic acid**, $\text{O}=\text{C}(\text{O})\text{c}1\text{cccc}(\text{Cl})\text{c}1$.

An alkene epoxidation would remove the two alkene-carbon signals and retain the ketone carbonyl; that does not match the observed spectrum.

7.2 — Reduction, acetylation, and configurations of E

Lithium aluminium hydride, $[\text{Li}^+].[\text{AlH}_4^-]$, reduces the lactone carbonyl and opens the lactone:



The acyl-oxygen bond is broken. The oxygen already attached to C_2 becomes its hydroxyl group, while the former carbonyl carbon becomes the terminal carbon of the $-\text{CH}_2\text{CH}_2\text{OH}$ side chain at C_1 . Consequently, the two substituents remain **cis**.

For the chosen drawing, both substituent bonds are solid wedges and both stereocentre hydrogens point away. The CIP priorities are:

Centre	Priority 1	Priority 2	Priority 3	Priority 4
C_1	Ring path through C_2	Hydroxyethyl side chain	Ring path through C_6	H
C_2	OH	Ring path through C_1	Ring path through C_3	H

At C_1 , the side chain outranks the path through C_6 because its terminal carbon encounters oxygen before the competing ring path does. In the specified projection, $1 \rightarrow 2 \rightarrow 3$ is counterclockwise at both centres with H away. Therefore,

$$C_1 = S, \quad C_2 = S.$$

These centres are positions 6 and 1, respectively, in the systematic name of **E**. The mirror-image choice would give *R, R*.

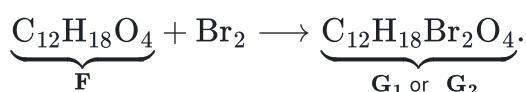
Acetyl chloride, CC(=O)Cl, acetylates both alcohols. Pyridine, n1cccc1, captures the hydrogen chloride as pyridinium chloride, [Cl-].[nH+]1cccc1:



Acetylation changes the oxygen substituents without breaking either stereogenic carbon–oxygen bond, giving **F** with unchanged configurations.

7.3 — Bromination to G_1 and G_2

Bromine, BrBr, adds across $C_4 = C_5$:



The alkene forms a bridged bromonium intermediate. Bromide opens it from the opposite face, so addition is **anti** and the two bromines are **trans**.

The two faces of the alkene are diastereotopic because **F** already contains stereocentres. Addition from the alternative faces therefore gives the two diastereomers listed in the Answers:

$$\begin{aligned} \mathbf{G}_1 : (C_4\text{-Br}, C_5\text{-Br}) &= (+, -), \\ \mathbf{G}_2 : (C_4\text{-Br}, C_5\text{-Br}) &= (-, +). \end{aligned}$$

7.4 — Double elimination to **H**

DBU, **1,8-diazabicyclo[5.4.0]undec-7-ene**, has SMILES C1CCC2=NCCCN2CC1.

In a reactive chair conformation of either dibromide, the vicinal trans bromines can occupy axial positions. Each then has an antiperiplanar axial hydrogen on an adjacent methylene carbon. Two E2 eliminations remove:

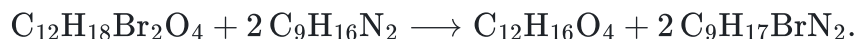
- the bromine at C_4 and a hydrogen at C_3 ;
- the bromine at C_5 and a hydrogen at C_6 .

This gives the conjugated diene

$$C_3 = C_4 - C_5 = C_6.$$

Both dibromides converge to **H**, since the stereocentres created during bromination become trigonal alkene carbons.

The balanced reaction is

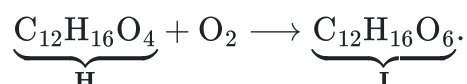


The salt is **DBU hydrobromide**, $[\text{Br}^-] \cdot \text{C}_1\text{CCC}2=[\text{NH}^+]\text{CCCN}2\text{CC}1$. The original configurations at C_1 and C_2 are retained.

7.5 — Endoperoxide formation and completion of the carbasugars

Formation of I. Singlet dioxygen has connectivity SMILES $\text{O}=\text{O}$; its $^1\Delta_g$ electronic state must be specified separately because ordinary SMILES does not encode that state.

It undergoes [4+2] cycloaddition with the conjugated diene:

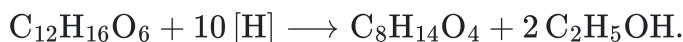


The two new carbon–oxygen bonds form at C_3 and C_6 , and the remaining double bond is $C_4 = C_5$. The cis C_1 and C_2 substituents occupy the + face. Approach from the opposite face minimizes the stated steric and electronic repulsions. Thus the peroxide bridge has both carbon–oxygen bonds –.

Formation of J. Excess lithium aluminium hydride reduces the peroxide bond and both acetate groups. The carbon–oxygen bonds at C_3 and C_6 remain intact, so both resulting hydroxyl groups retain the – configuration.

Reduction of each acetate requires four formal hydrogen equivalents and releases **ethanol**, CCO.

Peroxide cleavage requires two more:



The product therefore has:

- a hydroxyethyl side chain at C_1 , +;
- OH at C_2 , +;
- OH at C_3 and C_6 , both –;
- one double bond, $C_4 = C_5$.

This gives the stated formula $\text{C}_8\text{H}_{14}\text{O}_4$. Its eight carbons are inequivalent, and precisely two are sp^2 , as required by the NMR data.

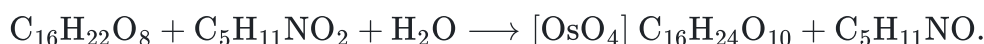
Formation of K. All four hydroxyl groups are acetylated:



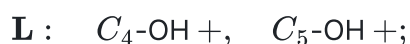
Thus **K** is the tetraacetate of **J**, with unchanged stereochemistry and the same $C_4 = C_5$ double bond.

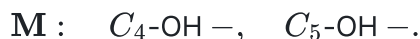
Formation of L and M. Osmium tetroxide, $\text{O}=[\text{Os}](=\text{O})(=\text{O})=\text{O}$, adds to the alkene through a cyclic osmate ester. Hydrolysis produces a **syn vicinal diol**.

The co-oxidant is **4-methylmorpholine 4-oxide**, $\text{C}[\text{N}^+]\text{1}([\text{O}^-])\text{CCOCC}1$; its reduced product is **4-methylmorpholine**, $\text{CN1CCOCC}1$. The balanced net transformation, including hydrolytic work-up, is



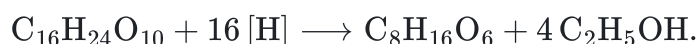
Addition from either face gives:





All previously established configurations remain unchanged.

Formation of 1a and 1b. Finally, excess lithium aluminium hydride removes the four acetate protecting groups. For either diastereomer,



The transformations are therefore



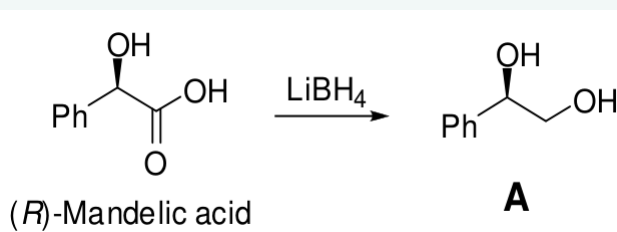
Each final product contains five ring hydroxyl groups and one terminal side-chain hydroxyl group. The two carbasugars differ at C_4 and C_5 , the centres introduced during osmium-mediated syn dihydroxylation.

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

Problem 8: Click chemistry

Click chemistry is a chemical concept introduced by K. B. Sharpless in 2001 and describes a set of chemical reactions that generate substances quickly, reliably and quantitatively by joining molecules through small units under mild conditions. This methodology has recently been applied as a key step in the following synthesis of bicyclic compounds.

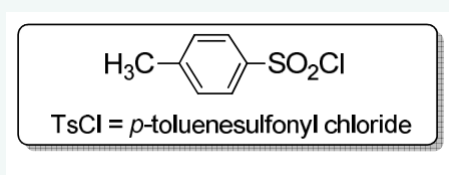
Mandelic acid is a versatile natural compound and widely used as a “chiral pool” in synthesis. The reduction of (*R*)-mandelic acid with LiBH_4 affords **A**.



Reaction of **A** with one equivalent of *p*-toluenesulfonyl chloride gives **B** (Scheme 8.1). Heating **B** in pyridine yields **C**. During this transformation, compounds **B** and **C** retain their absolute configurations.



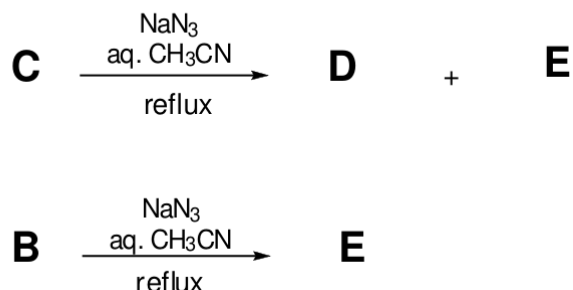
Scheme 8.1:



8.1 Draw the structures of **B** and **C** with the correct stereochemistry. Use dashed-wedged line notation throughout this problem.

Reaction of **C** with sodium azide in aqueous acetonitrile gives a mixture of enantiopure regioisomers **D** and **E** in a ratio of 3 : 1 (Scheme 8.2). On the other hand, the compound **B** affords **E** as the sole product under the same condition.

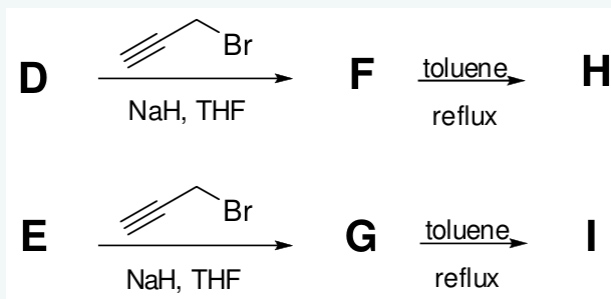
Scheme 8.2:



Scheme 8.2:

8.2 Draw the structures of **D** and **E** with the correct stereochemistry.

Part I: Compounds **D** and **E** are separately subjected to NaH mediated reaction with 3-bromoprop-1-yne to afford **F** and **G**, respectively (Scheme 8.3). Heating **F** and **G** separately in toluene gives the bicyclic products **H** and **I**, respectively.

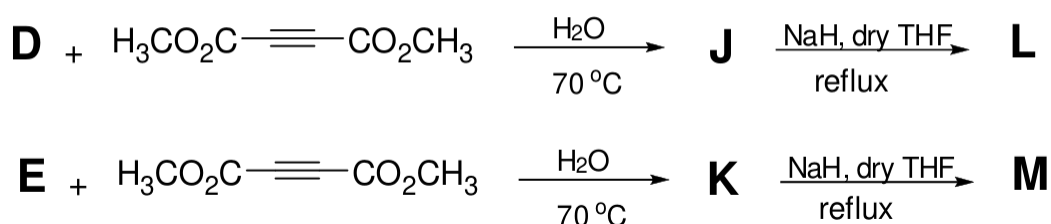


Scheme 8.3:

8.3 Draw the structure of compounds **F**, **G**, **H** and **I** with the correct stereochemistry.

Part II: Reaction of **D** and **E** separately with dimethyl acetylenedicarboxylate in water at 70°C forms the optically active monocyclic regioisomers **J** and **K**, respectively (Scheme 8.4). Subsequent treatment of **J** and **K** with NaH gives final bicyclic products **L** and **M**, respectively, both having the formula $\text{C}_{13}\text{H}_{11}\text{N}_3\text{O}_4$.

Scheme 8.4:



Scheme 8.4:

8.4 Draw the structures of compounds **J**, **K**, **L** and **M** with the correct stereochemistry.

Official English text of the problem.

Answers

All configurations below refer to the phenyl-bearing stereocenter. The bicyclic names describe the fused heterocyclic core explicitly.

- **8.1**

B: (2*R*)-2-Hydroxy-2-phenylethyl 4-methylbenzenesulfonate.

SMILES: Cc1ccc(S(=O)(=O)OC[C@H](O)c2ccccc2)cc1

C: (2*R*)-2-Phenyloxirane, also called (*R*)-styrene oxide.

SMILES: c1ccccc1[C@@H]1CO1

- **8.2**

D: (2*S*)-2-Azido-2-phenylethan-1-ol, the major product.

SMILES: OC[C@@H](N=[N+]=[N-])c1ccccc1

E: (1*R*)-2-Azido-1-phenylethan-1-ol, the minor product from **C** and sole product from **B**.

SMILES: [N-]=[N+]=NC[C@H](O)c1ccccc1

- **8.3**

F: 3-[(2*S*)-2-Azido-2-phenylethoxy]prop-1-yne.

SMILES: C#CCOC[C@@H](N=[N+]=[N-])c1ccccc1

G: 3-[(1*R*)-2-Azido-1-phenylethoxy]prop-1-yne.

SMILES: C#CCO[C@H](CN=[N+]=[N-])c1ccccc1

H: (2*S*)-2-Phenyl-4-oxa-1,8,9-triazabicyclo[4.3.0]nona-6,8-diene.

SMILES: c1nnn2[C@@H](c3ccccc3)COCc12

I: (3*R*)-3-Phenyl-4-oxa-1,8,9-triazabicyclo[4.3.0]nona-6,8-diene.

SMILES: c1nnn2C[C@@H](c3ccccc3)OCc12

- **8.4**

J: Dimethyl 1-[(1*S*)-2-hydroxy-1-phenylethyl]-1*H*-1,2,3-triazole-4,5-dicarboxylate.

SMILES: COC(=O)c1nnn([C@H](CO)c2ccccc2)c1C(=O)OC

K: Dimethyl 1-[(2*R*)-2-hydroxy-2-phenylethyl]-1*H*-1,2,3-triazole-4,5-dicarboxylate.

SMILES: COC(=O)c1nnn(C[C@H](O)c2ccccc2)c1C(=O)OC

L: Methyl (2*S*)-5-oxo-2-phenyl-4-oxa-1,8,9-triazabicyclo[4.3.0]nona-6,8-diene-7-carboxylate.

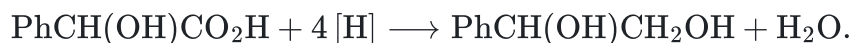
SMILES: COC(=O)c1nnn2[C@@H](c3ccccc3)COC(=O)c12

M: Methyl (3*R*)-5-oxo-3-phenyl-4-oxa-1,8,9-triazabicyclo[4.3.0]nona-6,8-diene-7-carboxylate.
SMILES: COC(=O)c1nnn2C[C@@H](c3ccccc3)OC(=O)c12

Solution

Here Ph denotes phenyl, Me methyl, and Ts *p*-toluenesulfonyl.

The starting material is (*R*)-mandelic acid, O=C(O)[C@H](O)c1ccccc1. Reduction gives **A**, (1*R*)-1-phenylethane-1,2-diol, OC[C@H](O)c1ccccc1. The formal organic reduction balance is



Here [*H*] represents reducing equivalents supplied by lithium borohydride, [Li+].[BH4-], followed by protonation during workup; water has SMILES O. The existing stereocenter is retained.

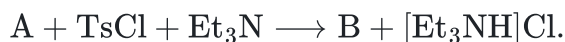
Wedge-dash drawing convention. For each product, place the phenyl group to the lower left and the carbon side chain to the lower right of the stereocenter, using ordinary bonds as in the drawing of **A**. Place the directly attached oxygen or nitrogen above that carbon:

- For **B, C, E, G, I, K and M**, draw this heteroatom bond as a **solid wedge**, with hydrogen directed away.
- For **D, F, H, J and L**, draw it as a **dashed wedge**, with hydrogen directed toward the viewer.

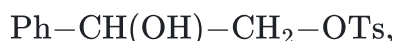
In this orientation these are, respectively, the *R* and *S* configurations. The ring connections are specified below; the drawings do not imply a fixed conformation of the flexible rings.

8.1 — Identification of B and C

One equivalent of *p*-toluenesulfonyl chloride, Cc1ccc(S(=O)(=O)Cl)cc1, converts the less hindered primary hydroxyl group of **A** into a tosylate:



Triethylamine, CCN(CC)CC, accepts the proton, forming triethylammonium chloride, CC[NH+](CC)CC.[Cl-]. Thus **B** has the connectivity



with the original *R* stereocenter.

On heating, the remaining hydroxyl oxygen attacks the primary carbon bearing the tosylate group. Intramolecular displacement closes the three-membered epoxide ring, while pyridine accepts the hydroxyl proton:



Pyridine is n1ccccc1; pyridinium is c1cc[nH+]cc1; *p*-toluenesulfonate is Cc1ccc(S(=O)(=O)[O-])cc1.

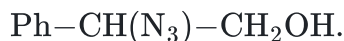
The substitution occurs at the terminal, nonstereogenic carbon. The benzylic carbon-oxygen bond remains intact, so **C** is (*R*)-2-phenyloxirane.

To draw **C**, connect the hydroxyl oxygen of the original **A** skeleton to its adjacent terminal carbon, producing the triangle containing oxygen, the phenyl-bearing carbon and CH2. The stated retention also excludes a pathway involving displacement at the benzylic stereocenter.

8.2 — Identification of D and E

Sodium azide, $[\text{Na}^+] \cdot [\text{N}_3^-] = [\text{N}^+] = [\text{N}^-]$, supplies azide ion, $[\text{N}_3^-] = [\text{N}^+] = [\text{N}^-]$. Backside attack can open **C** at either carbon.

1. **Attack at the benzylic carbon:** the benzylic carbon–oxygen bond breaks, and that stereocenter undergoes inversion. The original epoxide oxygen remains on the terminal carbon and is protonated. This gives **D**, the *S* azido alcohol:



2. **Attack at the terminal carbon:** the terminal carbon–oxygen bond breaks, while the benzylic carbon–oxygen bond is retained. This gives **E**, the *R* azido alcohol:

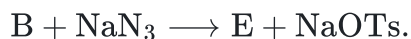


The separately balanced opening pathways are



Sodium hydroxide is $[\text{Na}^+] \cdot [\text{OH}^-]$. The supplied product ratio is **D : E = 3 : 1**.

The reaction of **B** independently establishes the identity of **E**. Azide replaces the terminal tosylate directly:



Sodium *p*-toluenesulfonate is $[\text{Na}^+] \cdot \text{Cc1ccc(S(=O)(=O)[O-])cc1}$. Since this substitution does not occur at the stereocenter, its *R* configuration is retained.

8.3 — Identification of F, G, H and I

Sodium hydride, $[\text{Na}^+] \cdot [\text{H}^-]$, removes the alcohol proton. The resulting oxygen nucleophile displaces bromide from 3-bromoprop-1-yne, or propargyl bromide, $\text{C}\equiv\text{CCBr}$. These Williamson ether syntheses give



Sodium bromide is $[\text{Na}^+] \cdot [\text{Br}^-]$, and hydrogen is $[\text{H}][\text{H}]$.

Consequently:

- **F** has connectivity $\text{Ph}-\text{CH}(\text{N}_3)-\text{CH}_2-\text{O}-\text{CH}_2-\text{C}\equiv\text{CH}$, retaining *S*.
- **G** has connectivity $\text{Ph}-\text{CH}(\text{OCH}_2\text{C}\equiv\text{CH})-\text{CH}_2\text{N}_3$, retaining *R*.

Heating brings about an **intramolecular azide–alkyne [3 + 2] cycloaddition**:



All three azide nitrogens and both alkyne carbons become the five atoms of a 1,2,3-triazole; no atoms are eliminated.

For the following drawing instructions, number the triazole consecutively **N1–N2–N3–C4–C5–N1**, with N1 being the nitrogen originally attached to the carbon chain. These are triazole positions, distinct from the bicyclic numbering used in the names above.

The tether favors closure of a six-membered second ring. The alkyne carbon carrying the CH₂O tether becomes **C5**, adjacent to N1; the original terminal alkyne carbon becomes **C4**, bearing hydrogen.

The precise fused-ring connections are:

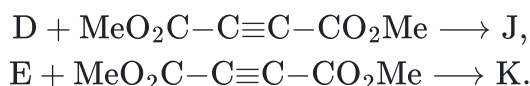
- **H**: Starting at N1, follow the six-membered ring through the *S* phenyl-bearing carbon, then CH₂–O–CH₂, then C5, and back to N1.
- **I**: Starting at N1, follow the six-membered ring through CH₂, then the *R* phenyl-bearing carbon, then O–CH₂, then C5, and back to N1.

Both products therefore share the **N1–C5 bond** between their triazole and six-membered ether rings. One valid Kekulé drawing has double bonds between N2 and N3 and between C4 and C5.

Neither cycloaddition changes a bond at the stereocenter. Thus **H** retains *S*, and **I** retains *R*. Their formulas remain C₁₁H₁₁N₃O, identical to those of **F** and **G**.

8.4 – Identification of J, K, L and M

Dimethyl acetylenedicarboxylate, COC(=O)C#CC(=O)OC, undergoes an intermolecular azide–alkyne cycloaddition with each azido alcohol:



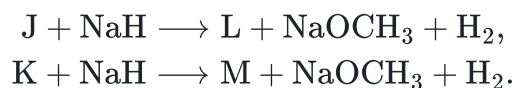
Because the alkyne is symmetric, both triazole carbon atoms bear a methyl ester group. Using the triazole numbering defined above:

- **J** has a CH(Ph)CH₂OH substituent attached through its *S* benzylic carbon to N1, with CO₂Me at both C4 and C5.
- **K** has a CH₂CH(OH)Ph substituent attached through its terminal CH₂ to N1, again with CO₂Me at both C4 and C5. Its benzylic center remains *R*.

The regioisomerism between **J** and **K** comes from the different connectivities of **D** and **E**.

Next, sodium hydride removes the remaining alcohol proton. The oxygen nucleophile attacks the carbonyl carbon of the **C5 ester**, producing a six-membered cyclic ester. Collapse of the tetrahedral intermediate expels methoxide. The **C4 methyl ester remains intact**.

The balanced reactions under the basic conditions are



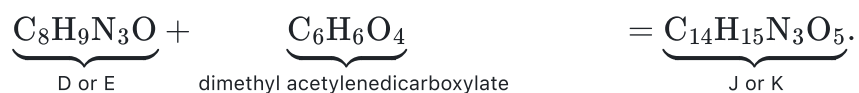
Sodium methoxide is [Na⁺]·C[O[–]].

For precise drawings of the products:

- **L**: Starting at triazole N1, follow the new six-membered ring through the *S* phenyl-bearing carbon, then CH₂–O–C(=O), then triazole C5, and back to N1.
- **M**: Starting at triazole N1, follow the new six-membered ring through CH₂, then the *R* phenyl-bearing carbon, then O–C(=O), then triazole C5, and back to N1.

In both drawings, retain the CO₂Me substituent on triazole C4. No substitution occurs at the stereocenter, so **L** remains *S*, and **M** remains *R*.

The formula check is



Cyclization removes from the organic molecule the elements of methanol, CO:



in agreement with the formula specified for both **L** and **M**.

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