

IChO 2017

Theory problems and solutions · Nakhon Pathom, Thailand · 11 theory problems with complete solutions

eulersolve.org/icho/2017/

Problem 1: Production of propene using heterogeneous catalysts

Propene or propylene is one of the most valuable chemicals for the petrochemical industry in Thailand and around the world. One good example of the commercial use of propene is for the production of polypropylene (PP).

Part A.

Propene can be synthesized via a direct dehydrogenation of propane in the presence of a heterogeneous catalyst. However, such a reaction is not economically feasible due to the nature of the reaction itself. Provide a concise explanation to each of the questions below. Additional information: $H_{\text{bond}}(\text{C}=\text{C}) = 1.77H_{\text{bond}}(\text{C}-\text{C})$, $H_{\text{bond}}(\text{H}-\text{H}) = 1.05H_{\text{bond}}(\text{C}-\text{H})$, and $H_{\text{bond}}(\text{C}-\text{H}) = 1.19H_{\text{bond}}(\text{C}-\text{C})$, where H_{bond} refers to average bond enthalpy of the indicated chemical bond.

1.1 What is the enthalpy change of the direct dehydrogenation of propane? Show your calculation and express your answer in terms of $H_{\text{bond}}(\text{C}-\text{C})$.

1.2 It is difficult to increase the amount of propene by increasing pressure at constant temperature. Which law or principle can best explain this phenomenon? Select your answer by marking "✓" in **one** of the open circles.

- ☐ Boyle's law
- ☐ Charles' law
- ☐ Dalton's law
- ☐ Raoult's law
- ☐ Le Chatelier's principle

1.3 Initially, the system is in equilibrium. Consistent with question **1.1**, what is/are correct set(s) of signs for the following thermodynamic variables of the system for the direct dehydrogenation of propane? Select your answer(s) by marking „✓" in any of the open square(s).

	ΔH	ΔS	ΔG	T^*
☐	–	+	+	lower
☐	–	+	–	higher
☐	–	–	+	lower
☐	–	–	–	higher
☐	+	+	+	lower
☐	+	+	–	higher

	ΔH	ΔS	ΔG	T^*
☐	+	-	+	lower
☐	+	-	-	higher

☐ None of the above is correct

* Relative to the initial temperature at the same partial pressure.

Part B.

A better reaction to produce large quantity of propene is the *oxidative dehydrogenation* (ODH) using solid catalysts, such as vanadium oxides, under molecular oxygen gas. Although this type of reaction is still under intense research development, its promise toward the production of propene at an industrial scale eclipses that of the direct dehydrogenation.

1.4 The overall rate of propane consumption in the reaction is

$$r_{\text{C}_3\text{H}_6} = \frac{1}{\frac{p^0}{k_{\text{red}} p_{\text{C}_3\text{H}_6}} + \frac{p^0}{k_{\text{ox}} p_{\text{O}_2}}}$$

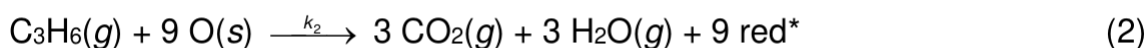
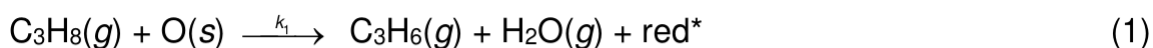
where k_{red} and k_{ox} are the rate constants for the reduction of metal oxide catalyst by propane and for the oxidation of the catalyst by molecular oxygen, respectively, and p^0 is the standard pressure of 1 bar. Some experiments found that the rate of oxidation of the catalyst is 100,000 times faster than that of the propane oxidation. The experimental

$$r_{\text{C}_3\text{H}_8} = k_{\text{obs}} \frac{p_{\text{C}_3\text{H}_6}}{p^0}$$

where k_{obs} is the observed rate constant (0.062 mol s^{-1}). If the reactor containing the catalyst is continuously passed through with propane and oxygen at a total pressure of 1 bar, determine the value of k_{red} and k_{ox} when the partial pressure of propane is 0.10 bar. Assume that the partial pressure of propene is negligible.

Part C.

The metal oxide catalyst contains oxygen atoms on its surface that serve as active sites for the ODH. Denoting red* as a reduced site and O(s) as an oxygen atom on the surface of the catalyst, one of the proposed mechanisms for the ODH in the presence of the catalyst can be written as follows:



Given

$$\beta = \frac{\text{number of reduced sites}}{\text{total number of active sites}}$$

The rate laws for the above 3 steps are:

$$r_1 = k_1 p_{\text{C}_2\text{H}_8} (1 - \beta)$$

$$r_2 = k_2 p_{\text{C}_3\text{H}_6} (1 - \beta)$$

and

$$r_3 = k_3 p_{\text{O}_2} \beta$$

1.5 Assuming that the amount of oxygen atoms on the surface stays constant at any time of reaction, calculate β as a function of

$$k_1, k_2, k_3, p_{\text{C}_2\text{H}_8}, p_{\text{C}_3\text{H}_6}, \text{ and } p_{\text{O}_2}.$$

Official English text of the problem.

Answers

- **1.1:** $\Delta H \approx +0.36 H_{\text{bond}}(\text{C}-\text{C})$. The reaction is endothermic.
- **1.2:** Check **Le Chatelier's principle**.
- **1.3:** Check the **fifth and sixth rows**: (+, +, +, lower) and (+, +, −, higher), in the order ($\Delta H, \Delta S, \Delta G, T^*$).
- **1.4:** $k_{\text{red}} \approx 0.062 \text{ mol s}^{-1}$ and $k_{\text{ox}} \approx 6.9 \times 10^2 \text{ mol s}^{-1}$.
- **1.5:** Using the corrected propane subscript,

$$\beta = \frac{k_1 p_{\text{C}_3\text{H}_8} + 9k_2 p_{\text{C}_3\text{H}_6}}{k_1 p_{\text{C}_3\text{H}_8} + 9k_2 p_{\text{C}_3\text{H}_6} + 2k_3 p_{\text{O}_2}}.$$

Solution

The molecular species used below are propane CCC, propene C=CC, hydrogen [H][H], molecular oxygen O=O, water O, and carbon dioxide O=C=O. The adsorbed oxygen atoms and reduced catalyst sites belong to an unspecified solid surface, so their surface bonding has no uniquely defined molecular SMILES.

1.1 — Enthalpy of direct dehydrogenation

The balanced reaction is



Propane contains two carbon–carbon single bonds and eight carbon–hydrogen bonds. The products contain one carbon–carbon single bond, one carbon–carbon double bond, six carbon–hydrogen bonds, and one hydrogen–hydrogen bond.

Using average bond enthalpies,

$$\begin{aligned} \Delta H &\approx [2H_{\text{bond}}(\text{C}-\text{C}) + 8H_{\text{bond}}(\text{C}-\text{H})] \\ &\quad - [H_{\text{bond}}(\text{C}-\text{C}) + H_{\text{bond}}(\text{C}=\text{C}) + 6H_{\text{bond}}(\text{C}-\text{H}) + H_{\text{bond}}(\text{H}-\text{H})] \\ &= H_{\text{bond}}(\text{C}-\text{C}) + 2H_{\text{bond}}(\text{C}-\text{H}) - H_{\text{bond}}(\text{C}=\text{C}) - H_{\text{bond}}(\text{H}-\text{H}). \end{aligned}$$

Let $D = H_{\text{bond}}(\text{C}-\text{C})$. The supplied ratios give

$$\begin{aligned}\Delta H &\approx [1 + 2(1.19) - 1.77 - 1.05(1.19)]D \\ &= 0.3605D \\ &\approx \boxed{+0.36H_{\text{bond}}(\text{C}-\text{C})}.\end{aligned}$$

The result has the same molar-energy units as the bond enthalpy. Its positive sign identifies an **endothermic** reaction.

1.2 — Effect of pressure

The forward reaction increases the number of gas molecules from one to two:



According to **Le Chatelier's principle**, increasing pressure by compression at constant temperature favors the side with fewer gas molecules. The equilibrium therefore shifts toward propane, reducing the equilibrium amount of propene.

Check **Le Chatelier's principle**.

1.3 — Thermodynamic signs after changing temperature

From 1.1,

$$\Delta H > 0.$$

At the initial equilibrium temperature T_0 ,

$$\Delta G(T_0) = \Delta H - T_0\Delta S = 0.$$

Consequently,

$$\Delta S(T_0) = \frac{\Delta H}{T_0} > 0,$$

consistent with the increase in the number of gaseous molecules.

At fixed partial pressures,

$$\left(\frac{\partial \Delta G}{\partial T}\right)_{\{p_i\}} = -\Delta S < 0.$$

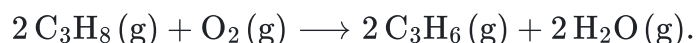
Thus, changing the temperature from the initial equilibrium gives:

Temperature change	ΔH	ΔS	ΔG
Lower temperature	+	+	+
Higher temperature	+	+	−

Check the **fifth and sixth rows**. These signs describe the temperature perturbation at the specified partial pressures. Once the composition reaches its new equilibrium, the reaction Gibbs energy is again zero.

1.4 — Reduction and oxidation rate constants

The balanced overall oxidative dehydrogenation is



The kinetic expressions must use the **propane** partial pressure, $p_{\text{C}_3\text{H}_8}$, wherever they describe propane consumption.

For the stated propane–oxygen mixture with negligible products,

$$p_{\text{O}_2} = 1.00 - 0.10 = 0.90 \text{ bar}.$$

The experimental consumption rate is

$$r = k_{\text{obs}} \frac{p_{\text{C}_3\text{H}_8}}{p^0} = (0.062 \text{ mol s}^{-1}) \frac{0.10 \text{ bar}}{1 \text{ bar}} = 6.2 \times 10^{-3} \text{ mol s}^{-1}.$$

Define the two pressure-weighted kinetic terms

$$a = k_{\text{red}} \frac{p_{\text{C}_3\text{H}_8}}{p^0}, \quad b = k_{\text{ox}} \frac{p_{\text{O}_2}}{p^0}.$$

Then the given rate expression becomes

$$r = \frac{1}{1/a + 1/b} = \frac{ab}{a + b}.$$

Interpreting the stated speed comparison as $b = 10^5 a$,

$$r = \frac{a}{1 + 10^{-5}} = \frac{k_{\text{red}}}{1 + 10^{-5}} \frac{p_{\text{C}_3\text{H}_8}}{p^0}.$$

Comparison with the experimental expression gives

$$k_{\text{red}} = k_{\text{obs}}(1 + 10^{-5}) \approx \boxed{0.062 \text{ mol s}^{-1}}.$$

The oxidation constant follows from the same rate comparison:

$$\frac{k_{\text{ox}} p_{\text{O}_2}}{k_{\text{red}} p_{\text{C}_3\text{H}_8}} = 10^5,$$

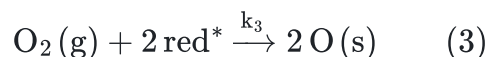
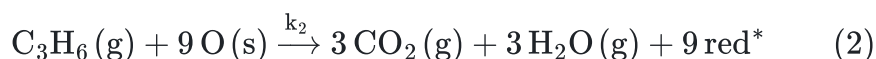
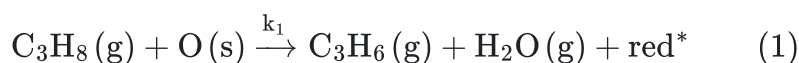
so

$$\begin{aligned} k_{\text{ox}} &= 10^5 k_{\text{red}} \frac{p_{\text{C}_3\text{H}_8}}{p_{\text{O}_2}} \\ &= 10^5 (0.06200062) \frac{0.10}{0.90} \text{ mol s}^{-1} \\ &\approx \boxed{6.9 \times 10^2 \text{ mol s}^{-1}}. \end{aligned}$$

Both constants have units of mol s^{-1} , because the pressure factors in these expressions are dimensionless.

1.5 — Steady-state fraction of reduced sites

The three supplied reactions are



Here $\text{O}(\text{s})$ denotes an oxygen atom on the catalyst surface, as defined in the question.

Each occurrence of step 1 consumes one surface oxygen atom; step 2 consumes nine; step 3 supplies two. Constancy of the surface oxygen population therefore requires

$$2r_3 - r_1 - 9r_2 = 0.$$

Using the supplied rate laws, with the propane subscript corrected,

$$2k_3 p_{\text{O}_2} \beta = k_1 p_{\text{C}_3\text{H}_8} (1 - \beta) + 9k_2 p_{\text{C}_3\text{H}_6} (1 - \beta).$$

Factor the right-hand side:

$$2k_3p_{O_2}\beta = (k_1p_{C_3H_8} + 9k_2p_{C_3H_6})(1 - \beta).$$

Solving for β ,

$$\beta = \frac{k_1p_{C_3H_8} + 9k_2p_{C_3H_6}}{k_1p_{C_3H_8} + 9k_2p_{C_3H_6} + 2k_3p_{O_2}}.$$

The factors 9 and 2 arise from the oxygen-atom balance. The pressure and coverage exponents remain those explicitly supplied in the question.

The solution was checked against the official solution.

Problem 2: Kinetic isotope effect (KIE) and zero-point vibrational energy (ZPE)

Calculation of ZPE and KIE

Kinetic isotope effect (KIE) is a phenomenon associated with a change in rate constant of the reaction when one of the atoms is replaced by its isotope. KIE can be used to confirm whether a particular bond to hydrogen is broken in the reaction. Harmonic oscillator model is used to estimate the difference in the rate between C–H and C–D bond activation (D – deuterium).

The vibrational frequency (ν) represented by harmonic oscillator model is

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

where k is the force constant and μ is the reduced mass.

The vibrational energies of the molecule are given by

$$E_n = \left(n + \frac{1}{2}\right) h\nu$$

where n is vibrational quantum number with possible values of 0, 1, 2, ... The energy of the lowest vibrational energy level (E_n at $n = 0$) is called **zero-point vibrational energy (ZPE)**.

2.1 Calculate the reduced mass of C–H (μ_{CH}) and C–D (μ_{CD}) in atomic mass unit.

Assume that the mass of deuterium is twice that of hydrogen.

Note: If a student is unable to calculate the values for μ_{CH} and μ_{CD} he/she can use $\mu_{CH} = 1.008$ and $\mu_{CD} = 2.016$ for the subsequent parts of the question. The given values are not necessarily be close to the correct values.

2.2 Given that the force constant (k) for C–H stretching is the same as that for the C–D stretching and the C–H stretching frequency is 2900 cm^{-1} , find the corresponding C–D stretching frequency (in cm^{-1}).

2.3 According to the C–H and C–D stretching frequencies in question **2.2**, calculate the zero-point vibrational energies (ZPE) of C–H and C–D stretching in kJ mol^{-1} .

Note: If a student is unable to calculate the values for ZPE in **2.3**, he/she can use $ZPE_{CH} = 7.23 \text{ kJ mol}^{-1}$ and $ZPE_{CD} = 2.15 \text{ kJ mol}^{-1}$ for the subsequent parts of the question. The given values are not necessarily be close to the correct values.

Kinetic isotope effect (KIE)

Due to the difference in zero-point vibrational energies, a protonated compound and its corresponding deuterated compounds are expected to react at different rates.

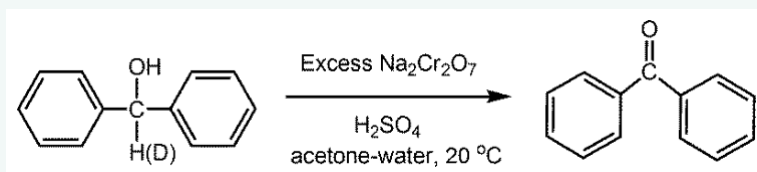
For the C–H and C–D bond dissociation reactions, the energies of both transition states and both products are identical. Then, the isotope effect is controlled by the difference in the ZPE's of the C–H and C–D bonds.

2.4 Calculate the difference in the bond dissociation energy (BDE) between C–D bond and C–H bond ($BDE_{CD} - BDE_{CH}$) in kJ mol^{-1} .

2.5 Assume that the activation energy (E_a) for the C–H/C–D bond cleavage is approximately equal to the bond dissociation energy and the Arrhenius factor is the same for both C–H and C–D bond cleavage. Find the relative rate constant for the C–H/C–D bond cleavage (k_{CH}/k_{CD}) at 25°C .

Using KIE to study reaction mechanism

The oxidation of nondeuterated and deuterated diphenylmethanol using an excess of chromic acid was studied.



2.6 Let C_0 be the initial concentration of either nondeuterated diphenylmethanol or deuterated diphenylmethanol and C_t its concentration at time t . The experiment led to two plots (Figure 2a and Figure 2b), from which the first-order rate constant can be determined.

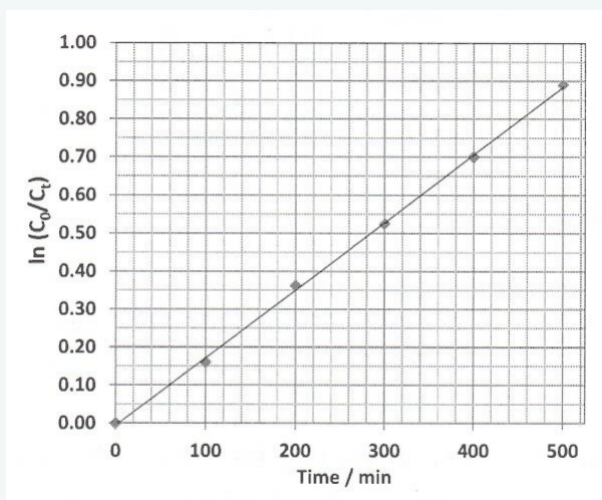


Figure 2a

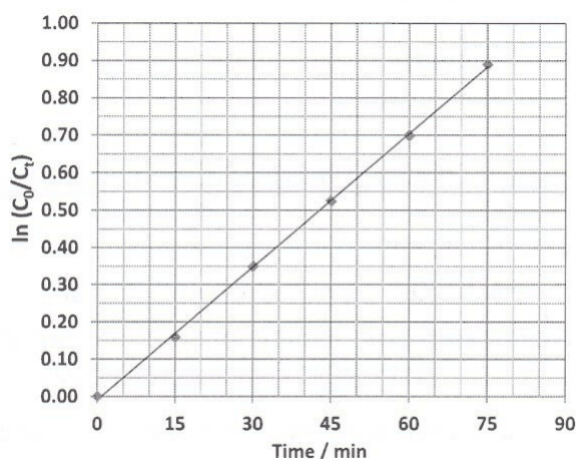


Figure 2b

Which plot should be for the oxidation of nondeuterated diphenylmethanol and which one is for the oxidation of deuterated diphenylmethanol?

For each statement, select your answer by marking "✓" in one of the square.

The oxidation of nondeuterated diphenylmethanol:

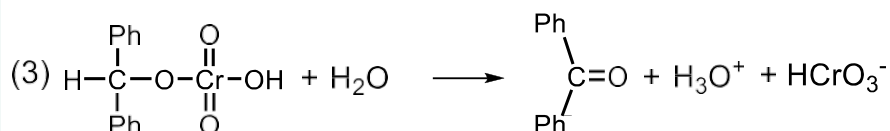
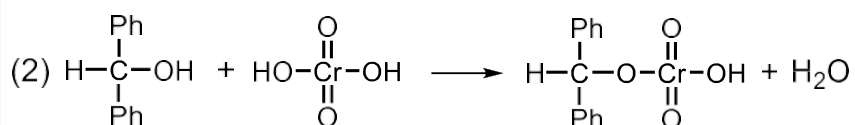
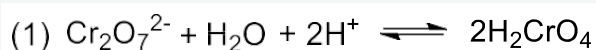
- ☐ Figure 2a
☐ Figure 2b

The oxidation of deuterated

- ☐ Figure 2a
☐ Figure 2b

2.7 Determine k_{CH} , k_{CD} (in min^{-1}), and the k_{CH}/k_{CD} of this reaction from the plots in question **2.6**.

2.8 The mechanism has been proposed as follows:



According to the information in **2.6** and **2.7**, which step should be the rate determining step?

Select your answer by marking "✓" in one of the corresponding squares:

- ☐ Step (1)
☐ Step (2)
☐ Step (3)

Answers

- 2.1: $\mu_{CH} = 0.9299 \text{ u}, \quad \mu_{CD} = 1.726 \text{ u}.$
- 2.2: $\tilde{\nu}_{CD} = 2.13 \times 10^3 \text{ cm}^{-1}.$
- 2.3: $ZPE_{CH} = 17.35 \text{ kJ mol}^{-1}, \quad ZPE_{CD} = 12.73 \text{ kJ mol}^{-1}.$
- 2.4: $BDE_{CD} - BDE_{CH} = +4.61 \text{ kJ mol}^{-1}.$
- 2.5: $k_{CH}/k_{CD} = 6.43$ at $25^\circ\text{C}.$
- 2.6: Nondeuterated diphenylmethanol: **Figure 2b**. Deuterated diphenylmethanol: **Figure 2a**.
- 2.7: $k_{CH} \approx 1.2 \times 10^{-2} \text{ min}^{-1}, \quad k_{CD} \approx 1.8 \times 10^{-3} \text{ min}^{-1}, \quad k_{CH}/k_{CD} \approx 6.7.$
- 2.8: **Step (3)** is the rate determining step.

Solution

The calculations use the standard atomic masses

$$m_C = 12.01 \text{ u}, \quad m_H = 1.008 \text{ u}, \quad m_D = 2m_H = 2.016 \text{ u},$$

and the constants

$$\begin{aligned} h &= 6.62607015 \times 10^{-34} \text{ J s}, \\ c &= 2.99792458 \times 10^{10} \text{ cm s}^{-1}, \\ N_A &= 6.02214076 \times 10^{23} \text{ mol}^{-1}, \\ R &= 8.314462618 \text{ J mol}^{-1} \text{ K}^{-1}. \end{aligned}$$

Here $\tilde{\nu} = \nu/c$ denotes the spectroscopic wavenumber in cm^{-1} .

2.1 — Reduced masses

For two bonded atoms,

$$\mu = \frac{m_1 m_2}{m_1 + m_2}.$$

Therefore,

$$\begin{aligned} \mu_{CH} &= \frac{(12.01)(1.008)}{12.01 + 1.008} \text{ u} = \boxed{0.9299 \text{ u}}, \\ \mu_{CD} &= \frac{(12.01)(2.016)}{12.01 + 2.016} \text{ u} = \boxed{1.726 \text{ u}}. \end{aligned}$$

2.2 — C–D stretching wavenumber

For equal force constants, both frequency and wavenumber are proportional to $\mu^{-1/2}$. Thus,

$$\frac{\tilde{\nu}_{CD}}{\tilde{\nu}_{CH}} = \sqrt{\frac{\mu_{CH}}{\mu_{CD}}}.$$

Using unrounded reduced masses,

$$\tilde{\nu}_{CD} = (2900 \text{ cm}^{-1}) \sqrt{\frac{0.9299493}{1.7262341}} = 2128.52 \text{ cm}^{-1}.$$

Hence,

$$\boxed{\tilde{\nu}_{CD} \approx 2.13 \times 10^3 \text{ cm}^{-1}}.$$

The greater reduced mass lowers the stretching frequency.

2.3 — Zero-point vibrational energies

At $n = 0$, the energy per oscillator is $\frac{1}{2}h\nu$. The molar zero-point energy is therefore

$$ZPE = \frac{1}{2}N_A h\nu = \frac{1}{2}N_A hc\tilde{\nu}.$$

With c expressed in cm s^{-1} ,

$$\frac{1}{2}N_A hc = 5.9813283 \times 10^{-3} \text{ kJ cm mol}^{-1}.$$

Consequently,

$$ZPE_{CH} = (5.9813283 \times 10^{-3})(2900) = \boxed{17.35 \text{ kJ mol}^{-1}},$$

$$ZPE_{CD} = (5.9813283 \times 10^{-3})(2128.52) = \boxed{12.73 \text{ kJ mol}^{-1}}.$$

The unrounded values, 17.34585 and 12.73138 kJ mol^{-1} , are retained for the following calculations.

2.4 — Difference in bond dissociation energies

Let D_e be the energy difference between the minimum of the bond potential and the dissociated products. Under the stated assumptions, D_e is the same for both isotopes. Dissociation begins from the vibrational ground state, so

$$BDE_{CH} = D_e - ZPE_{CH}, \quad BDE_{CD} = D_e - ZPE_{CD}.$$

Subtracting gives

$$\begin{aligned} BDE_{CD} - BDE_{CH} &= ZPE_{CH} - ZPE_{CD} \\ &= 17.34585 - 12.73138 \\ &= \boxed{+4.61 \text{ kJ mol}^{-1}}. \end{aligned}$$

The C–D bond requires more energy to dissociate because its vibrational ground state lies lower.

2.5 — Relative rate constant at 25 °C

The Arrhenius equation is

$$k = A \exp\left(-\frac{E_a}{RT}\right).$$

With equal pre-exponential factors,

$$\frac{k_{CH}}{k_{CD}} = \exp\left(\frac{E_{a,CD} - E_{a,CH}}{RT}\right).$$

Using $E_a \approx BDE$, the activation-energy difference is 4.61447 kJ mol^{-1} . At $T = 298.15 \text{ K}$,

$$\frac{k_{CH}}{k_{CD}} = \exp\left[\frac{4.61447 \times 10^3 \text{ J mol}^{-1}}{(8.314462618 \text{ J mol}^{-1} \text{ K}^{-1})(298.15 \text{ K})}\right] = \boxed{6.43}.$$

Thus, this model predicts that C–H cleavage is about 6.4 times faster.

2.6 — Identification of the plots

The organic compounds are:

Compound	SMILES
Nondeuterated diphenylmethanol, also called benzhydrol	<chem>OC(c1ccccc1)c1ccccc1</chem>
Diphenylmethanol deuterated at the methine carbon	<chem>OC([2H])(c1ccccc1)c1ccccc1</chem>
Benzophenone, the oxidation product	<chem>O=C(c1ccccc1)c1ccccc1</chem>

The deuterium is attached to carbon, as shown in the reaction scheme. Neither substrate has a stereogenic center because the two phenyl groups are identical.

For first-order disappearance,

$$-\frac{dC}{dt} = kC, \quad \ln\left(\frac{C_0}{C_t}\right) = kt.$$

Therefore, the slope of each graph is its rate constant. With the oxidant in excess, these are observed pseudo-first-order rate constants.

Figure 2b reaches the same value of $\ln(C_0/C_t)$ in a much shorter time than Figure 2a. It therefore represents the faster, nondeuterated substrate.

The answer-sheet selections are:

- **Nondeuterated diphenylmethanol:** mark **Figure 2b**.
- **Deuterated diphenylmethanol:** mark **Figure 2a**.

2.7 — Rate constants from the plots

Using the origin and the clearly readable points near $\ln(C_0/C_t) = 0.70$:

For Figure 2b,

$$k_{CH} \approx \frac{0.70}{60 \text{ min}} = 1.17 \times 10^{-2} \text{ min}^{-1} \approx \boxed{1.2 \times 10^{-2} \text{ min}^{-1}}.$$

For Figure 2a,

$$k_{CD} \approx \frac{0.70}{400 \text{ min}} = 1.75 \times 10^{-3} \text{ min}^{-1} \approx \boxed{1.8 \times 10^{-3} \text{ min}^{-1}}.$$

Taking the ratio before rounding,

$$\frac{k_{CH}}{k_{CD}} \approx \frac{0.70/60}{0.70/400} = \frac{400}{60} = \boxed{6.7}.$$

These are graphical estimates for the oxidation experiment at 20 °C.

2.8 — Rate determining step

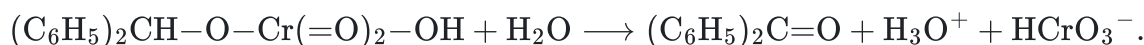
The large normal isotope effect, $k_{CH}/k_{CD} \approx 6.7$, indicates that cleavage of the carbon–hydrogen or carbon–deuterium bond contributes directly to the rate-controlling transition state.

In the proposed mechanism:

- **Step (1)** is an inorganic acid–base equilibrium and involves no substrate C–H bond.

- **Step (2)** forms the chromate ester while retaining the methine C–H bond.
- **Step (3)** breaks that C–H bond as the carbonyl group forms.

The chromate ester is **diphenylmethyl hydrogen chromate(VI)**, $O=[Cr](=O)(O)OC(c1ccccc1)c1ccccc1$. Its elimination is represented by the balanced equation



The additional species are water, O ; hydronium, $[OH_3^+]$; and hydrogen trioxidochromate(IV), $HCrO_3^-$, $[O^-][Cr](=O)O$.

In the proposed elimination, water accepts the methine hydrogen, the electrons of the C–H bond form the carbonyl π bond, and the O–Cr bond breaks with its electron pair transferred toward chromium. The chromium SMILES specify formal connectivity; they do not encode this electron flow, coordination geometry, or spin state.

Accordingly, within the proposed mechanism, mark

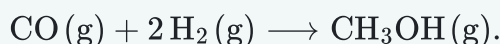
Step (3).

The solution was checked against the official solution.

Problem 3: Thermodynamics of chemical reactions

Part A.

Methanol is produced commercially by using a mixture of carbon monoxide and hydrogen over zinc oxide/copper oxide catalyst:



The standard enthalpy of formation (ΔH_f°) and the absolute entropy (S°) for each of the three gases at room temperature (298 K) and at a standard pressure of 1 bar are given as follows.

Gas	ΔH_f° (kJ mol ⁻¹)	S° (J K ⁻¹ mol ⁻¹)
CO(g)	-111	198
H ₂ (g)	0	131
CH ₃ OH(g)	-201	240

3.1 Calculate ΔH° , ΔS° , ΔG° , and K_p for the reaction at 298 K.

(If you are unable to calculate K_p at 298 K in problem 3.1, use $K_p = 9 \times 10^5$ later on.)

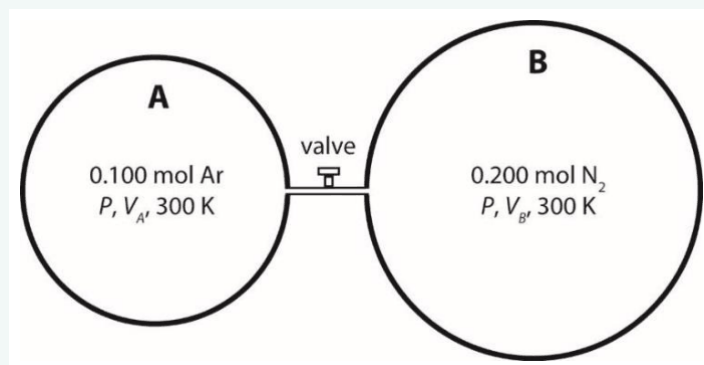
3.2 A commercial reactor is operated at a temperature of 600 K. Calculate the value of K_p at this temperature, assuming that ΔH° and ΔS° are independent on temperature.

(If you are unable to calculate K_p at 600 K in problem 3.2, use $K_p = 1.0 \times 10^{-2}$ later on.)

3.3 Production of methanol in industry is based on flowing of the gas comprising 2.00 moles of H₂ for each mole of CO into the reactor. The mole fraction of methanol in the exhaust gas from the reactor was found to be 0.18. Assuming that equilibrium is established, what is the total pressure in the reactor at a high temperature of 600 K?

Part B.

3.4 Consider the following closed system at 300 K. The system comprises 2 compartments, separated by a closed valve, which has negligible volume (see next figure). At the same pressure P , compartment A and compartment B contain 0.100 mol argon gas and 0.200 mol nitrogen gas, respectively. The volumes of the two compartments, V_A and V_B , are selected so that the gases behave as ideal gases.



After opening the valve slowly, the system is allowed to reach equilibrium. It is assumed that the two gases form an ideal gas mixture. Calculate the change in Gibbs free energy at 300 K, ΔG .

If you are unable to calculate K_p at 298 K in problem 3.1, use $K_p = 9 \times 10^5$ later on.

Official English text of the problem.

Answers

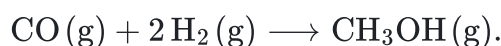
- **3.1:** $\Delta H^\circ = -90\text{ kJ mol}^{-1}$; $\Delta S^\circ = -220\text{ J K}^{-1}\text{ mol}^{-1}$; $\Delta G^\circ = -24.4\text{ kJ mol}^{-1}$; $K_p(298\text{ K}) = 1.9 \times 10^4$.
- **3.2:** $K_p(600\text{ K}) = 2.2 \times 10^{-4}$.
- **3.3:** $P = 1.0 \times 10^2\text{ bar}$.
- **3.4:** $\Delta G = -476\text{ J} = -0.476\text{ kJ}$ for the whole system.

Solution

Use $R = 8.314\text{ J mol}^{-1}\text{ K}^{-1}$ and standard pressure $p^\circ = 1\text{ bar}$. Equilibrium constants defined using p_i/p° are dimensionless.

3.1 — Thermodynamic quantities and equilibrium constant at 298 K

Carbon monoxide ($[\text{C-}]\#[\text{O+}]$) reacts with hydrogen ($[\text{H}][\text{H}]$) to produce methanol (CO):



The standard reaction enthalpy is the sum of the product formation enthalpies minus that of the reactants, including stoichiometric coefficients:

$$\begin{aligned}\Delta H^\circ &= \Delta H_f^\circ(\text{CH}_3\text{OH(g)}) - \Delta H_f^\circ(\text{CO(g)}) - 2\Delta H_f^\circ(\text{H}_2(\text{g})) \\ &= -201 - (-111) - 2(0) \\ &= \boxed{-90\text{ kJ mol}^{-1}}.\end{aligned}$$

Similarly,

$$\begin{aligned}\Delta S^\circ &= S^\circ(\text{CH}_3\text{OH}(\text{g})) - S^\circ(\text{CO}(\text{g})) - 2S^\circ(\text{H}_2(\text{g})) \\ &= 240 - 198 - 2(131) \\ &= \boxed{-220 \text{ J K}^{-1} \text{ mol}^{-1}}.\end{aligned}$$

Thus, at 298 K,

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= -90 - (298)(-0.220) \\ &= -24.44 \text{ kJ mol}^{-1} \\ &\approx \boxed{-24.4 \text{ kJ mol}^{-1}}.\end{aligned}$$

Using $\Delta G^\circ = -RT \ln K_p$,

$$K_p = \exp\left(\frac{24440}{8.314 \times 298}\right) = 1.9235 \times 10^4 \approx \boxed{1.9 \times 10^4}.$$

3.2 — Equilibrium constant at 600 K

With the specified assumption that ΔH° and ΔS° are temperature independent,

$$\begin{aligned}\Delta G^\circ(600 \text{ K}) &= -90 - (600)(-0.220) \\ &= +42.0 \text{ kJ mol}^{-1}.\end{aligned}$$

Therefore,

$$K_p(600 \text{ K}) = \exp\left(-\frac{42000}{8.314 \times 600}\right) = 2.2052 \times 10^{-4} \approx \boxed{2.2 \times 10^{-4}}.$$

The decrease in K_p with increasing temperature is consistent with the reaction being exothermic.

The optional fallback constants printed in the question differ from those calculated from the table. The following calculation uses the calculated value $K_p(600 \text{ K}) = 2.2052 \times 10^{-4}$.

3.3 — Total reactor pressure

The feed contains hydrogen and carbon monoxide in the same 2 : 1 ratio in which they are consumed. Consequently, the unreacted gases retain this ratio at equilibrium:

$$y_{\text{H}_2} = 2y_{\text{CO}}.$$

Since $y_{\text{CH}_3\text{OH}} = 0.18$,

$$y_{\text{CO}} + y_{\text{H}_2} = 1 - 0.18 = 0.82.$$

Hence,

$$y_{\text{CO}} = \frac{0.82}{3} = 0.273333, \quad y_{\text{H}_2} = \frac{2(0.82)}{3} = 0.546667.$$

For ideal gases, $p_i = y_i P$, so

$$\begin{aligned}K_p &= \frac{p_{\text{CH}_3\text{OH}}/p^\circ}{(p_{\text{CO}}/p^\circ)(p_{\text{H}_2}/p^\circ)^2} \\ &= \frac{y_{\text{CH}_3\text{OH}}}{y_{\text{CO}} y_{\text{H}_2}^2} \left(\frac{p^\circ}{P}\right)^2.\end{aligned}$$

Solving for P ,

$$\begin{aligned}
 P &= p^\circ \sqrt{\frac{y_{\text{CH}_3\text{OH}}}{K_p y_{\text{CO}} y_{\text{H}_2}^2}} \\
 &= (1 \text{ bar}) \sqrt{\frac{0.18}{(2.2052 \times 10^{-4})(0.273333)(0.546667)^2}} \\
 &= 99.96 \text{ bar}.
 \end{aligned}$$

Thus,

$$\boxed{P = 1.0 \times 10^2 \text{ bar}}.$$

3.4 — Gibbs free energy change on mixing

The gases are argon, Ar ([Ar]), and nitrogen, N₂ (N#N).

Initially, both compartments have the same temperature and pressure. The ideal-gas law therefore gives

$$V_A = \frac{n_{\text{Ar}} RT}{P}, \quad V_B = \frac{n_{\text{N}_2} RT}{P}.$$

After opening the valve, the total amount and total volume are unchanged. At the same temperature, the final total pressure is

$$P_f = \frac{(n_{\text{Ar}} + n_{\text{N}_2}) RT}{V_A + V_B} = P.$$

The final mole fractions are

$$y_{\text{Ar}} = \frac{0.100}{0.300} = \frac{1}{3}, \quad y_{\text{N}_2} = \frac{0.200}{0.300} = \frac{2}{3}.$$

For an ideal gas,

$$\mu_i(T, p_i) = \mu_i^\circ(T) + RT \ln\left(\frac{p_i}{p^\circ}\right).$$

Each gas initially has pressure P , and its final partial pressure is $y_i P$. Therefore,

$$\begin{aligned}
 \Delta G &= \sum_i n_i (\mu_{i,f} - \mu_{i,i}) \\
 &= RT \sum_i n_i \ln\left(\frac{y_i P}{P}\right) \\
 &= RT (n_{\text{Ar}} \ln y_{\text{Ar}} + n_{\text{N}_2} \ln y_{\text{N}_2}).
 \end{aligned}$$

Substitution gives

$$\begin{aligned}
 \Delta G &= (8.314)(300) \left[0.100 \ln\left(\frac{1}{3}\right) + 0.200 \ln\left(\frac{2}{3}\right) \right] \text{ J} \\
 &= -476.28 \text{ J}.
 \end{aligned}$$

Thus, for the whole system,

$$\boxed{\Delta G = -476 \text{ J} = -0.476 \text{ kJ}}.$$

The negative value reflects spontaneous mixing. For this ideal-gas mixture, $\Delta H_{\text{mix}} = 0$, and the entropy increases by

$$\Delta S_{\text{mix}} = -\frac{\Delta G}{T} = 1.59 \text{ J K}^{-1}.$$

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 4: Electrochemistry

Part A. Galvanic cell

The experiment is performed at 30.00°C. The electrochemical cell is composed of a hydrogen half-cell $[\text{Pt}(\text{s}) \mid \text{H}_2(\text{g}) \mid \text{H}^+(\text{aq})]$ containing a metal platinum electrode immersed in a buffer solution under a pressure of hydrogen gas. This hydrogen half-cell is connected to a half-cell of a metal (**M**) strip dipped in an unknown concentration of $\text{M}^{2+}(\text{aq})$ solution. The two half-cells are connected *via* a salt bridge as shown in Figure 1.

Note: The standard reduction potentials are given in Table 1.

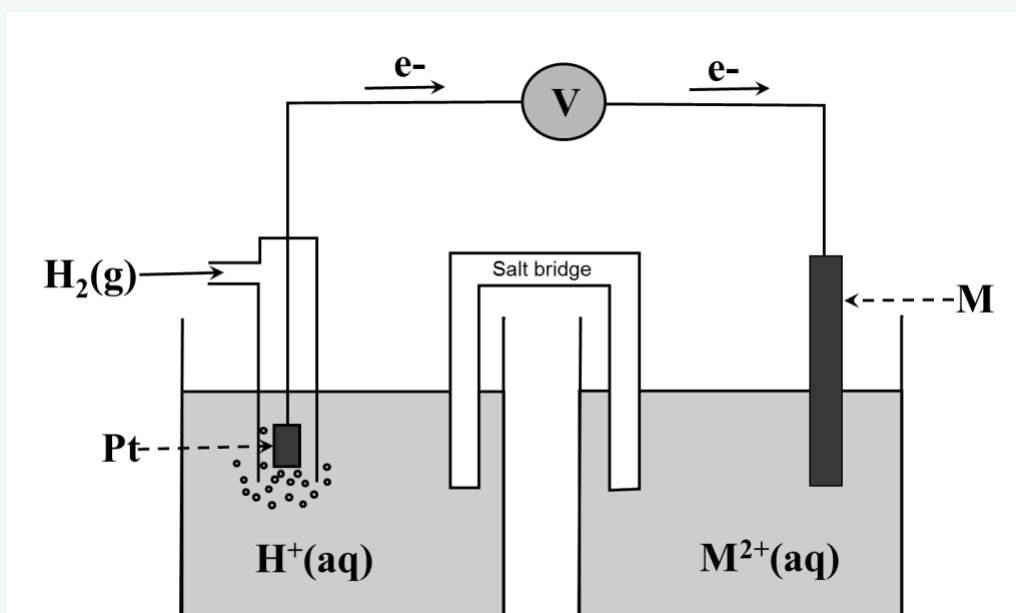


Figure 1 The galvanic cell

Table 1. Standard reduction potential (range 298-308 K)

Half-reaction	E° (V)-
$\text{Ba}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Ba}(\text{s})$	-2.912
$\text{Sr}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Sr}(\text{s})$	2.899
$\text{Ca}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Ca}(\text{s})$	-2.868
$\text{Er}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Er}(\text{s})$	-2.000
$\text{Ti}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Ti}(\text{s})$	-1.630
$\text{Mn}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Mn}(\text{s})$	-1.185
$\text{V}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{V}(\text{s})$	-1.175
$\text{Cr}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Cr}(\text{s})$	-0.913

Half-reaction	E° (V)-
$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Fe}(\text{s})$	-0.447
$\text{Cd}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cd}(\text{s})$	-0.403
$\text{Co}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Co}(\text{s})$	-0.280
$\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Ni}(\text{s})$	-0.257
$\text{Sn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Sn}(\text{s})$	-0.138
$\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Pb}(\text{s})$	-0.126
$2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$	0.000
$\text{Sn}^{4+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Sn}^{2+}(\text{aq})$	+0.151
$\text{Cu}^{2+}(\text{aq}) + \text{e}^- \rightarrow \text{Cu}^+(\text{aq})$	+0.153
$\text{Ge}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Ge}(\text{s})$	+0.240
$\text{VO}^{2+}(\text{aq}) + 2\text{H}^+(\text{aq}) + \text{e}^- \rightarrow \text{V}^{3+}(\text{aq}) + \text{H}_2\text{O}(\text{l})$	+0.337
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$	+0.340
$\text{Tc}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Tc}(\text{s})$	+0.400
$\text{Ru}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Ru}(\text{s})$	+0.455
$\text{I}_2(\text{s}) + 2\text{e}^- \rightarrow 2\text{I}^-(\text{aq})$	+0.535
$\text{UO}_2^{2+}(\text{aq}) + 4\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{U}^{4+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$	+0.612
$\text{PtCl}_4^{2-}(\text{aq}) + 2\text{e}^- \rightarrow \text{Pt}(\text{s}) + 4\text{Cl}^-(\text{aq})$	+0.755
$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightarrow \text{Fe}^{2+}(\text{aq})$	+0.770
$\text{Hg}_2^{2+}(\text{aq}) + 2\text{e}^- \rightarrow 2\text{Hg}(\text{l})$	+0.797
$\text{Hg}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Hg}(\text{l})$	+0.851
$2\text{Hg}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Hg}_2^{2+}(\text{aq})$	+0.920
$\text{Pt}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Pt}(\text{s})$	+1.180
$\text{MnO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$	+1.224
$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6\text{e}^- \rightarrow 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$	+1.360
$\text{Co}^{3+}(\text{aq}) + \text{e}^- \rightarrow \text{Co}^{2+}(\text{aq})$	+1.920
$\text{S}_2\text{O}_8^{2-}(\text{aq}) + 2\text{e}^- \rightarrow 2\text{SO}_4^{2-}(\text{aq})$	+2.010

4.1 If the reaction quotient (Q) of the whole galvanic cell is equal to 2.18×10^{-4} at 30.00°C , the electromotive force is $+0.450\text{ V}$. Calculate the value of standard reduction potential (E°) and identify the metal "M".

Note: $\Delta G = \Delta G^\circ + RT \ln Q$

4.2 Write the balanced equation of the spontaneous redox reaction of the galvanic cell.

4.3 The unknown concentration of $\text{M}^{2+}(\text{aq})$ solution in the cell (Figure 1) can be analyzed by a iodometric titration. A 25.00 cm^3 aliquot of $\text{M}^{2+}(\text{aq})$ solution is added into a conical flask and an excess of KI is added. A volume of 25.05 cm^3 of a sodium thiosulfate solution with a concentration of 0.800 mol dm^{-3} is required to reach the equivalent point. Write all the redox reactions associated with this titration and calculate the concentration of $\text{M}^{2+}(\text{aq})$ solution.

Note: If a student cannot find the answer, the student can use $0.950 \text{ mol dm}^{-3}$ as the concentration of M^{2+} for further calculations.

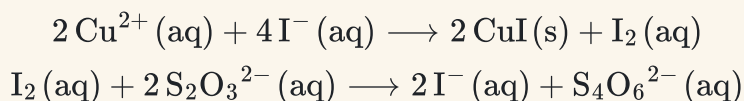
4.4 In Figure 1, if the hydrogen half-cell is under 0.360 bar hydrogen gas and the platinum electrode is immersed in a 500 cm^3 buffer solution containing 0.050 mol lactic acid ($\text{HC}_3\text{H}_5\text{O}_3$) and 0.025 mol sodium lactate ($\text{C}_3\text{H}_5\text{O}_3\text{Na}$), the electromotive force of the galvanic cell measured is +0.534 V. Calculate the pH of the buffer solution and the dissociation constant (K_a) of lactic acid at 30.00°C .

Note: If a student cannot find the answer, the student can use 3.46 as the buffer pH for further calculations.

Official English text of the problem.

Answers

- **4.1:** $E^\circ = +0.340 \text{ V}$; the metal **M is copper**, Cu.
- **4.2:** $\text{H}_2(\text{g}) + \text{Cu}^{2+}(\text{aq}) \longrightarrow 2\text{H}^+(\text{aq}) + \text{Cu}(\text{s})$.
- **4.3:** $[\text{Cu}^{2+}] = 0.802 \text{ mol dm}^{-3}$. The reactions are:



- **4.4:** $\text{pH} = 3.50$ and $K_a = 1.6 \times 10^{-4}$.

Solution

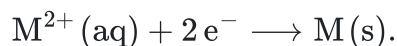
Use $T = 303.15 \text{ K}$, $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$, and $F = 96485 \text{ C mol}^{-1}$. Thus,

$$\frac{RT}{2F} = 0.0130610 \text{ V}, \quad \frac{RT \ln 10}{F} = 0.0601483 \text{ V}.$$

For the concentration calculations, activities are approximated by concentrations divided by $c^\circ = 1 \text{ mol dm}^{-3}$; gas pressure is divided by $p^\circ = 1 \text{ bar}$.

4.1

The electron-flow arrows show that the hydrogen electrode is the anode and the metal electrode is the cathode. Reduction of one metal ion requires two electrons:



Therefore $n = 2$. Combining

$$\Delta G = -nFE, \quad \Delta G^\circ = -nFE^\circ$$

with the given relation gives the Nernst equation:

$$E = E^\circ - \frac{RT}{nF} \ln Q.$$

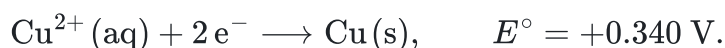
Hence,

$$\begin{aligned}
 E_{\text{cell}}^{\circ} &= E + \frac{RT}{2F} \ln Q \\
 &= 0.450 \text{ V} + (0.0130610 \text{ V}) \ln(2.18 \times 10^{-4}) \\
 &= 0.339882 \text{ V} \\
 &\approx \boxed{+0.340 \text{ V}}.
 \end{aligned}$$

Since the standard hydrogen reduction potential is zero,

$$E_{\text{cell}}^{\circ} = E_{\text{metal}}^{\circ} - E_{\text{hydrogen}}^{\circ} = E_{\text{metal}}^{\circ}.$$

The matching entry is the reduction of copper(II) ions, Cu^{2+} , SMILES [Cu+2], to copper:



Thus $\boxed{\text{M} = \text{Cu}}$.

4.2

Hydrogen, H_2 , SMILES [H][H], is oxidized to hydrogen ions (protons), H^{+} , SMILES [H+].

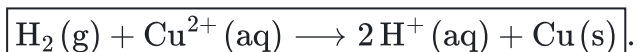
Anode:



Cathode:



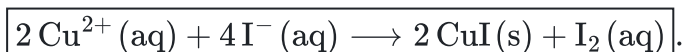
Adding the half-reactions gives



Atoms and charge are balanced, and the positive cell potential confirms that this direction is spontaneous under the stated conditions. Platinum conducts electrons and catalyzes the hydrogen electrode reaction.

4.3

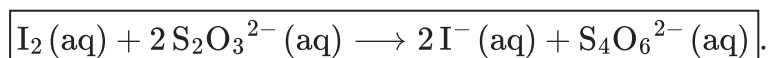
Iodide ions, I^{-} , SMILES [I-], reduce copper(II) to copper(I), Cu^{+} , SMILES [Cu+]. Copper(I) precipitates as sparingly soluble copper(I) iodide, which drives the reaction:



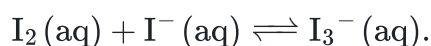
Copper(I) iodide can be represented compositionally as $[\text{Cu}+] \cdot [\text{I}-]$; this represents an ionic formula unit, not the solid's crystal lattice.

Each copper(II) ion accepts one electron. Two iodide ions lose two electrons to form one iodine molecule, while two further iodide ions enter the precipitate.

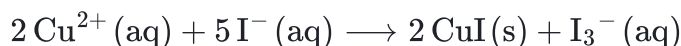
The liberated iodine, I_2 , SMILES I I, is titrated with thiosulfate, $\text{S}_2\text{O}_3^{2-}$, SMILES [O-]S(=O)(=O)[O-]. Thiosulfate is oxidized to tetrathionate, $\text{S}_4\text{O}_6^{2-}$, SMILES [O-]S(=O)(=O)SSS(=O)(=O)[O-]:



In excess iodide, iodine forms triiodide, I_3^{-} , SMILES I [I-] I:



This is a complex-formation equilibrium, not an additional redox reaction. Triiodide is linear; the SMILES does not specify that geometry. Equivalently, the two redox steps can be written as



and



Both representations give the same stoichiometry:

$$n(\text{Cu}^{2+}) = 2n(\text{liberated iodine}) = n(\text{S}_2\text{O}_3^{2-}).$$

The amount of thiosulfate used is

$$n(\text{S}_2\text{O}_3^{2-}) = (0.800 \text{ mol dm}^{-3})(25.05 \times 10^{-3} \text{ dm}^3) = 0.02004 \text{ mol}.$$

Therefore,

$$[\text{Cu}^{2+}] = \frac{0.02004 \text{ mol}}{25.00 \times 10^{-3} \text{ dm}^3} = 0.8016 \text{ mol dm}^{-3},$$

or, to three significant figures,

$$\boxed{[\text{Cu}^{2+}] = 0.802 \text{ mol dm}^{-3}}.$$

4.4

For the overall reaction in 4.2, the activity of solid copper is unity, so

$$Q = \frac{a_{\text{H}^+}^2}{a_{\text{Cu}^{2+}}(p_{\text{H}_2}/p^\circ)}.$$

Using the tabulated copper potential, $E^\circ = 0.340 \text{ V}$, and retaining the unrounded concentration from 4.3,

$$0.534 = 0.340 - 0.0130610 \ln \left(\frac{a_{\text{H}^+}^2}{0.8016(0.360)} \right).$$

Since $\ln a_{\text{H}^+} = -(\ln 10)\text{pH}$,

$$E = E^\circ + \frac{RT}{2F} \ln[a_{\text{Cu}^{2+}}(p_{\text{H}_2}/p^\circ)] + \frac{RT \ln 10}{F} \text{pH}.$$

Thus,

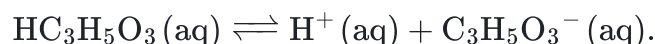
$$\begin{aligned} \text{pH} &= \frac{0.534 - 0.340 - 0.0130610 \ln(0.8016 \times 0.360)}{0.0601483} \\ &= 3.49523. \end{aligned}$$

Therefore,

$$\boxed{\text{pH} = 3.50}, \quad [\text{H}^+] \approx 3.1972 \times 10^{-4} \text{ mol dm}^{-3}.$$

Lactic acid, $\text{HC}_3\text{H}_5\text{O}_3$, is 2-hydroxypropanoic acid, SMILES CC(O)C(=O)O. Its conjugate base is lactate, $\text{C}_3\text{H}_5\text{O}_3^-$, SMILES CC(O)C(=O)[O-]. Sodium lactate has the component SMILES CC(O)C(=O)[O-].[Na+]. The problem specifies no stereoisomer, so no stereochemical tags are assigned.

The acid dissociation is



The formal concentrations in 0.500 dm^3 are

$$C_{\text{acid}} = \frac{0.050}{0.500} = 0.100 \text{ mol dm}^{-3},$$

$$C_{\text{lactate}} = \frac{0.025}{0.500} = 0.050 \text{ mol dm}^{-3}.$$

Using the usual buffer approximation,

$$K_a \approx \frac{[\text{H}^+]}{c^\circ} \frac{[\text{C}_3\text{H}_5\text{O}_3^-]}{[\text{HC}_3\text{H}_5\text{O}_3]}$$

$$= (3.1972 \times 10^{-4}) \frac{0.050}{0.100}$$

$$= 1.5986 \times 10^{-4}.$$

Retaining the small additional dissociation of lactic acid, with $h = [\text{H}^+]$ and negligible water autoionization, gives

$$K_a \approx \frac{h}{c^\circ} \frac{0.050 \text{ mol dm}^{-3} + h}{0.100 \text{ mol dm}^{-3} - h} = 1.6140 \times 10^{-4}.$$

Both treatments give, at the precision of the buffer amounts,

$$\boxed{K_a = 1.6 \times 10^{-4}}.$$

Here K_a is dimensionless, using concentrations normalized by c° .

The solution was checked against the official solution.

Problem 5: Phosphate and silicate in soil

Distribution and mobility of phosphorus in soil are usually studied by sequential extraction. Sequential extraction is performed by the use of acid or alkaline reagents to fractionate inorganic phosphorus in soil. Soil sample was extracted and analyzed as follows:

Part A. Determination of total phosphate (PO_4^{3-}) and silicate (SiO_4^{4-})

A 5.00 gram of soil sample is digested to give a final volume of 50.0 cm^3 digesting solution which dissolves total phosphorus and silicon. The extract is analyzed for the total concentrations of phosphorus and silicon. The concentrations of phosphorus and silicon are found to be 5.16 mg dm^{-3} and 5.35 mg dm^{-3} , respectively.

5.1.1 Determine the mass of PO_4^{3-} in mg per 1.00 g of soil.

5.1.2 Determine the mass of PO_4^{3-} in mg per 1.00 g of soil.

Part B. Determination of available PO_4^{3-} in acid extract

Phosphate can be analyzed by using molybdenum blue method. One mole of phosphate is converted into one mole of molybdenum blue compound. This method is used for determination of phosphate in the acid extract. Absorbance (A) and transmittance (T) are recorded at 800 nm.

The molar absorptivity of the molybdenum blue compound is $6720 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ and all measurement is carried out in a 1.00-cm cuvette.

Transmittance and absorbance are given by the following equations:

$$T = I/I_o$$

$$A = \log(I_o/I)$$

where I is the intensity of the transmitted light and I_o is the intensity of the incident light.

5.2.1 When the sample containing high concentration of phosphate is analyzed, a reference solution of $7.5 \times 10^{-5} \text{ mol dm}^{-3}$ of molybdenum blue compound is used for adjusting zero absorbance. The transmittance of the sample solution is then measured to be 0.55. Calculate the concentration of phosphate (mol dm^{-3}) in the sample solution.

Part C. Determination of PO_4^{3-} and SiO_4^{4-} in alkaline extract

Both phosphate and silicate ions can react with molybdate in alkaline solution, producing the yellow molybdophosphate and molybdatosilicate. Further reduction with ascorbic acid produces intense color molybdenum blue compounds. Both complexes exhibit maximum absorption at 800 nm. Addition of tartaric acid helps preventing interference from silicate in the determination of phosphate.

Two series of phosphate standard are treated with and without tartaric acid whereas a series of silicate standard is not treated with tartaric acid. Linear equations obtained from those calibration curves are as follows:

Conditions	Linear equations
Phosphate with and without tartaric acid	$y = 6720x_1$
Silicate without tartaric acid	$y = 868x_2$

y is absorbance at 800 nm,

x_1 is concentration of phosphate as mol dm^{-3} ,

x_2 is concentration of silicate as mol dm^{-3}

Absorbance at 800 nm of the alkaline fraction of the soil extract after treated with and without tartaric acid are 0.267 and 0.510, respectively.

5.3.1 Calculate the phosphate concentration in the alkaline soil extract in mol dm^{-3} and calculate the corresponding phosphorus in mg dm^{-3} .

5.3.2 Calculate the silicate concentration from the soil sample in the alkaline fraction in mol dm^{-3} and calculate the corresponding silicon in mg dm^{-3} .

Part D. Preconcentration of ammonium phosphomolybdate

A 100 cm^3 of aqueous sample of ammonium phosphomolybdate $((\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40})$ compound is extracted with 5.0 cm^3 of an organic solvent. The organic-water partition coefficient (K_{ow}) is defined as the ratio of concentration of the compound in the organic phase (c_o) to that in the water phase (c_w). K_{ow} of the ammonium phosphomolybdate is 5.0.

The molar absorptivity of ammonium phosphomolybdate in the organic phase is $5000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$.

5.4 If the absorbance in the organic phase is 0.200, calculate the total mass of phosphorus (in mg unit) in the original aqueous sample solution. The optical pathlength of the cuvette is 1.00 cm.

Official English text of the problem.

Answers

- **5.1.1:** 0.158 mg of phosphate, PO_4^{3-} , per 1.00 g of soil.
- **5.1.2:** As printed, 0.158 mg of phosphate per 1.00 g of soil. If the intended species is silicate, SiO_4^{4-} , the answer is 0.175 mg per 1.00 g of soil.
- **5.2.1:** $c(\text{PO}_4^{3-}) = 1.14 \times 10^{-4} \text{ mol dm}^{-3}$.
- **5.3.1:** $c(\text{PO}_4^{3-}) = 3.97 \times 10^{-5} \text{ mol dm}^{-3}$, corresponding to 1.23 mg dm^{-3} of phosphorus.
- **5.3.2:** $c(\text{SiO}_4^{4-}) = 2.80 \times 10^{-4} \text{ mol dm}^{-3}$, corresponding to 7.86 mg dm^{-3} of silicon.
- **5.4:** $m(\text{P}) = 0.031 \text{ mg}$ in the original aqueous sample.

Solution

The ions quantified are **phosphate (orthophosphate)**, PO_4^{3-} , SMILES O=P([O-])([O-])[O-], and **orthosilicate**, SiO_4^{4-} , SMILES [O-][Si]([O-])([O-])[O-]. Both have tetrahedral arrangements of oxygen atoms around the central atom. The phosphate SMILES represents one localized Lewis structure; it does not convey resonance delocalization.

For mass conversions, use the standard atomic molar masses

$$M(\text{P}) = 30.97, \quad M(\text{Si}) = 28.09, \quad M(\text{O}) = 16.00 \text{ g mol}^{-1}.$$

Thus,

$$M(\text{PO}_4^{3-}) = 94.97 \text{ g mol}^{-1}, \quad M(\text{SiO}_4^{4-}) = 92.09 \text{ g mol}^{-1}.$$

5.1.1

The digest volume is

$$50.0 \text{ cm}^3 = 0.0500 \text{ dm}^3.$$

The phosphorus mass in the entire 5.00 g soil sample is

$$m(\text{P}) = (5.16 \text{ mg dm}^{-3})(0.0500 \text{ dm}^3) = 0.258 \text{ mg}.$$

Each phosphate ion contains one phosphorus atom. Therefore, the phosphate mass per gram of soil is

$$\frac{m(\text{PO}_4^{3-})}{m_{\text{soil}}} = \frac{0.258 \text{ mg}}{5.00 \text{ g}} \frac{94.97}{30.97} = 0.158 \text{ mg g}^{-1}.$$

5.1.2

Taken literally, this repeats 5.1.1, so the answer is again

$$0.158 \text{ mg of } \text{PO}_4^{3-} \text{ per } 1.00 \text{ g of soil}.$$

If the intended question concerns silicate, the silicon mass in the digest is

$$m(\text{Si}) = (5.35 \text{ mg dm}^{-3})(0.0500 \text{ dm}^3) = 0.2675 \text{ mg}.$$

Each orthosilicate ion contains one silicon atom, giving

$$\frac{m(\text{SiO}_4^{4-})}{m_{\text{soil}}} = \frac{0.2675 \text{ mg}}{5.00 \text{ g}} \frac{92.09}{28.09} = \boxed{0.175 \text{ mg g}^{-1}}.$$

5.2.1

Beer–Lambert’s law is

$$A = \varepsilon \ell c.$$

Because the instrument is zeroed against a solution containing molybdenum blue, the measured transmittance is the sample intensity divided by the reference intensity:

$$T_{\text{meas}} = \frac{I_{\text{sample}}}{I_{\text{reference}}} = 10^{-\varepsilon \ell (c_{\text{sample}} - c_{\text{reference}})}.$$

Consequently,

$$-\log_{10} T_{\text{meas}} = \varepsilon \ell (c_{\text{sample}} - c_{\text{reference}}).$$

The measured absorbance difference is

$$\Delta A = -\log_{10}(0.55) = 0.259637.$$

Hence,

$$\begin{aligned} c_{\text{sample}} &= c_{\text{reference}} + \frac{\Delta A}{\varepsilon \ell} \\ &= 7.5 \times 10^{-5} \text{ mol dm}^{-3} + \frac{0.259637}{(6720 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})(1.00 \text{ cm})} \\ &= 1.13637 \times 10^{-4} \text{ mol dm}^{-3}. \end{aligned}$$

The stated phosphate-to-molybdenum-blue conversion is 1:1, so

$$\boxed{c(\text{PO}_4^{3-}) = 1.14 \times 10^{-4} \text{ mol dm}^{-3}}.$$

5.3.1

Tartaric acid suppresses the silicate contribution while leaving the phosphate calibration unchanged. Thus, the absorbance with tartaric acid measures phosphate alone:

$$0.267 = 6720 c(\text{PO}_4^{3-}),$$

where concentration is in mol dm^{-3} .

Therefore,

$$c(\text{PO}_4^{3-}) = \frac{0.267}{6720} = \boxed{3.97 \times 10^{-5} \text{ mol dm}^{-3}}.$$

There is one phosphorus atom per phosphate ion, so the corresponding phosphorus mass concentration is

$$\begin{aligned} \rho(\text{P}) &= (3.97321 \times 10^{-5} \text{ mol dm}^{-3})(30.97 \text{ g mol}^{-1})(1000 \text{ mg g}^{-1}) \\ &= \boxed{1.23 \text{ mg dm}^{-3}}. \end{aligned}$$

5.3.2

Without tartaric acid, the two absorbance contributions add:

$$A_{\text{without}} = 6720c(\text{PO}_4^{3-}) + 868c(\text{SiO}_4^{4-}).$$

Subtracting the phosphate contribution gives

$$A_{\text{silicate}} = 0.510 - 0.267 = 0.243.$$

Thus,

$$c(\text{SiO}_4^{4-}) = \frac{0.243}{868} = \boxed{2.80 \times 10^{-4} \text{ mol dm}^{-3}}.$$

Each silicate ion contains one silicon atom:

$$\begin{aligned} \rho(\text{Si}) &= (2.79954 \times 10^{-4} \text{ mol dm}^{-3})(28.09 \text{ g mol}^{-1})(1000 \text{ mg g}^{-1}) \\ &= \boxed{7.86 \text{ mg dm}^{-3}}. \end{aligned}$$

5.4

First determine the equilibrium concentration of ammonium phosphomolybdate in the organic phase:

$$c_o = \frac{A}{\varepsilon \ell} = \frac{0.200}{(5000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})(1.00 \text{ cm})} = 4.00 \times 10^{-5} \text{ mol dm}^{-3}.$$

Using the partition coefficient,

$$K_{\text{ow}} = \frac{c_o}{c_w} = 5.0,$$

the concentration remaining in water is

$$c_w = \frac{4.00 \times 10^{-5}}{5.0} = 8.0 \times 10^{-6} \text{ mol dm}^{-3}.$$

Conservation of solute requires counting both phases:

$$\begin{aligned} n_{\text{initial}} &= c_o V_o + c_w V_w \\ &= (4.00 \times 10^{-5} \text{ mol dm}^{-3})(0.0050 \text{ dm}^3) \\ &\quad + (8.0 \times 10^{-6} \text{ mol dm}^{-3})(0.100 \text{ dm}^3) \\ &= 2.0 \times 10^{-7} + 8.0 \times 10^{-7} \\ &= 1.0 \times 10^{-6} \text{ mol}. \end{aligned}$$

Thus only 20% of the compound is extracted into the organic phase. Each formula unit of $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}$ contains one phosphorus atom, so

$$\begin{aligned} m(\text{P}) &= (1.0 \times 10^{-6} \text{ mol})(30.97 \text{ g mol}^{-1})(1000 \text{ mg g}^{-1}) \\ &= 0.03097 \text{ mg} \\ &\approx \boxed{0.031 \text{ mg}}. \end{aligned}$$

The solution was checked against the official solution.

Problem 6: Iron

Iron (Fe) is the fourth most abundant element in the Earth's crust and has been used for more than 5,000 years.

Part A.

Pure iron is easily oxidized, which limits its utilization. Element **X** is one of the alloying elements that is added to improve the oxidation resistance property of iron.

6.1 Below is some information about the element **X**:

- (1) In first ionization, an electron with quantum numbers $n_1 = 4 - l_1$ is removed.
- (2) In second ionization, an electron with quantum numbers $n_2 = 5 - l_2$ is removed.
- (3) The atomic mass of **X** is lower than that of Fe.

What is the element **X**?

(Answer by writing the proper symbol according to the periodic table.)

6.2 Both Fe and **X** crystallize in the body centered cubic structure. Approximating the Fe atoms as hard-spheres, the volume taken up by the Fe atoms inside the unit cell is $1.59 \times 10^{-23} \text{ cm}^3$. The volume of the unit cell of **X** is 0.0252 nm^3 . A complete substitutional solid solution usually occurs when

$$\Delta R = \left(\frac{|R_X - R_{\text{Fe}}|}{R_{\text{Fe}}} \right) \times 100$$

is less than or equal to 15, where R_X and R_{Fe} are the atomic radii of **X** and Fe, respectively. Can **X** and Fe form a complete substitutional solid solution?

Tick the relevant box ☐ YES ☐ NO.

Show your calculation. The volume of sphere is $4/3\pi r^3$.

Part B.

Iron in natural water is in the form of $\text{Fe}(\text{HCO}_3)_2$, which ionizes to Fe^{2+} and HCO_3^- . To remove iron from water, $\text{Fe}(\text{HCO}_3)_2$ is oxidized to an insoluble complex $\text{Fe}(\text{OH})_3$, which can be filtered out of the water.

6.3 Fe^{2+} can be oxidized by KMnO_4 in a basic solution to yield $\text{Fe}(\text{OH})_3$ and MnO_2 precipitates. Write the balanced ionic equation for this reaction in a basic solution.

6.4 Under this condition, HCO_3^- ions are converted to CO_3^{2-} . Write the balanced ionic equation for this reaction in a basic solution.

6.5 A covalent compound **A** which contains more than 2 atoms and, a potential oxidizing agent, can be prepared by the reaction between diatomic halogen molecule (X_2) and NaQO_2



where x , y and z are the coefficients for the balanced equation. Among the binary compounds between hydrogen and halogen, HX has the lowest boiling point. Identify **X** and if **A** has an unpaired electron, draw a Lewis structure of compound **A** with zero formal charge on all atoms.

6.6 Compound **D** is an unstable oxidizing agent that can be used to remove $\text{Fe}(\text{HCO}_3)_2$ from natural water. It consists of elements **G**, **Z** and hydrogen and the oxidation number of **Z** is +1. In this compound, hydrogen is connected to the element having the higher electronegativity among them. Below is some information about the elements **G** and **Z**:

(1) **G** exists in its normal state as a diatomic molecule, G_2 .

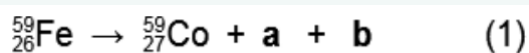
(2) **Z** has one proton fewer than that of element **E**. **E** exists as a gas under standard conditions. Z_2 is a volatile solid.

(3) The compound EG_3 has a pyramidal shape.

Identify the elements **G** and **Z** and draw a molecular structure of compound **D**.

Part C.

^{59}Fe is a radiopharmaceutical isotope which is used in the study of iron metabolism in the spleen. This isotope decays to ^{59}Co as follows:



6.7 What are **a** and **b** in equation (1)? (Mark $\checkmark$ in the appropriate boxes.)

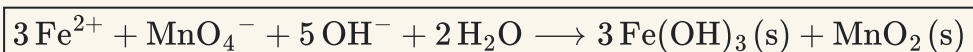
proton	neutron	beta	positron	alpha	gamma

6.8 Consider equation (1), if the ^{59}Fe isotope is left for 178 days which is n times of its half-life ($t_{1/2}$), the mole ratio of ^{59}Co to ^{59}Fe is 15 : 1. If n is an integer, what is the half-life of ^{59}Fe in day(s)? Show your calculation.

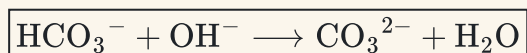
Official English text of the problem.

Answers

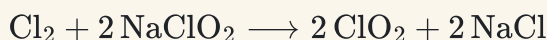
- **6.1:** $\boxed{X = \text{Cr}}$, chromium.
- **6.2:** **YES**, according to the stated criterion. $R_{\text{Fe}} = 0.124 \text{ nm}$, $R_X = 0.127 \text{ nm}$; the radius mismatch is approximately 2.5%.
- **6.3:**



- **6.4:**



- **6.5:** $X = \text{Cl}$; **A** is chlorine dioxide, ClO_2 , SMILES $\text{o}=[\text{Cl}]=\text{o}$.



The requested Lewis structure has two chlorine–oxygen double bonds, two lone pairs on each oxygen, and one lone pair plus one unpaired electron on chlorine. All formal charges are zero.

- **6.6:** $G = \text{O}$, $Z = \text{I}$. **D** is hypoiodous acid, HOI , SMILES $[\text{H}]\text{OI}$. Its structure is $\text{H}-\text{O}-\text{I}$, bent at oxygen.
- **6.7:** Mark **beta** and **gamma**: $a = \beta^-$, $b = \gamma$, with their order interchangeable.
- **6.8:** $n = 4$, and $t_{1/2} = 44.5 \text{ days}$.

Solution

6.1

The quantum-number conditions are

$$n_1 + l_1 = 4, \quad n_2 + l_2 = 5.$$

The allowed subshells satisfying the first condition are $4s$ and $3p$; those satisfying the second are $5s$, $4p$, and $3d$. For an element lighter than iron, the relevant successive removals are from $4s$ and then $3d$.

Chromium has the ground-state configuration



Removing its single $4s$ electron gives chromium(I), Cr^+ , SMILES $[\text{Cr}^+]$, with configuration $[\text{Ar}] 3d^5$. The next electron is removed from $3d$, producing chromium(II), Cr^{2+} , SMILES $[\text{Cr}^{+2}]$, with configuration $[\text{Ar}] 3d^4$.

Thus,

$$(n_1, l_1) = (4, 0), \quad (n_2, l_2) = (3, 2),$$

which satisfy both conditions. Chromium also has a lower atomic mass than iron. Therefore,

$$X = \text{Cr}.$$

6.2

A body centered cubic unit cell contains

$$8 \left(\frac{1}{8} \right) + 1 = 2$$

atoms. The given volume for iron is the volume occupied by these two atomic spheres, so

$$2 \left(\frac{4}{3} \pi R_{\text{Fe}}^3 \right) = 1.59 \times 10^{-23} \text{ cm}^3.$$

Consequently,

$$R_{\text{Fe}} = \left(\frac{3(1.59 \times 10^{-23} \text{ cm}^3)}{8\pi} \right)^{1/3} = 1.23811 \times 10^{-8} \text{ cm} = 0.123811 \text{ nm}.$$

For **X**, the given value is the entire unit-cell volume. Its edge length is

$$a_X = (0.0252 \text{ nm}^3)^{1/3} = 0.293179 \text{ nm}.$$

In a body centered cubic structure, atoms touch along the body diagonal:

$$4R_X = \sqrt{3} a_X.$$

Therefore,

$$R_X = \frac{\sqrt{3}}{4}(0.293179 \text{ nm}) = 0.126950 \text{ nm}.$$

Using the unrounded radii,

$$\Delta R = \frac{|0.126950 - 0.123811|}{0.123811} \times 100 = 2.5356.$$

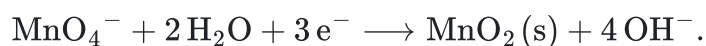
The radius mismatch is approximately 2.5%, below the stated 15% limit. Therefore, tick **YES**.

6.3

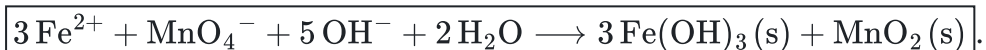
Iron is oxidized from oxidation state +2 to +3:



Manganese is reduced from +7 in permanganate to +4 in manganese dioxide:



Multiplying the iron half-reaction by three, adding, and cancelling electrons and hydroxide gives



The total charge on the left is $3(2) - 1 - 5 = 0$, equal to that on the right.

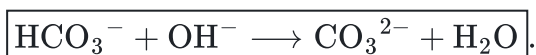
The species names and SMILES are:

Formula	Name	SMILES
Fe^{2+}	Iron(II) ion	[Fe+2]
MnO_4^-	Permanganate ion	[O-] [Mn] (=O) (=O) =O
OH^-	Hydroxide ion	[OH-]
H_2O	Water	O
$\text{Fe}(\text{OH})_3$	Iron(III) hydroxide	[Fe+3] . [OH-] . [OH-] . [OH-]
MnO_2	Manganese(IV) oxide, or manganese dioxide	[Mn+4] . [O-2] . [O-2]

For the two precipitates, the disconnected SMILES represent formal ionic formula units. They do not describe the extended solid structures or metal coordination geometries.

6.4

Hydroxide removes a proton from hydrogen carbonate:



This is an acid–base reaction; carbon remains in oxidation state +4.

Hydrogen carbonate, also called bicarbonate, HCO_3^- , has SMILES O=C(O)[O-]. Carbonate, CO_3^{2-} , has SMILES O=C([O-])[O-]. These SMILES show individual resonance representations; the carbonate ion is planar, with equivalent oxygen positions in the free ion.

6.5

Here **X** is a halogen and is independent of the label **X** in Part A.

Among the hydrogen halides:

- Hydrogen fluoride, **HF**, SMILES [H]F, has an unusually high boiling point because of hydrogen bonding.
- Hydrogen chloride, **HCl**, SMILES [H]Cl, has the lowest boiling point.
- Hydrogen bromide, **HBr**, SMILES [H]Br, and hydrogen iodide, **HI**, SMILES [H]I, have stronger dispersion interactions than hydrogen chloride.

Thus,

$$\boxed{X = \text{Cl}}.$$

To identify the odd-electron compound **A**, let it contain p chlorine atoms and q oxygen atoms. Using the displayed reaction scheme, conservation of sodium gives $z = x$. Conservation of chlorine and oxygen then gives

$$2 + x = py + z \Rightarrow py = 2, \quad 2x = qy.$$

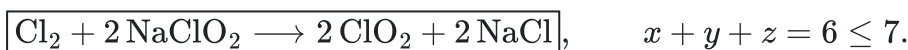
An odd total number of valence electrons requires $7p + 6q$ to be odd, so p is odd. Since $py = 2$, this gives

$$p = 1, \quad y = 2, \quad q = x = z.$$

The requirement of more than two atoms gives $q \geq 2$. The coefficient bound gives

$$x + y + z = 2q + 2 \leq 7,$$

so $q = 2$. Hence **A** is chlorine dioxide:



The reactants and products are chlorine, Cl_2 , SMILES ClCl; sodium chlorite, NaClO_2 , SMILES [Na+] . [O-] Cl=O; chlorine dioxide, ClO_2 , SMILES O=[Cl]=O; and sodium chloride, NaCl , SMILES [Na+] . [Cl-].

Chlorine dioxide has

$$7 + 2(6) = 19$$

valence electrons. For the requested zero-formal-charge Lewis structure, place chlorine centrally, with a double bond to each oxygen. Give each oxygen two lone pairs, and give chlorine one lone pair and one unpaired electron.

The formal charges are

$$\text{FC}(\text{Cl}) = 7 - 3 - \frac{8}{2} = 0, \quad \text{FC}(\text{O}) = 6 - 4 - \frac{4}{2} = 0.$$

The molecule is bent. The SMILES does not display the lone pairs or the bond angle; the electron placement above specifies the requested Lewis representation.

6.6

The volatile solid consisting of diatomic molecules is iodine, I_2 , SMILES I I. Therefore,

$$Z = \text{I}.$$

Iodine has atomic number 53, so the element with one more proton is xenon, Xe, atomic number 54, which is a gas under standard conditions.

The pyramidal compound is xenon trioxide, XeO₃, SMILES O=[Xe](=O)=O. Its xenon center has three bonding regions and one lone pair, giving a trigonal pyramidal molecular geometry. Therefore,

$$G = \text{O}.$$

This also satisfies the diatomic-element clue: oxygen occurs as dioxygen, O₂, SMILES O=O. That simple SMILES does not encode dioxygen's triplet electronic state.

The compound containing hydrogen, oxygen, and iodine with iodine in oxidation state +1 is **hypoiodous acid**, HOI, SMILES [H]OI:

$$(+1)_{\text{H}} + (-2)_{\text{O}} + (+1)_{\text{I}} = 0.$$

Oxygen is more electronegative than iodine, so hydrogen bonds to oxygen. The requested drawing is therefore H—O—I, bent at oxygen. Oxygen has two lone pairs, and iodine has three lone pairs.

$$\boxed{G = \text{O}, \quad Z = \text{I}, \quad D = \text{HOI}}.$$

6.7

The mass number stays at 59, while the atomic number increases from 26 to 27. This identifies beta-minus decay:

$$59 = 59 + 0, \quad 26 = 27 - 1.$$

The emitted beta particle is an electron. Of the listed choices, gamma radiation supplies the second emission with zero charge and zero mass number, corresponding to de-excitation of the daughter nucleus.

Thus, in the schematic notation of the question,



Mark **beta** and **gamma**. Physically, beta-minus decay also emits an electron antineutrino, $\bar{\nu}_e$, which the problem's schematic omits.

6.8

For an initially pure sample containing N_0 iron-59 nuclei, after n half-lives,

$$N_{\text{Fe}} = \frac{N_0}{2^n}.$$

The number of cobalt-59 nuclei formed is

$$N_{\text{Co}} = N_0 - \frac{N_0}{2^n}.$$

The mole ratio equals the ratio of nucleus counts, so

$$\frac{N_{\text{Co}}}{N_{\text{Fe}}} = \frac{N_0 - N_0/2^n}{N_0/2^n} = 2^n - 1 = 15.$$

Therefore,

$$2^n = 16, \quad n = 4,$$

and

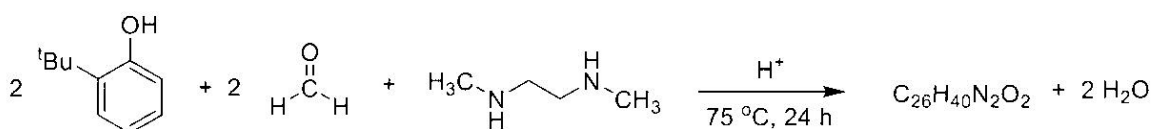
$$t_{1/2} = \frac{178 \text{ days}}{4} = 44.5 \text{ days}.$$

The solution was checked against the official solution.

Problem 7: Chemical Structure Puzzles

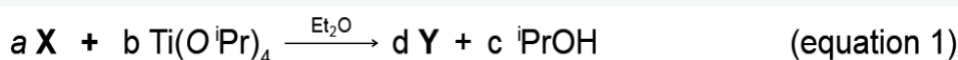
Titanium complexes have been investigated for their antitumor activity. Many factors including isomerism and sizes have shown to affect the potency of the complexes. This question deals with the synthesis and characterization of some titanium complexes.

7.1 A reaction of 2 equivalents of 2-tert-butylphenol, 2 equivalents of formaldehyde, and *N,N'*-dimethylethylene-1,2-diamine under acidic conditions at 75 °C affords three major products with the same chemical formula of $C_{26}H_{40}N_2O_2$, as shown in the equation below. Draw the structure of each product.



7.2 If 2,4-di-tert-butylphenol is used as a substrate instead of 2-tert-butylphenol using the same stoichiometry as that in **7.1**, only one product **X** was obtained. Draw the structure of **X**.

A reaction between **X** from **7.2** and $Ti(O^iPr)_4$ [*i*Pr = isopropyl] in diethyl ether under an inert atmosphere resulted in the six-coordinate Ti complex **Y**, as a yellow crystalline solid and isopropanol at room temperature.



UV-VIS spectra of **X**, $Ti(O^iPr)_4$, and **Y** reveal that only the product **Y** has an absorption at $\lambda = 370 \text{ nm}$. By varying the volumes of **X** and $Ti(O^iPr)_4$, each with the concentration of 0.50 mol dm^{-3} , and using benzene as the solvent, the absorbance data at $\lambda = 370 \text{ nm}$ are given below:

Volume of X (cm ³)	Volume of $Ti(O^iPr)_4$ (cm ³)	Volume of benzene (cm ³)	Absorbance
0	1.20	1.80	0.05
0.20	1.00	1.80	0.25
0.30	0.90	1.80	0.38
0.50	0.70	1.80	0.59
0.78	0.42	1.80	0.48
0.90	0.30	1.80	0.38
1.10	0.10	1.80	0.17
1.20	0	1.80	0.02

7.3 Fill in appropriate values in the table provided below.

$\frac{\text{mol of X}}{\text{mol of X} + \text{mol of Ti(O}^i\text{Pr)}_4}$	Absorbance
	0.05
	0.25
	0.38
	0.59
	0.48
	0.38
	0.17
	0.02

Next figure: Plot a graph showing a relationship between

$$\frac{\text{mole of X}}{\text{mole of X} + \text{mole of Ti(O}^i\text{Pr)}_4}$$

and absorbance in the space provided below.

The value of

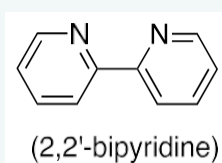
$$\frac{\text{mole of X}}{\text{mole of X} + \text{mole of Ti(O}^i\text{Pr)}_4}$$

which maximizes the amount of the product **Y** represents the stoichiometry of **X** in the chemical formula of **Y**. Based on the graph above, show what is the molar ratio Ti : X in the complex **Y**.

7.4 The titanium complex **Y** is six-coordinated. The IR spectrum of **Y** does not contain a broad absorption band in the range of 3200–3600 cm^{−1}. **Y** exists as three diastereomers. Ignoring stereochemistry at N atoms, draw clearly the structures of all three diastereomers.

Note that you do not need to draw the complete structure of the ligand. Only identify donor atoms that involve in coordination with titanium and the ligand framework between the donor atoms can be drawn as follows:

For example:



(2,2'-bipyridine)

can be drawn as:



****If you did not get a structure of X from 7.2, use the following ligand symbol to represent X (A and Z are donor atoms):**



7.5 Under certain conditions, the reaction shown in **equation 1** affords only one diastereomer of **Y**. Given that structures of **Y** are "fixed" (no intramolecular movement), the ^1H NMR spectrum of **Y** in CDCl_3 shows four singlet resonances at δ 1.25, 1.30, 1.66, and 1.72 corresponding to the tert-butyl groups. Draw a structure of the only possible diastereomer of **Y**.

(You do not need to draw the complete structure of the ligand. Only identify donor atoms that involve in coordination and the ligand framework between the donor atoms can be drawn as shown in **7.4**).

Official English text of the problem.

Answers

- **7.1:** The three products are the **ortho/ortho**, **ortho/para**, and **para/para** bis-Mannich products. Their names and complete SMILES are given in **Solution 7.1**.
- **7.2:** **X** is *N*, *N'*-bis(3,5-di-tert-butyl-2-hydroxybenzyl)-*N*, *N'*-dimethylethane-1,2-diamine, $\text{C}_{34}\text{H}_{56}\text{N}_2\text{O}_2$:
CN(Cc1c(O)c(C(C)(C)C)cc(C(C)(C)C)c1)CCN(C)Cc1c(O)c(C(C)(C)C)cc(C(C)(C)C)c1
- **7.3:** The mole fractions, in order, are 0, 0.167, 0.250, 0.417, 0.650, 0.750, 0.917, 1.000. The graph peaks near 0.50, giving **Ti : X = 1 : 1**.
- **7.4:** Writing $\text{X} = \text{H}_2\text{L}$, **Y** is the titanium(IV) bis(isopropoxide) complex $[\text{Ti}(\text{L})(\text{O}^i\text{Pr})_2]$, with formula $\text{C}_{40}\text{H}_{68}\text{N}_2\text{O}_4\text{Ti}$. Its three geometric diastereomers have: **I**, trans isopropoxide donors and cis phenolate donors; **II**, cis isopropoxide donors and trans phenolate donors; **III**, both pairs cis. Exact structures and stereochemical SMILES appear in **Solution 7.4**. Equation 1 has $a = b = d = 1$, $c = 2$.
- **7.5: Isomer III**, with both the isopropoxide pair and the phenolate pair cis, is selected. Its two aromatic rings are inequivalent, allowing four distinct tert-butyl resonances.

Solution

7.1 — The three Mannich products

The starting structures are:

- 2-tert-Butylphenol: Oc1c(C(C)(C)C)cccc1
- Formaldehyde: C=O
- *N*, *N'*-Dimethylethane-1,2-diamine: CNCCNC

The reaction is a Mannich aminomethylation. Each secondary amine group reacts with one formaldehyde molecule and one phenol ring, installing an aromatic $-\text{CH}_2-\text{N}$ linkage and eliminating water, O.

Number each starting phenol ring with the hydroxyl group at C1 and tert-butyl at C2. The hydroxyl group activates the ortho and para positions. C2 is occupied, so the available positions are **C6, ortho**, and **C4, para**.

The common product framework is



Choosing ortho or para attachment independently on the two rings gives three distinct combinations; exchanging the two ends makes ortho/para and para/ortho identical.

Ortho/ortho product, P_{oo} :

N, N'-Bis(3-tert-butyl-2-hydroxybenzyl)-*N, N'*-dimethylethane-1,2-diamine.



For the drawing, attach both aminomethyl groups at C6 of their respective starting phenol rings.

Ortho/para product, P_{op} :

N-(3-tert-Butyl-2-hydroxybenzyl)-*N'*-(3-tert-butyl-4-hydroxybenzyl)-*N, N'*-dimethylethane-1,2-diamine.



Attach one aminomethyl group at C6 and the other at C4.

Para/para product, P_{pp} :

N, N'-Bis(3-tert-butyl-4-hydroxybenzyl)-*N, N'*-dimethylethane-1,2-diamine.



Attach both aminomethyl groups at C4.

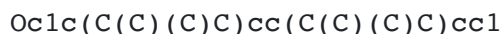
For each product, the balanced overall equation under the stated acidic conditions is



Thus all three structures have the required molecular formula.

7.2 — Identification of X

The new starting phenol is 2,4-di-tert-butylphenol:



Its C2 ortho position and C4 para position are both occupied. Aminomethylation therefore occurs at the remaining ortho position, C6, on each ring.

Consequently, **X** is the ortho/ortho product named and specified in the Answers section. To draw it, use the same diamine bridge as in P_{oo} , retaining tert-butyl substituents at C2 and C4 of each phenol ring.

The balanced synthesis is



X contains two phenolic hydroxyl groups and two tertiary amine nitrogen atoms. These supply the eventual four-donor sequence



where each curved connection represents the ligand framework between consecutive donors.

7.3 — Continuous-variation plot and stoichiometry

Let x_X denote the mole fraction requested in the table. Since both stock solutions have the same concentration,

$$x_X = \frac{cV_X}{cV_X + cV_{\text{Ti}}} = \frac{V_X}{V_X + V_{\text{Ti}}} = \frac{V_X}{1.20 \text{ cm}^3}.$$

The combined amount of the two reagents is constant:

$$n_X + n_{\text{Ti}} = (0.50 \text{ mol dm}^{-3})(1.20 \times 10^{-3} \text{ dm}^3) = 6.0 \times 10^{-4} \text{ mol}.$$

Every mixture also has the same total volume, 3.00 cm^3 . Thus the absorbances can be compared directly in a Job plot.

The completed table is:

x_X	Absorbance at 370 nm
0.000	0.05
0.167	0.25
0.250	0.38
0.417	0.59
0.650	0.48
0.750	0.38
0.917	0.17
1.000	0.02

For the requested graph, place x_X on the horizontal axis from 0 to 1 and absorbance on the vertical axis. Plot these eight points. The rising and falling branches are approximately straight, and their intersection lies near $x_X = 0.50$.

For a numerical check, least-squares lines through the first four and last four points are

$$A_{\text{left}} \approx 0.0454 + 1.3062x_X, \quad A_{\text{right}} \approx 1.3406 - 1.3003x_X.$$

Their intersection is

$$x_{X,\text{max}} = \frac{1.3406 - 0.0454}{1.3062 + 1.3003} \approx 0.497, \quad A_{\text{max}} \approx 0.69.$$

The peak falls between the sampled compositions. For a complex containing a ligands X per b titanium atoms,

$$x_{X,\text{max}} = \frac{a}{a + b}.$$

Hence

$$\text{Ti} : \text{X} = (1 - x_{X,\text{max}}) : x_{X,\text{max}} \approx 0.503 : 0.497 \approx \boxed{1 : 1}.$$

7.4 — Composition and three octahedral diastereomers

Write the neutral ligand as H_2L . The absence of the broad hydroxyl absorption indicates that both phenolic groups have lost their protons.

The resulting ligand is the **bis(phenolate) dianion of X**, L^{2-} , with formula $\text{C}_{34}\text{H}_{54}\text{N}_2\text{O}_2^{2-}$:

CN(Cc1c([O-])c(C(C)(C)C)cc(C(C)(C)C)c1)CCN(C)Cc1c([O-])c(C(C)(C)C)cc(C(C)(C)C)c1

Its two phenolate oxygen atoms and two tertiary amine nitrogen atoms bind titanium. Two isopropoxide oxygen donors complete the six-coordinate, octahedral complex.

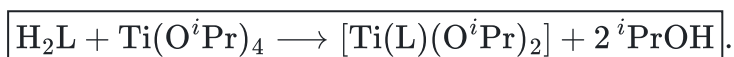
The reagent is **titanium(IV) isopropoxide**:

CC(C)O[Ti](OC(C)C)(OC(C)C)OC(C)C

The eliminated alcohol is **propan-2-ol (isopropanol)**:

CC(O)C

The balanced complexation reaction is



Therefore,

$$\boxed{a = b = d = 1, \quad c = 2}.$$

Charge balance is consistent with a neutral complex:

$$(+4)_{\text{Ti}} + (-2)_{\text{L}} + 2(-1)_{\text{isopropoxide}} = 0.$$

The molecular formula is consequently $\text{C}_{40}\text{H}_{68}\text{N}_2\text{O}_4\text{Ti}$.

For the geometry, label the phenolate donors O_1, O_2 , their respective amine donors N_1, N_2 , and the two isopropoxide oxygen donors $\text{O}_{a1}, \text{O}_{a2}$. The ligand connections are always



Each consecutive donor pair must occupy cis sites because it forms a chelate ring. There are three resulting geometric classes:

Isomer	Isopropoxide oxygen pair	Phenolate oxygen pair
I	trans	cis
II	cis	trans
III	cis	cis

The following table specifies an exact drawing of one representative of each class. Put Ti at the origin, with $+x$ right, $-x$ left, $+y$ up, $-y$ down, $+z$ toward the reader, and $-z$ away. Draw the $+z$ bond as a solid wedge and the $-z$ bond as a dashed wedge, then add the three ligand-framework connections.

Isomer	$+x$	$-x$	$+y$	$-y$	$+z$	$-z$
I	N_1	O_2	N_2	O_1	O_{a1}	O_{a2}
II	N_1	O_{a1}	N_2	O_{a2}	O_1	O_2
III	N_1	O_{a1}	N_2	O_1	O_2	O_{a2}

Complete stereochemical SMILES for these representatives follow. They use the extended @OH notation for octahedral stereochemistry and -> for nitrogen-to-titanium dative bonds. Nitrogen configurations are intentionally unspecified, as requested.

I — trans-Isopropoxide isomer of the titanium(IV) complex:

```
[Ti@OH23]123(OC(C)C)(OC(C)C)Oc4c(C(C)(C)C)cc(C(C)(C)C)cc4CN->1(C)CCN-  
>2(C)Cc1cc(C(C)(C)C)cc(C(C)(C)C)c1O3
```

II — cis-Isopropoxide/trans-phenolate isomer of the titanium(IV) complex:

```
[Ti@OH16]123(OC(C)C)(OC(C)C)Oc4c(C(C)(C)C)cc(C(C)(C)C)cc4CN->1(C)CCN-  
>2(C)Cc1cc(C(C)(C)C)cc(C(C)(C)C)c1O3
```

III — cis-Isopropoxide/cis-phenolate isomer of the titanium(IV) complex:

```
[Ti@OH21]123(OC(C)C)(OC(C)C)Oc4c(C(C)(C)C)cc(C(C)(C)C)cc4CN->1(C)CCN-  
>2(C)Cc1cc(C(C)(C)C)cc(C(C)(C)C)c1O3
```

At the donor-framework level, II and III each have mirror-related forms. Drawing either enantiomer represents the corresponding diastereomeric class.

7.5 — Selection from the tert-butyl NMR signals

There are four tert-butyl groups: one ortho and one para to the phenolate oxygen on each aromatic ring.

In **I** and **II**, symmetry interchanges the two ligand arms. Consequently, the two ortho tert-butyl groups are equivalent to each other, and the two para tert-butyl groups are equivalent to each other. These arrangements predict **two tert-butyl resonances**, each accounting for 18 H.

In **III**, the two phenolate donors have different trans partners:

- O_1 is trans to the opposite arm's amine donor, N_2 .
- O_2 is trans to an isopropoxide oxygen, O_{a2} .

No symmetry operation interchanges the two aromatic rings. All four tert-butyl groups can therefore be chemically inequivalent, giving **four singlets**, each accounting for 9 H.

Thus the required drawing is precisely **isomer III** in the coordinate table:

cis isopropoxide donors; cis phenolate donors; inequivalent ligand arms.

Its name and stereochemical SMILES are given under III above. Either enantiomer, or a racemic mixture, gives the same spectrum in achiral $CDCl_3$; these data do not assign absolute configuration.

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

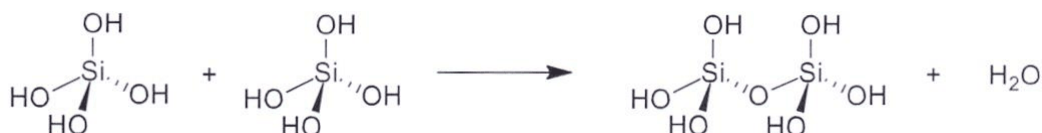
Problem 8: Silica Surface

Silica exists in various forms like amorphous and crystalline. Silica can be synthesized *via* sol- gel process by using silicon alkoxides like tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS) as the details below:

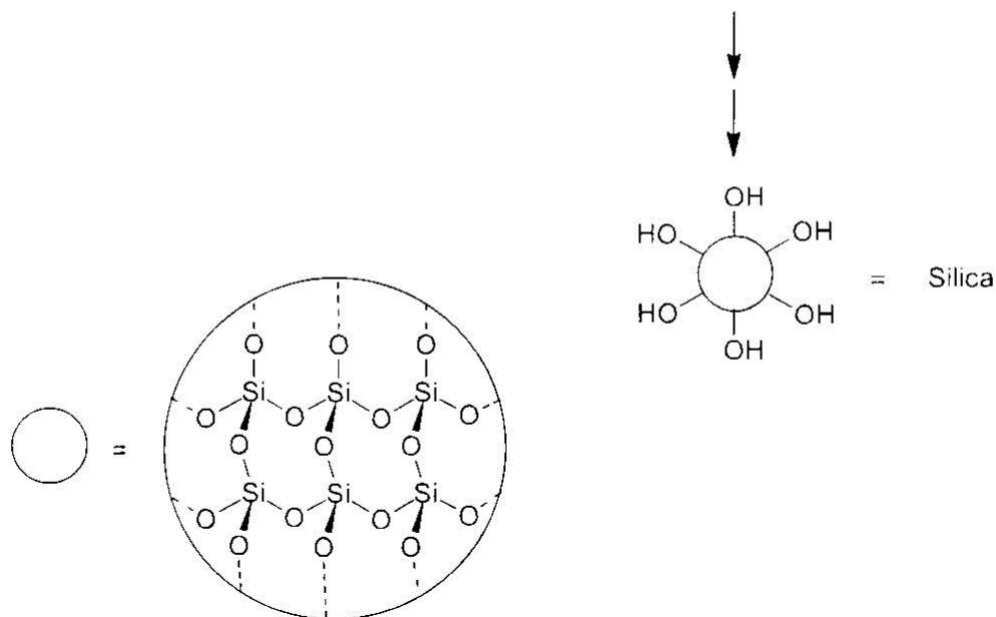
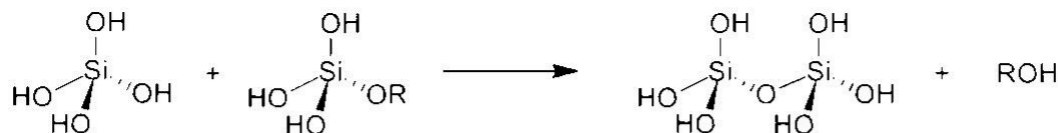
a. Hydrolysis



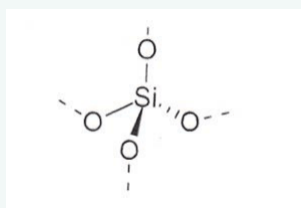
b. Water condensation



c. Alcohol condensation



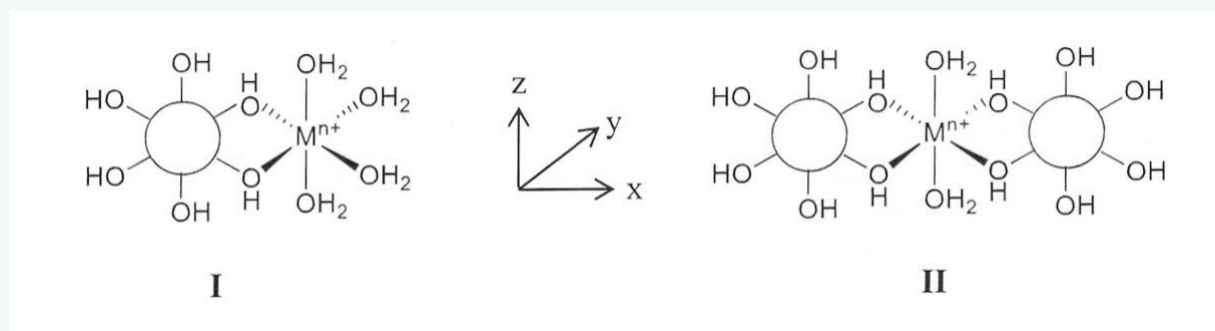
In bulk silica, all silicon atoms are tetrahedrally bonded to four oxygen atoms giving three-dimensional solid network. The silicon environments found inside silica is presented below:



8.1 Three silicon atom environments (similar to the example above) are commonly observed at the silica **surface**. The three structures of the silicon environments must be **drawn** in the provided boxes.



Silica can be used as an effective metal ion adsorbent in water. The proposed structure for metal-silica complex is as follows:



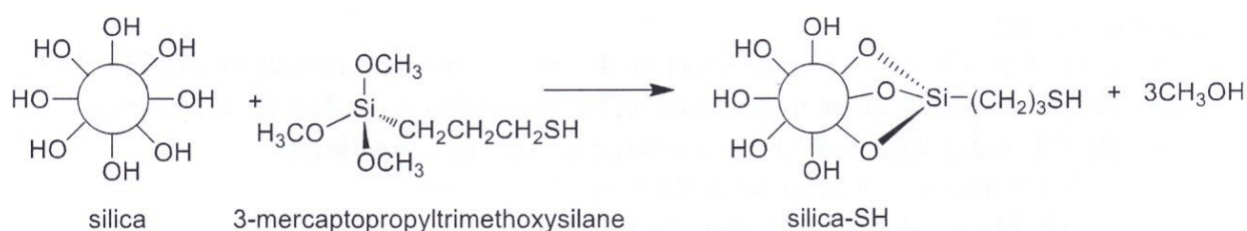
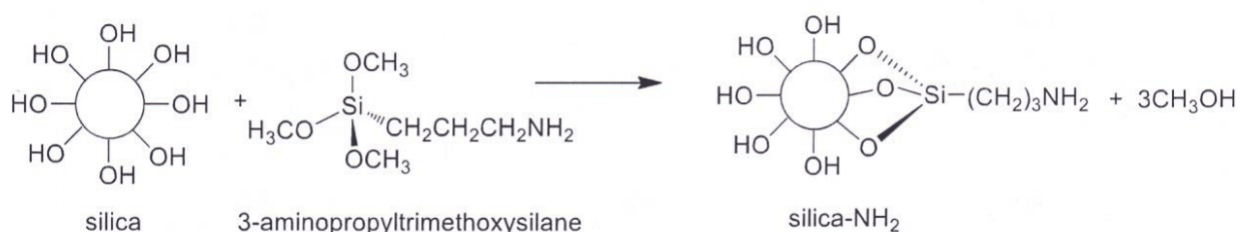
8.2 After Cu^{2+} is being adsorbed, the color of silica changes from white to pale blue. The visible spectrum shows a broad absorption band (with a shoulder) at $\lambda_{\text{max}} = 550 \text{ nm}$.

If Cu^{2+} can bind with silica and adopt the structure similar to **II**, draw the splitting diagram of the d - orbitals of Cu^{2+} ion including the label of the d orbitals in the complex and **specify** the corresponding electronic transition(s) for the visible absorption.

8.3 If the first row transition metal ions form complexes with silica analogous to Cu^{2+} , which metal ion(s) do(es) have the analogous to electronic transition(s) to Cu^{2+} ?

The metal ion(s) must be in +2 or +3 oxidation state. Please note that the silanol groups ($\text{Si}-\text{OH}$) and water are weak field ligands.

However, silica is randomly bonded to various types of metal ion. To increase the selectivity, modification of silica surface has been performed by grafting with various organic molecules like 3-aminopropyltrimethoxysilane and 3-mercaptopropyltrimethoxy-silane.



8.4 If Hg^{2+} is only bonding to sulfur binding sites in silica-SH, the **symmetric** complex of $[\text{Hg}(\text{silica-SH})_2]^{2+}$ is formed. Draw the structure of $[\text{Hg}(\text{silica-SH})_2]^{2+}$, specify the direction of the bond axes, and draw the corresponding d -orbital splitting. (You may use R-SH instead of drawing the whole structure of silica-SH.).

The structure: d -orbital splitting diagram :

8.5 Specify whether the following statements are true or false:

a) $d-d$ transition is found in $[(\text{Hg}(\text{silica-SH})_x)]^{2+}$

☐ True ☐ False

b) The $[\text{Cu}(\text{silica-NH}_2)_x]^{2+}$ in a similar geometry, is expected to have a color similar to other copper(II) amine complexes.

☐ True ☐ False

c) In the visible absorption spectra, λ_{max} of $[\text{Cu}(\text{silica-NH}_2)_x]^{2+}$ is greater than that of $[\text{Cu}(\text{silica-OH})_x]^{2+}$.

☐ True ☐ False

Official English text of the problem.

Answers

In the surface-fragment SMILES below, $[*]$ represents an attachment to the remaining structure. These fragments describe local connectivity, not the complete silica network.

- **8.1:** The three hydroxylated tetrahedral silicon environments are:
- **Monohydroxyl site, Q^3 :** three bridging oxygens and one hydroxyl; fragment SMILES $\text{O}[\text{Si}](\text{O}[*])(\text{O}[*])(\text{O}[*])$.
- **Geminal dihydroxyl site, Q^2 :** two bridging oxygens and two hydroxyls; fragment SMILES $\text{O}[\text{Si}](\text{O})(\text{O}[*])(\text{O}[*])$.
- **Trihydroxyl site, Q^1 :** one bridging oxygen and three hydroxyls; fragment SMILES $\text{O}[\text{Si}](\text{O})(\text{O})(\text{O}[*])$.
- **8.2:** Copper(II), Cu^{2+} , $[\text{Cu}+2]$, is $3d^9$. For the usual tetragonally elongated octahedron, a conventional ordering is

$$d_{xz} = d_{yz} < d_{xy} < d_{z^2} < d_{x^2-y^2}.$$

The highest orbital is singly occupied; all others are doubly occupied. The absorption comprises

$$d_{z^2} \rightarrow d_{x^2-y^2}, \quad d_{xy} \rightarrow d_{x^2-y^2}, \quad (d_{xz}, d_{yz}) \rightarrow d_{x^2-y^2}.$$

The relative order of the two intermediate levels depends on the distortion strength.

- **8.3: Chromium(II), Cr^{2+} , $[\text{Cr}+2]$, and manganese(III), Mn^{3+} , $[\text{Mn}+3]$.** Both are high-spin $3d^4$.

- **8.4: Linear bis(thiol)mercury(II)**, $[\text{Hg}(\text{RSH})_2]^{2+}$; coordination-fragment SMILES $[\text{*}] [\text{SH}] \rightarrow [\text{Hg}+2] \leftarrow [\text{SH}] [\text{*}]$. Place the two sulfur donors on the $+z$ and $-z$ axes:

$$\angle \text{S}-\text{Hg}-\text{S} = 180^\circ, \quad d_{xy} = d_{x^2-y^2} < d_{xz} = d_{yz} < d_{z^2}.$$

All five orbitals are doubly occupied.

- **8.5: (a) False; (b) True; (c) False.**

Solution

8.1 — Surface silicon environments

Each silicon remains tetrahedrally coordinated to four oxygen atoms. In the interior, all four oxygens bridge to other silicon atoms. At a hydroxylated surface, some of these positions terminate as silanol groups instead.

The notation Q^n counts the number of bridging oxygens attached to a silicon atom. Thus the three partially condensed, surface-connected possibilities are:

Site	Local structural formula	Bridging oxygens	Terminal hydroxyls
Monohydroxyl, Q^3	$\text{Si}(\text{OH})(\text{O}-\text{Si})_3$	3	1
Geminal dihydroxyl, Q^2	$\text{Si}(\text{OH})_2(\text{O}-\text{Si})_2$	2	2
Trihydroxyl, Q^1	$\text{Si}(\text{OH})_3(\text{O}-\text{Si})$	1	3

These formulas denote fragments: each outer silicon continues into the solid.

To fill the boxes, draw a central silicon with four tetrahedrally directed bonds to oxygen. In the first box, label one oxygen as a hydroxyl and continue the other three into the network; in the second, use two of each; in the third, use three hydroxyls and one network connection. The corresponding fragment SMILES are given in the Answers section.

A site with no bridging oxygen would be a detached, fully hydroxylated silicon species, rather than a silicon atom connected to the silica surface.

8.2 — Copper orbital splitting and absorption

Copper(II), Cu^{2+} , $[\text{Cu}+2]$, has configuration

$$[\text{Ar}] 3d^9.$$

In structure II, four surface silanol oxygen donors surround the metal in the xy plane, while two water ligands occupy the axial positions along z . Water, H_2O , has SMILES o .

The copper surface complex can be represented by the coordination-fragment SMILES $[\text{Cu}+2] (<-\text{[OH2]}) (<-\text{[OH2]}) (<-\text{[OH] [*]}) (<-\text{[OH] [*]}) (<-\text{[OH] [*]}) (<-\text{[OH] [*]})$, where each wildcard is a surface silicon. Dative arrows record oxygen-to-metal donation; the SMILES does not specify the octahedral geometry or bond lengths.

In an ideal octahedral field, the configuration is

$$t_{2g}^6 e_g^3.$$

The uneven occupation of the e_g orbitals makes this configuration Jahn–Teller active. The usual copper(II) distortion is axial elongation: the two bonds along z are longer than the four equatorial bonds.

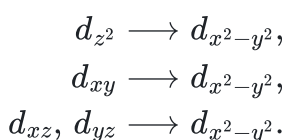
Consequently:

- $d_{x^2-y^2}$, directed toward the four equatorial donors, becomes the highest orbital.
- d_{z^2} is lowered relative to $d_{x^2-y^2}$.
- d_{xz} and d_{yz} are lowered relative to d_{xy} , remaining mutually degenerate.

For a conventional moderate elongation, draw the following levels, with energy increasing upward:

Position	Orbital(s)	Occupancy
Highest	$d_{x^2-y^2}$	$\uparrow$
Next	d_{z^2}	$\uparrow\downarrow$
Next	d_{xy}	$\uparrow\downarrow$
Lowest	d_{xz}, d_{yz}	$\uparrow\downarrow \quad \uparrow\downarrow$

Draw upward absorption arrows from each lower energy level to $d_{x^2-y^2}$:



Each promotion fills the vacancy in $d_{x^2-y^2}$ and leaves a vacancy in a lower orbital. There are three distinct transition energies because d_{xz} and d_{yz} are degenerate.

These transitions can overlap into the observed broad band with a shoulder. The supplied 550 nm maximum does not determine a separate wavelength for each transition.

8.3 — Other ions with analogous transitions

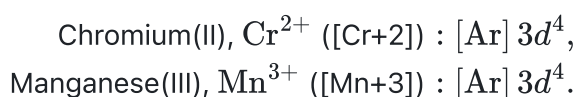
The relevant analogy is the availability of the same orbital promotions into the highest $d_{x^2-y^2}$ orbital.

A high-spin d^4 ion places one electron in each of the four lower orbitals and leaves $d_{x^2-y^2}$ empty:

Orbital(s)	Copper(II), d^9	High-spin d^4
$d_{x^2-y^2}$	$\uparrow$	Empty
d_{z^2}	$\uparrow\downarrow$	$\uparrow$
d_{xy}	$\uparrow\downarrow$	$\uparrow$
d_{xz}, d_{yz}	$\uparrow\downarrow \quad \uparrow\downarrow$	$\uparrow \quad \uparrow$

Thus the same three types of promotion shown in 8.2 are possible without changing the total spin. High-spin d^4 , with octahedral configuration $t_{2g}^3 e_g^1$, also has uneven e_g occupation and is strongly Jahn–Teller active.

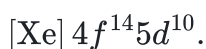
The first-row ions in the permitted oxidation states with this configuration are:



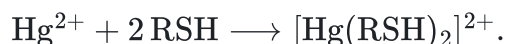
The weak-field qualification ensures that these d^4 ions are high spin. Their transition wavelengths need not equal those of copper(II).

8.4 — Mercury complex and orbital splitting

Mercury(II), Hg^{2+} , [Hg+2], has configuration



The ligand is a neutral surface-tethered thiol, RSH , represented by fragment SMILES [*]S. Sulfur donates a lone pair without loss of its hydrogen:



The product is bis(thiol)mercury(II), with coordination-fragment SMILES [*][SH]->[Hg+2]<-[SH][*].

For the requested drawing:

1. Place mercury at the origin.
2. Place one sulfur donor on $+z$ and the other on $-z$.
3. Draw a sulfur-to-mercury coordination bond from each ligand. Each sulfur also retains its bonds to hydrogen and R .
4. Make the coordination unit linear, with $\angle \text{S}-\text{Hg}-\text{S} = 180^\circ$. Choose x and y perpendicular to this axis.

For the conventional linear crystal field, draw:

Position	Orbital(s)	Occupancy
Highest	d_{z^2}	$\uparrow\downarrow$
Intermediate	d_{xz}, d_{yz}	$\uparrow\downarrow$ $\uparrow\downarrow$
Lowest	$d_{xy}, d_{x^2-y^2}$	$\uparrow\downarrow$ $\uparrow\downarrow$

The d_{z^2} orbital points directly toward the two donors and experiences the greatest destabilization. The two orbitals confined to the perpendicular plane are lowest. Cylindrical symmetry about the bond axis gives the indicated degeneracies.

8.5 — True or false

(a) False. Mercury(II) is d^{10} . Every d orbital is filled, so there is no vacant d -orbital state into which a d electron can be promoted.

(b) True. The surface primary amine group, RNH_2 , has fragment SMILES [*]N; its copper coordination can be represented locally as [*]N->[Cu+2]. Nitrogen coordination gives a ligand field similar to that of other copper(II) amine complexes when the coordination geometries are comparable, so a similar color is expected.

(c) False. Amine nitrogen donors generally produce a stronger ligand field than silanol oxygen donors. For comparable geometries, the relevant transition energies therefore increase:

$$\Delta_{\text{amine}} > \Delta_{\text{silanol}}.$$

Since

$$E = \frac{hc}{\lambda},$$

the expected wavelength relationship is

$$\lambda_{\text{max,amine}} < \lambda_{\text{max,silanol}}.$$

The statement gives the opposite inequality.

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

Problem 9: Into the Unknown

Organic compound **A** is **chiral** and contains only three elements with the molecular weight (MW) of 149 (rounded to an integer).

^1H NMR spectrum of compound **A** shows among others, three types of aromatic protons, and its ^{13}C NMR spectrum shows eight signals, of which four signals are in the range of 120–140 ppm.

Compound **A** can be prepared by treating a carbonyl compound with methylamine followed by NaBH_3CN .

9.1 Write all possible structural formulae of compound **A**. No stereochemistry is required, and **do not** include stereoisomers.

9.2 One of the position isomers of compound **A** (structure **A1**, **A2** or **A3**) can be synthesized from compound **B** or **C** and **D** as shown in the diagram below. Write down the structural formulae of compounds **B–F**, and the position isomer of compound **A**.

9.3 Compound **A** is the (*R*)-form of one of structures **A1–A3**. It can be prepared from vicinal diols **X** and **Y** as shown in the diagram below. Both diols are structural isomers, and each structure contains one carbon less than that of compound **A**.

Write down the structural formulae of compounds **G–N**, **X**, **Y** and the (*R*)-form of compound **A**. You must show stereochemistry of all compounds.

Official English text of the problem.

Answers

The labels **A1–A3** below are assigned for this solution. Ph denotes the phenyl group, attachment-point SMILES `[*]c1ccccc1`.

- 9.1.** The three intended constitutional isomers are:

Label	Name	Condensed structure	SMILES
A1	N-Methyl-1-phenylpropan-1-amine	$\text{PhCH}(\text{NHCH}_3)\text{CH}_2\text{CH}_3$	<code>CCC(NC)c1ccccc1</code>
A2	N-Methyl-1-phenylpropan-2-amine	$\text{PhCH}_2\text{CH}(\text{NHCH}_3)\text{CH}_3$	<code>CC(NC)Cc1ccccc1</code>
A3	N-Methyl-2-phenylpropan-1-amine	$\text{PhCH}(\text{CH}_3)\text{CH}_2\text{NHCH}_3$	<code>CC(CNC)c1ccccc1</code>

- 9.2. B–F and the selected position isomer cannot be identified uniquely:** the reaction diagram containing their relationships and reagents is not printed in the problem.

- **9.3. X and Y each contain nine carbon atoms.** Their structures and stereochemistry, the assignments **G–N**, and the identity of the selected **A** cannot be determined without the missing diagram. The three possible (*R*)-configured final structures are:

Candidate	Name	Stereochemical SMILES
(<i>R</i>)- A1	(1 <i>R</i>)-N-Methyl-1-phenylpropan-1-amine	<chem>CC[C@H](NC)c1ccccc1</chem>
(<i>R</i>)- A2	(2 <i>R</i>)-N-Methyl-1-phenylpropan-2-amine	<chem>C[C@H](NC)Cc1ccccc1</chem>
(<i>R</i>)- A3	(2 <i>R</i>)-N-Methyl-2-phenylpropan-1-amine	<chem>C[C@H](CNC)c1ccccc1</chem>

Solution

9.1

Methylamine, CN , and sodium cyanoborohydride, $[\text{Na}^+] \cdot [\text{BH}_3^-] \text{C}\equiv\text{N}$, perform **reductive amination**. The carbonyl group is converted into a carbon bearing an N-methylamino group, $-\text{NHCH}_3$.

The balanced net transformation, with $2[\text{H}]$ representing the reducing equivalents supplied during reduction, is



The coproduct is water, O . For an aldehyde, one of the groups R^1 or R^2 is hydrogen.

Mechanistically, methylamine attacks the carbonyl carbon. Proton transfers and elimination of water generate an imine/iminium intermediate; hydride addition to its carbon produces the amine.

Since the product contains carbon, hydrogen and nitrogen, these account for its three elements.

The usual interpretation of the NMR pattern is a **monosubstituted benzene ring**:

- The aromatic protons occupy three environments: ortho, meta and para, normally corresponding to 2 : 2 : 1 protons.
- The aromatic carbons occupy four environments: ipso, ortho, meta and para.

Thus six aromatic carbon atoms account for four carbon signals. The other four signals correspond to four different nonaromatic carbon atoms, giving ten carbon atoms altogether. With one nitrogen atom, the molecular mass requires fifteen hydrogens:

$$10(12) + 15(1) + 14 = 149.$$

Hence the molecular formula is

$$\boxed{\text{C}_{10}\text{H}_{15}\text{N}}, \quad M \approx 149 \text{ g mol}^{-1}.$$

Its degree of unsaturation is

$$\text{DBE} = \frac{2(10) + 2 + 1 - 15}{2} = 4.$$

The benzene ring accounts for all four degrees of unsaturation. The remaining part must therefore be saturated and acyclic.

One of the four nonaromatic carbons belongs to the N-methyl group. Arranging the other three carbons between the phenyl and N-methylamino groups gives the three chiral structures listed in the answers:

- **A1**: the stereogenic carbon bears NHCH_3 , phenyl, ethyl and hydrogen.
- **A2**: the stereogenic carbon bears NHCH_3 , benzyl, methyl and hydrogen.
- **A3**: the stereogenic carbon bears CH_2NHCH_3 , phenyl, methyl and hydrogen.

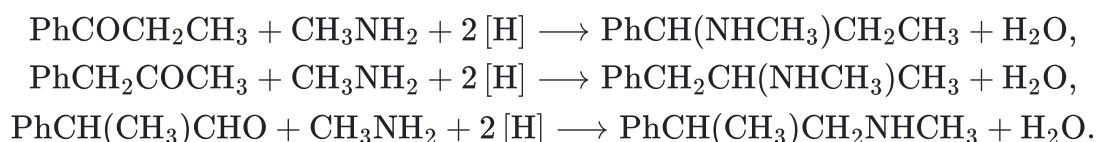
Each has four distinct nonaromatic carbon environments, consistent with eight carbon signals overall.

The other saturated arrangements do not satisfy the chirality requirement. N-Methyl-3-phenylpropan-1-amine, CNCCCCc1ccccc1, has no carbon stereocentre. N-Methyl-2-phenylpropan-2-amine, CNC(C)c1ccccc1, has two identical methyl groups on its substituted carbon; it also lacks the carbon-bound hydrogen introduced by ordinary reductive amination. Nitrogen inversion does not furnish a configurationally stable stereocentre in these ordinary acyclic amines.

The corresponding carbonyl precursors confirm the stated preparation:

Product	Carbonyl precursor	Precursor SMILES
A1	1-Phenylpropan-1-one, or propiophenone	<chem>CCC(=O)c1ccccc1</chem>
A2	1-Phenylpropan-2-one, or phenylacetone	<chem>CC(=O)Cc1ccccc1</chem>
A3	2-Phenylpropanal	<chem>CC(C=O)c1ccccc1</chem>

Their balanced net reactions are



For **A3**, the stereogenic carbon is already present in the aldehyde precursor.

9.2

The supplied text gives no structures, reagents, reaction conditions or connectivity between the labels **B–F**. Those details reside in the missing diagram.

The carbonyl precursors above establish possible preparations of all three candidates, but they cannot be assigned to **B–F** without the scheme. Nor does the remaining text select one position isomer. Providing specific assignments would therefore require inventing information.

9.3

From part 9.1, **A** contains ten carbon atoms. Therefore,

$$n_{\text{C}}(\text{X}) = n_{\text{C}}(\text{Y}) = 10 - 1 = \boxed{9}.$$

A vicinal diol has hydroxyl groups on adjacent carbon atoms. This condition, structural isomerism and the carbon count do not fix the carbon skeletons or absolute configurations of **X** and **Y**. The omitted reactions are also needed to determine where stereochemistry is retained, inverted or newly established in **G–N**.

The (*R*) requirement can nevertheless be specified precisely for each possible final structure. Their Cahn–Ingold–Prelog priorities are:

Candidate	Priority 1	Priority 2	Priority 3	Priority 4
A1	$-\text{NHCH}_3$	Phenyl	$-\text{CH}_2\text{CH}_3$	$-\text{H}$
A2	$-\text{NHCH}_3$	$-\text{CH}_2\text{Ph}$	$-\text{CH}_3$	$-\text{H}$

Candidate	Priority 1	Priority 2	Priority 3	Priority 4
A3	$-\text{CH}_2\text{NHCH}_3$	Phenyl	$-\text{CH}_3$	$-\text{H}$

For **A1**, phenyl outranks ethyl because the next comparison is (C, C, C) against (C, H, H), applying the multiple-bond duplication convention. For **A2**, benzyl similarly outranks methyl. For **A3**, the aminomethyl carbon has the comparison list (N, H, H), so it outranks the phenyl carbon.

To draw any of the required (*R*) structures, orient hydrogen away from the viewer and arrange priorities $1 \rightarrow 2 \rightarrow 3$ clockwise. The stereochemical SMILES in the answers encode these configurations. The missing diagram is necessary to choose which one is **A**.

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

Problem 10: Total Synthesis of Alkaloids

Alkaloids are a class of nitrogen-containing natural products. Their structural complexity and potent biological activities has drawn attentions. Two representative examples of alkaloids – sauristolactam and pancratistatin are highlighted in following questions.

Part A

Sauristolactam possesses excellent cytotoxicity against various cancer cell lines. It could be prepared by following synthetic sequence on the page. (^1H -NMR spectra were recorded in CDCl_3 at 300 MHz.)

10.1 Draw the structures of **A-G** in the sequence.

Part B

Pancratistatin, isolated from a Hawaiian native plant, spider lily, exhibits potent in vitro and in vivo inhibitory activity of cancer cell growth in addition to its excellent antiviral activity.



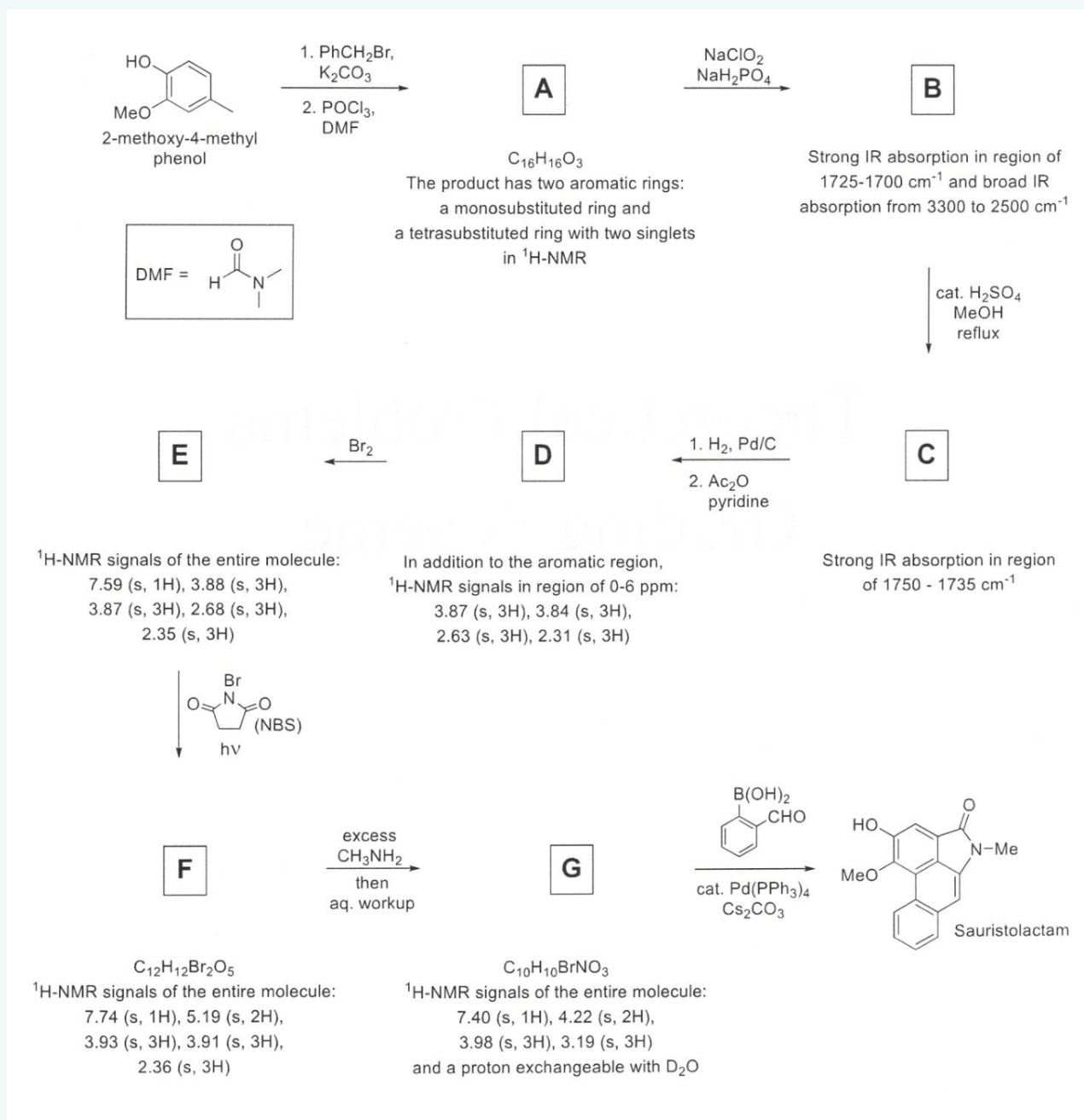
Pancratistatin

Pancratistatin could be successfully synthesized via intermediates **X1** and **X2**. The synthesis of these intermediates are shown in the attached scheme.

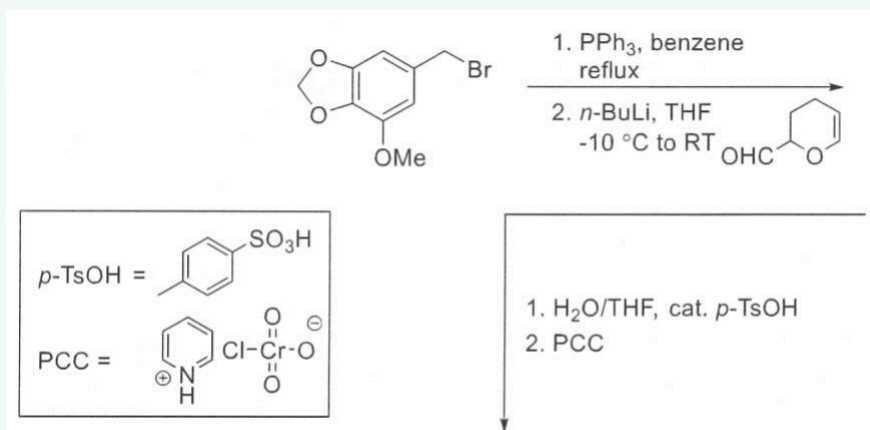
10.2 Draw the structures of **A** and **B**.

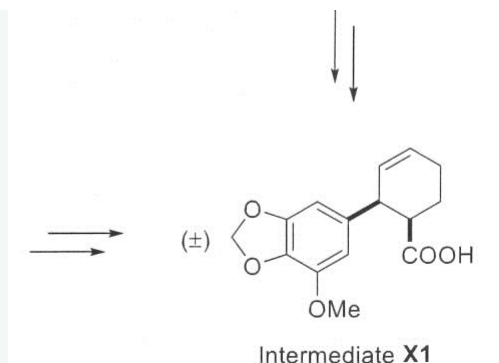
10.3 Intermediate **X1** (a single enantiomer with the stereochemistry shown) is labeled with deuterium with configuration as indicated below, propose the 3-D chair structure of compound **E** and the structure of compound **F**, with stereochemistry. Is **Y** a proton (^1H) or a deuterium (^2H)?

Syntetic sequence:



Scheme of the synthesis of Pancratistatin and structures of compound A and B:





Intermediate X1

Official English text of the problem.

Answers

- 10.1. The structures are:

Compound	Name	SMILES
A	5-(Benzyloxy)-4-methoxy-2-methylbenzaldehyde	<chem>COc1cc(C)c(C=O)cc1OCc1ccccc1</chem>
B	5-(Benzyloxy)-4-methoxy-2-methylbenzoic acid	<chem>COc1cc(C)c(C(=O)O)cc1OCc1ccccc1</chem>
C	Methyl 5-(benzyloxy)-4-methoxy-2-methylbenzoate	<chem>COc1cc(C)c(C(=O)OC)cc1OCc1ccccc1</chem>
D	Methyl 5-acetoxy-4-methoxy-2-methylbenzoate	<chem>COc1cc(C)c(C(=O)OC)cc1OC(C)=O</chem>
E	Methyl 5-acetoxy-3-bromo-4-methoxy-2-methylbenzoate	<chem>COc1c(Br)c(C)c(C(=O)OC)cc1OC(C)=O</chem>
F	Methyl 5-acetoxy-3-bromo-2-(bromomethyl)-4-methoxybenzoate	<chem>COc1c(Br)c(CBr)c(C(=O)OC)cc1OC(C)=O</chem>
G	4-Bromo-6-hydroxy-5-methoxy-2-methylisindolin-1-one	<chem>CN1Cc2c(Br)c(OC)c(O)cc2C1=O</chem>

- 10.2. The two visible operations give the following products. **Their assignment to A and B, respectively, is inferred: the labeled product boxes are outside the supplied crop.**

Inferred label	Name	SMILES
A, product of the Wittig reaction	2-[2-(7-Methoxy-1,3-benzodioxol-5-yl)ethenyl]-3,4-dihydro-2H-pyran	<chem>COc1cc(C=CC2CCC=CO2)cc2OCc12</chem>
B, product after aqueous acid and PCC	6-[2-(7-Methoxy-1,3-benzodioxol-5-yl)ethenyl]oxan-2-one, a six-membered lactone	<chem>COc1cc(C=CC2CCCC(=O)O2)cc2OCc12</chem>

These SMILES specify connectivity. The cropped scheme does not establish an *E/Z* designation or an absolute configuration for these products.

- **10.3. E, F, and the identity of Y cannot be determined uniquely from the problem as printed.** The deuterium-labeled structure and the reaction sequence defining these compounds are absent. The visible **X1** has **cis** aryl and carboxyl substituents and is explicitly shown as a racemate.

Solution

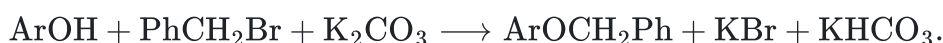
10.1. Identification of A–G

For **A–F**, number the aromatic ring so that the carbon bearing the aldehyde or carboxyl-derived group is C1. The original ring methyl group is then at C2, the methoxy group at C4, and the protected phenolic oxygen at C5.

Formation of A: protection and regioselective formylation

The starting material is 2-methoxy-4-methylphenol, COc1cc(C)ccc1O.

Benzyl bromide and potassium carbonate protect its phenolic hydroxyl group as a benzyl ether, giving 1-(benzyloxy)-2-methoxy-4-methylbenzene, COc1cc(C)ccc1OCC1CCCCC1. A balanced representation is



The POCl3/DMF treatment is a Vilsmeier–Haack formylation. Formylation occurs **para to methoxy and ortho to methyl**.

The NMR description fixes this position. In the starting phenol's numbering, introduction of the formyl group at C5 leaves hydrogens at C3 and C6. These are para to one another and appear as two aromatic singlets. The benzyl protecting group supplies the monosubstituted phenyl ring.

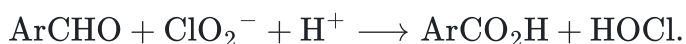
A formal balanced equation including aqueous workup is



Thus **A** is **5-(benzyloxy)-4-methoxy-2-methylbenzaldehyde**, with formula C16H16O3, as required.

A → B: aldehyde oxidation

Buffered sodium chlorite oxidizes the aldehyde to a carboxylic acid:

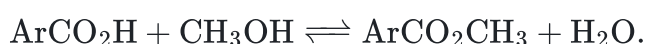


The strong carbonyl absorption at $1725\text{--}1700\text{ cm}^{-1}$, together with the broad $3300\text{--}2500\text{ cm}^{-1}$ absorption, identifies a carboxylic acid.

Therefore **B** is **5-(benzyloxy)-4-methoxy-2-methylbenzoic acid**.

B → C: esterification

Methanol and catalytic sulfuric acid give the methyl ester by Fischer esterification:



The reported $1750\text{--}1735\text{ cm}^{-1}$ carbonyl absorption supports the ester assignment.

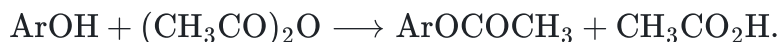
Thus **C** is **methyl 5-(benzyloxy)-4-methoxy-2-methylbenzoate**.

C → D: hydrogenolysis and acetylation

Hydrogen over palladium removes the benzyl protecting group:



The resulting phenol is acetylated:



Consequently, **D** is **methyl 5-acetoxy-4-methoxy-2-methylbenzoate**.

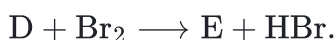
Its four three-proton singlets are consistent with:

Signals, δ /ppm	Assignment
3.87 and 3.84	Aromatic methoxy and methyl ester
2.63	Ring methyl
2.31	Acetate methyl

The two methoxy resonances need not be individually distinguished to identify the structure.

D → E: aromatic bromination

Bromination replaces the hydrogen at C3:



C3 is activated by the neighboring methoxy group. The remaining aromatic hydrogen is H6, adjacent to the ester, consistent with its relatively downfield singlet at $\delta 7.59$ ppm.

Thus **E** is **methyl 5-acetoxy-3-bromo-4-methoxy-2-methylbenzoate**.

Its spectrum accounts for one aromatic hydrogen and four methyl groups, matching $\text{C}_{12}\text{H}_{13}\text{BrO}_5$.

E → F: benzylic bromination

N-Bromosuccinimide under irradiation brominates the benzylic methyl group:



Here NBS is N-bromosuccinimide, $\text{O}=\text{C}1\text{CCC}(=\text{O})\text{N}1\text{Br}$; succinimide is $\text{O}=\text{C}1\text{CCC}(=\text{O})\text{N}1$.

The aryl bromine remains in place. Conversion of CH_3 to CH_2Br explains:

- disappearance of the benzylic three-proton signal;
- appearance of a two-proton singlet at $\delta 5.19$ ppm;
- the formula $\text{C}_{12}\text{H}_{12}\text{Br}_2\text{O}_5$.

Therefore **F** is **methyl 5-acetoxy-3-bromo-2-(bromomethyl)-4-methoxybenzoate**.

F → G: substitution, lactam formation, and deprotection

Methylamine first displaces the benzylic bromide, producing a tethered secondary amine. That amine attacks the adjacent methyl ester intramolecularly, eliminating methanol and forming a five-membered lactam.

Excess methylamine also removes the phenolic acetate by aminolysis; aqueous workup furnishes the phenol.

A balanced net equation for this pathway is



The organic by-products are methanol, CO, and N-methylacetamide, $\text{CNC}(\text{C})=\text{O}$; the salt is methylammonium bromide, $\text{C}[\text{NH}_3^+] \cdot [\text{Br}^-]$.

The product is **4-bromo-6-hydroxy-5-methoxy-2-methylisoindolin-1-one, G**.

To draw it, fuse a five-membered lactam to the benzene ring. Its nonaromatic sequence is



The aryl carbon adjacent to the methylene-bearing fusion carbon carries bromine; the next two aromatic carbons carry methoxy and hydroxyl groups, respectively.

Every reported NMR feature is accounted for:

Observation	Assignment in G
$\delta 7.40$, singlet, 1 H	Sole aromatic hydrogen
$\delta 4.22$, singlet, 2 H	Lactam-ring methylene
$\delta 3.98$, singlet, 3 H	Methoxy
$\delta 3.19$, singlet, 3 H	N-methyl
One exchangeable proton	Phenolic OH

The total is ten hydrogens, consistent with $\text{C}_{10}\text{H}_{10}\text{BrNO}_3$.

The final reaction provides a further connectivity check: Suzuki coupling replaces the aryl bromine with the ortho-formylphenyl group. Subsequent intramolecular condensation involving the lactam methylene closes the additional ring, giving **sauristolactam**, COc1c(O)cc2c3c(cc4cccc4c13)N(C)C2=O.

10.2. Products of the visible Part B reactions

The aromatic starting material is **6-(bromomethyl)-4-methoxy-1,3-benzodioxole**, COc1cc(CBr)cc2OCOc12.

For the following discussion, Ar denotes **7-methoxy-1,3-benzodioxol-5-yl**, represented as an attachment-point fragment by *c1cc(OC)c2OCOc2c1.

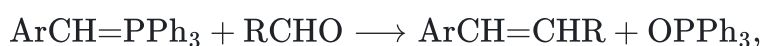
First visible operation: Wittig olefination

Triphenylphosphine converts the benzyl bromide into a phosphonium salt. Deprotonation with *n*-butyllithium gives the corresponding benzyl Wittig ylide.

Its charged-resonance representation is COc1cc([CH-][P+](c2ccccc2)(c2ccccc2)c2ccccc2)cc2OCOc12.

The aldehyde partner is **3,4-dihydro-2H-pyran-2-carbaldehyde**, O=CC1CCC=CO1.

The balanced olefination is



where *R* is the 3,4-dihydro-2H-pyran-2-yl group. The by-product is triphenylphosphine oxide, O=P(c1ccccc1)(c1ccccc1)c1ccccc1.

The aldehyde carbon becomes one carbon of the new alkene; the original benzylic carbon becomes the other. The existing enol-ether double bond remains unchanged.

The resulting structure, provisionally assigned as **A**, is therefore

COc1cc(C=CC2CCC=CO2)cc2OCOc12.

Second visible operation: hydration followed by lactone formation

Aqueous acid hydrates the cyclic enol ether, giving a cyclic hemiacetal, or lactol:

6-[2-(7-methoxy-1,3-benzodioxol-5-yl)ethenyl]oxan-2-ol,

COc1cc(C=CC2CCCC(O)O2)cc2OCOc12.

The formula change is



PCC oxidizes the hemiacetal carbon to an ester carbonyl, producing the six-membered lactone. The oxidation half-equation is

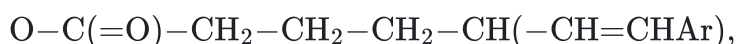


Thus the product, provisionally assigned as **B**, is

6-[2-(7-methoxy-1,3-benzodioxol-5-yl)ethenyl]oxan-2-one,

COc1cc(C=CC2CCCC(=O)O2)cc2OCOc12.

For the drawing, use a six-membered ring with the sequence



closed back to the ring oxygen. The aryl-alkene unit remains intact.

10.3. What the visible X1 establishes

The structure of X1 shown in the statement is **(±)-cis-2-(7-methoxy-1,3-benzodioxol-5-yl)cyclohex-3-ene-1-carboxylic acid**.

Its two enantiomers can be represented by:

- O=C(O)[C@H]1[C@@H](C2CC(OC)C3OCOC3C2)C=CCC1
- O=C(O)[C@@H]1[C@H](C2CC(OC)C3OCOC3C2)C=CCC1

Both the aryl and carboxyl bonds are drawn as solid wedges, establishing their **cis** relationship. The (±) label specifies the racemate.

However, question 10.3 refers to a separate drawing containing:

1. a specified single enantiomer of **X1**;
2. a deuterium atom at a specified position and configuration;
3. the transformations defining **E**, **F**, and **Y**.

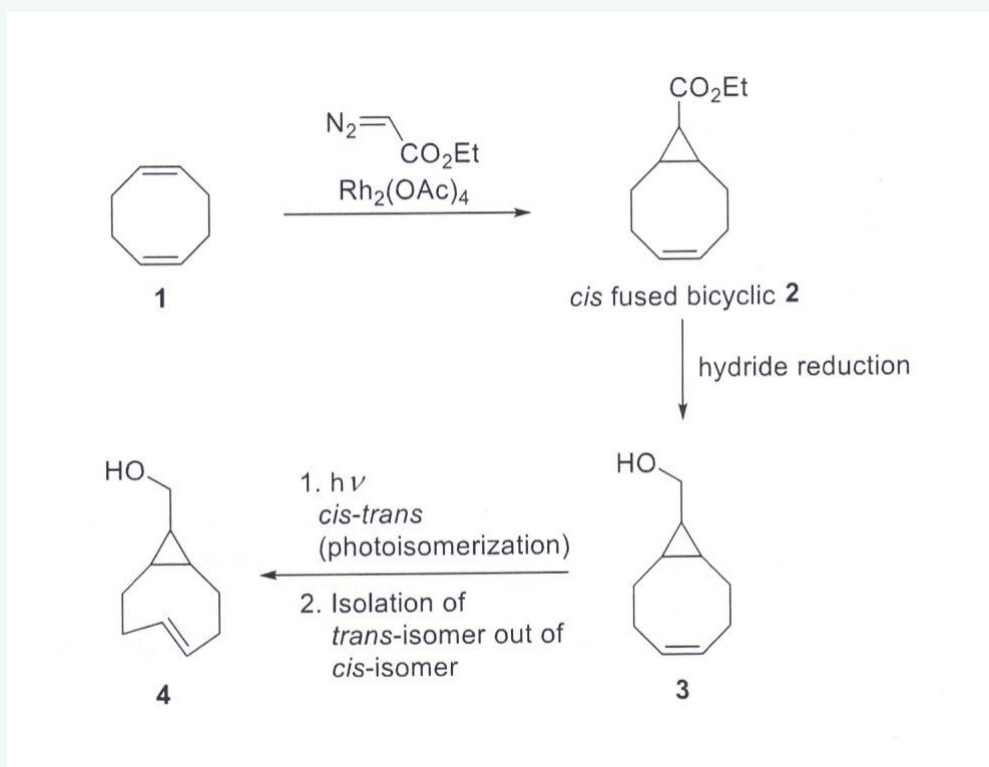
None of those details appears in the supplied fragments. Consequently, a unique chair conformation for **E**, stereochemical structure for **F**, or assignment of **Y** as ^1H or ^2H does not follow from the available information.

The answers were checked against the official answers published by the organisers. Where this solution differs from the official solution, the official solution contains an error or a misprint.

Problem 11: Twist & Chirality

trans-Cyclooctene has a chiral plane and a high barrier for racemization. The double bond of *trans*-cyclooctene is twisted, as a result, the molecule displays unusual reactivity in cycloaddition reactions.

In 2011, Fox and coworkers developed a photochemical synthesis towards a variety of *trans*-cyclooctene derivatives. The process is non-stereocontrolled and the synthetic scheme is as follow.



11.1 Draw all possible stereoisomers of compound **3** that could be obtained from the reduction of compound **2**. Not necessary to assign *R*, *S* configuration.

11.2 i) If one of the stereoisomers of compound **3** is converted to compound **4**, how many stereoisomeric form(s) of compound **4** will be obtained?

ii) The number of possible stereoisomeric form(s) of compound **4** =

iii) If there are more than one stereoisomer, is it possible to separate the obtained stereoisomers of compound **4** by achiral chromatography? Tick the relevant circle.

☐ Yes ☐ No

Official English text of the problem.

Answers

- 11.1:** Two *cis*-fused stereoisomers of [(4*Z*)-bicyclo[6.1.0]non-4-en-9-yl]methanol:
- Syn**, with CH₂OH on the same face as both bridgehead hydrogens:
OC[C@@H]1[C@H]2CC/C=C\CC[C@@H]12.

- **Anti**, with CH₂OH on the opposite face: OC[C@H]1[C@H]2CC/C=C\CC[C@@H]12.
- **11.2(i): Two**, forming an enantiomeric pair.
- **11.2(ii): 2** under the single-starting-stereoisomer condition in (i). Counting products from **both** stereoisomers of **3** gives **four** forms overall.
- **11.2(iii): No**. Tick the **No** circle.

Solution

11.1

Number the bicyclic framework so that the cyclopropane bridgeheads are C1 and C8, and its substituent-bearing carbon is C9. The cis fusion requires the two bridgehead hydrogens to lie on the **same face** of the cyclopropane.

Compound **2** is ethyl (4Z)-bicyclo[6.1.0]non-4-ene-9-carboxylate. For example, its cis-fused syn stereoisomer is CCOC(=O)[C@@H]1[C@H]2CC/C=C\CC[C@@H]12. Hydride reduction converts the ester substituent into CH₂OH, preserving the cyclopropane's relative configurations. The newly formed methylene carbon bears two hydrogens, so this reduction creates no new stereogenic centre.

There are two possibilities for the hydroxymethyl substituent relative to the bridgehead hydrogens:

Stereoisomer of 3	Precise drawing instructions
3-syn	Draw both bridgehead H bonds as solid wedges. Draw the C9–CH ₂ OH bond as a solid wedge and the C9–H bond as a hashed wedge.
3-anti	Keep both bridgehead H bonds as solid wedges. Draw the C9–CH ₂ OH bond as a hashed wedge and the C9–H bond as a solid wedge.

In both drawings, retain the **cis**, or *Z*, double bond.

The two configurations are **diastereomeric**, but each is achiral: the symmetry relating the two halves of the ring makes its mirror image equivalent to itself. Reversing every wedge and dash therefore does not produce additional stereoisomers. Ordinary interconverting ring conformations are not counted separately.

Thus,

$$N(\mathbf{3}) = 2.$$

11.2(i)

Photoisomerization changes the double bond from *Z* to *E*, while retaining the cyclopropane's relative configuration. The trans double bond forces the eight-membered ring into a twisted arrangement with **planar chirality**.

For either individual stereoisomer of **3**, two opposite, mirror-related twists are possible. Because the starting stereoisomer is achiral, these products form an **enantiomeric pair**, produced as a racemate under achiral conditions.

Compound **4** is the corresponding cis-fused **[(4E)-bicyclo[6.1.0]non-4-en-9-yl]methanol**:

Starting stereoisomer	Product family and SMILES	Planar configurations
3-syn	Syn-4, <chem>OC[C@H]1[C@H]2CC/C=C/CC[C@H]12</chem>	Two opposite planar configurations, R_p and S_p
3-anti	Anti-4, <chem>OC[C@H]1[C@H]2CC/C=C/CC[C@@H]12</chem>	Two opposite planar configurations, R_p and S_p

These SMILES specify the cyclopropane stereochemistry and the E double bond. **Ordinary isomeric SMILES does not distinguish the two planar enantiomers:** each row additionally requires two drawings with opposite ring twists.

Consequently, from **one** stereoisomer of **3**,

$$N(\mathbf{4} \text{ obtained}) = 2.$$

11.2(ii)

Reading the box as the answer field for the experiment specified in (i), enter

$$2.$$

If instead all forms obtainable from **both** stereoisomers of **3** are counted, there are two enantiomeric pairs:

$$N(\mathbf{4} \text{ overall}) = 2 \text{ precursor configurations} \times 2 \text{ planar configurations} = 4.$$

11.2(iii)

The two products obtained from a single stereoisomer of **3** are enantiomers. They have identical interactions with an achiral stationary phase and an achiral mobile phase, so achiral chromatography cannot resolve them.

Therefore, tick **No**.

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