

IChO 1980

Theory problems and solutions · Linz, Austria · 6 theory problems with complete solutions

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Problem 1: Photodissociation of chlorine and the quantum yield of the H₂-Cl₂ reaction

The dissociation of (molecular) chlorine is an endothermic process, $\Delta H = 243.6 \text{ kJ mol}^{-1}$.

The dissociation can also be attained by the effect of light.

1.1 At what wavelength can the dissociating effect of light be expected?

1.2 Can this effect also be obtained with light whose wavelength is smaller or larger than the calculated critical wavelength?

1.3 What is the energy of the photon with the critical wavelength?

When light that can effect the chlorine dissociation is incident on a mixture of gaseous chlorine and hydrogen, hydrogen chloride is formed. The mixture is irradiated with a mercury UV-lamp ($\lambda = 253.6 \text{ nm}$). The lamp has a power input of 10 W. An amount of 2 % of the energy supplied is absorbed by the gas mixture (in a 10 litre vessel). Within 2.5 seconds of irradiation 65 millimoles of HCl are formed.

1.4 How large is the quantum yield (= the number of product molecules per absorbed photons)?

1.5 How can the value obtained be (qualitatively) explained? Describe the reaction mechanism.

Official English text of the problem.

Answers

- 1.1** The critical wavelength is $\lambda_{\text{crit}} = 491.1 \text{ nm}$, the maximum wavelength permitted by the dissociation-energy requirement.
- 1.2** Shorter wavelengths can cause dissociation if absorbed. Longer wavelengths cannot supply sufficient energy for single-photon dissociation.
- 1.3** $E_{\text{crit}} = 4.045 \times 10^{-19} \text{ J}$ per photon.
- 1.4** $\Phi \approx 6.1 \times 10^4$ hydrogen chloride (HCl) molecules per absorbed photon.
- 1.5** The reaction proceeds by a radical chain mechanism. Photodissociation initiates chains whose propagation repeatedly produces hydrogen chloride and regenerates the radical carriers. Radical recombination terminates the chains.

Solution

Use the standard constants

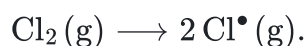
$$h = 6.62607015 \times 10^{-34} \text{ J s}, \quad c = 2.99792458 \times 10^8 \text{ m s}^{-1}, \\ N_A = 6.02214076 \times 10^{23} \text{ mol}^{-1}.$$

The chemical species used below are:

Name	Formula	SMILES
Molecular chlorine	Cl ₂	ClCl
Molecular hydrogen	H ₂	[H][H]
Hydrogen chloride	HCl	[H]Cl
Chlorine atom (chlorine radical)	Cl•	[Cl]
Hydrogen atom (hydrogen radical)	H•	[H]

1.1 — Critical wavelength

The dissociation is



Taking the given molar dissociation enthalpy as the required dissociation energy, one absorbed photon must supply at least

$$E_{\text{diss}} = \frac{\Delta H}{N_A}.$$

Since a photon has energy $E = hc/\lambda$, the threshold satisfies

$$\frac{hc}{\lambda_{\text{crit}}} = \frac{\Delta H}{N_A}.$$

Therefore,

$$\lambda_{\text{crit}} = \frac{N_A hc}{\Delta H} = \frac{N_A hc}{243.6 \times 10^3 \text{ J mol}^{-1}} = 4.91078 \times 10^{-7} \text{ m}.$$

Thus,

$$\boxed{\lambda_{\text{crit}} = 491.1 \text{ nm}}.$$

1.2 — Shorter and longer wavelengths

Photon energy is inversely proportional to wavelength:

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

Consequently:

- For $\lambda < \lambda_{\text{crit}}$, a photon has more than the minimum dissociation energy. Dissociation is energetically possible, provided the photon is absorbed in a suitable transition.
- For $\lambda > \lambda_{\text{crit}}$, a photon has insufficient energy. It cannot dissociate the molecule in the single-photon process considered here.

1.3 — Energy of a critical-wavelength photon

$$E_{\text{crit}} = \frac{\Delta H}{N_A} = \frac{243.6 \times 10^3 \text{ J mol}^{-1}}{6.02214076 \times 10^{23} \text{ mol}^{-1}}.$$

Hence,

$$E_{\text{crit}} = 4.045 \times 10^{-19} \text{ J}.$$

1.4 — Quantum yield

The energy absorbed during irradiation is

$$Q_{\text{abs}} = 0.02Pt = 0.02(10 \text{ J s}^{-1})(2.5 \text{ s}) = 0.50 \text{ J}.$$

At the lamp wavelength, the energy per photon is

$$E_{\text{UV}} = \frac{hc}{253.6 \times 10^{-9} \text{ m}} = 7.833 \times 10^{-19} \text{ J}.$$

The number of absorbed photons is therefore

$$N_{\text{abs}} = \frac{Q_{\text{abs}}}{E_{\text{UV}}} = \frac{0.50}{7.833 \times 10^{-19}} = 6.383 \times 10^{17}.$$

The number of hydrogen chloride molecules formed is

$$N_{\text{HCl}} = n_{\text{HCl}}N_A = (65 \times 10^{-3} \text{ mol})N_A = 3.914 \times 10^{22}.$$

Using the definition in the question,

$$\Phi = \frac{N_{\text{HCl}}}{N_{\text{abs}}} = \frac{3.914 \times 10^{22}}{6.383 \times 10^{17}} = 6.132 \times 10^4.$$

Thus,

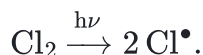
$$\Phi \approx 6.1 \times 10^4 \text{ hydrogen chloride molecules per absorbed photon}.$$

The vessel volume is unnecessary because the calculation uses total absorbed energy and total product amount.

1.5 — Explanation and reaction mechanism

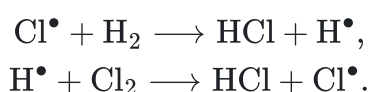
The very large quantum yield shows that one absorbed photon leads to many product-forming reactions through a radical chain.

Initiation:



Light causes homolytic cleavage of the chlorine–chlorine bond: one bonding electron goes to each chlorine atom.

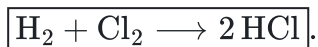
Propagation:



First, a chlorine radical abstracts a hydrogen atom from molecular hydrogen. The resulting hydrogen radical then abstracts a chlorine atom from molecular chlorine.

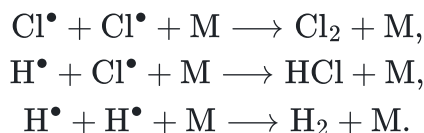
In each abstraction, the incoming radical's unpaired electron and one electron from the broken bond form the new bond; the other bond electron remains on the atom released as a radical. These electron movements are not depicted by the SMILES.

Adding the two propagation steps gives



The chlorine radical is regenerated, so this cycle can repeat many times without another photon.

Termination: radicals are removed by recombination, for example,



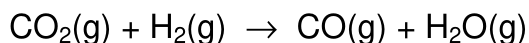
Here M denotes a third collision partner that carries away excess energy. Radicals may also be lost at the vessel walls.

Because propagation occurs many times before termination, approximately 6.1×10^4 hydrogen chloride molecules can be formed per absorbed photon. The photon initiates the chain; the overall exothermic chemical reaction supplies the energy released during its continuation.

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 2: Water gas equilibrium

The homogeneous gas reaction



is termed the water gas reaction.

Problems:

2.1 Calculate the Gibbs reaction energy, ΔG_{1000}^0 , for the water gas reaction at 1000 K from the reaction enthalpy:

$$\Delta H_{1000}^0 = 35040 \text{ J mol}^{-1}$$

and the reaction entropy:

$$\Delta S_{1000}^0 = 32.11 \text{ J mol}^{-1} \text{ K}^{-1}.$$

2.2 What is the value of the equilibrium constant K_p of the water gas reaction at 1000 K?

2.3 What are the values of the equilibrium constants K_x and K_c (x : mole fraction, c : concentration in mol dm^{-3} at the same temperature (1000 K)? (Note: The gas behaves ideally.)

2.4 A mixture of gases containing 35 vol. % of H_2 , 45 vol. % of CO and 20 vol. % of H_2O vapours is heated to 1000 K. What is the composition of the mixture after the establishment of the water gas equilibrium?

2.5 Calculate the reaction enthalpy value, ΔH_{1400}^0 , at 1400 K from the reaction enthalpy value, ΔH_{1000}^0 , and the values of the molar heat, c_p^0 , (valid in the temperature range 1000 K to 1400 K)

$$\Delta H_{1000}^0 = 35040 \text{ J mol}^{-1}$$

$$c_p^0(\text{CO}_2) = 42.31 + 10.09 \times 10^{-3} T \text{ J mol}^{-1} \text{ K}^{-1}$$

$$c_p^0(\text{H}_2) = 27.40 + 3.20 \times 10^{-3} T \text{ J mol}^{-1} \text{ K}^{-1}$$

$$c_p^0(\text{CO}) = 28.34 + 4.14 \times 10^{-3} T \text{ J mol}^{-1} \text{ K}^{-1}$$

$$c_p^0(\text{H}_2\text{O}) = 30.09 + 10.67 \times 10^{-3} T \text{ J mol}^{-1} \text{ K}^{-1}$$

(It holds that $\int_a^b (c_1 + c_2 x) dx = c_1(b - a) + 0.5c_2(b^2 - a^2)$)

2.6 What can you say on the basis of the above findings on ΔH^0 about the shift in the water gas equilibrium with increasing temperature?

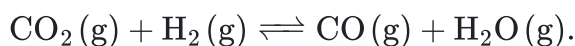
Official English text of the problem.

Answers

- **2.1:** $\Delta G_{1000}^0 = +2.93 \text{ kJ mol}^{-1}$.
- **2.2:** $K_p = 0.703$ at 1000 K.
- **2.3:** $K_x = K_c = K_p = 0.703$, all dimensionless.
- **2.4:** The equilibrium composition by volume is approximately **45.4% hydrogen** ($[\text{H}] [\text{H}]$), **34.6% carbon monoxide** ($[\text{C-}] \# [\text{O+}]$), **9.6% water vapour** (O), and **10.4% carbon dioxide** ($\text{O}=\text{C}=\text{O}$).
- **2.5:** $\Delta H_{1400}^0 = +31.26 \text{ kJ mol}^{-1}$.
- **2.6:** Increasing temperature shifts the equilibrium towards the products of the stated reaction, CO and H₂O; the equilibrium constant increases.

Solution

The balanced reaction, with all species gaseous, is



Reaction quantities below refer to one mole of reaction as written.

2.1 — Gibbs reaction energy

Using

$$\Delta G_T^0 = \Delta H_T^0 - T\Delta S_T^0,$$

we obtain

$$\begin{aligned} \Delta G_{1000}^0 &= 35040 \text{ J mol}^{-1} - (1000 \text{ K})(32.11 \text{ J mol}^{-1} \text{ K}^{-1}) \\ &= 2930 \text{ J mol}^{-1}. \end{aligned}$$

Thus

$$\Delta G_{1000}^0 = +2.93 \text{ kJ mol}^{-1}.$$

2.2 — Pressure equilibrium constant

For ideal gases, the dimensionless equilibrium constant is

$$K_p = \frac{(p_{\text{CO}}/p^0)(p_{\text{H}_2\text{O}}/p^0)}{(p_{\text{CO}_2}/p^0)(p_{\text{H}_2}/p^0)} = \frac{p_{\text{CO}}p_{\text{H}_2\text{O}}}{p_{\text{CO}_2}p_{\text{H}_2}}.$$

The standard Gibbs reaction energy satisfies

$$\Delta G^0 = -RT \ln K_p.$$

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

$$\ln K_p = -\frac{2930}{8.314 \times 1000} = -0.35242,$$

and hence

$$K_p = e^{-0.35242} = 0.70299 \approx 0.703.$$

2.3 — Mole-fraction and concentration equilibrium constants

The change in the total stoichiometric amount of gas is

$$\Delta \nu_{\text{gas}} = (1 + 1) - (1 + 1) = 0.$$

Since $p_i = x_i P$,

$$K_p = \frac{(x_{\text{CO}}P)(x_{\text{H}_2\text{O}}P)}{(x_{\text{CO}_2}P)(x_{\text{H}_2}P)} = \frac{x_{\text{CO}}x_{\text{H}_2\text{O}}}{x_{\text{CO}_2}x_{\text{H}_2}} = K_x.$$

Similarly, the ideal-gas relation $p_i = c_i RT$, with consistent units, gives

$$K_p = \frac{(c_{\text{CO}}RT)(c_{\text{H}_2\text{O}}RT)}{(c_{\text{CO}_2}RT)(c_{\text{H}_2}RT)} = \frac{c_{\text{CO}}c_{\text{H}_2\text{O}}}{c_{\text{CO}_2}c_{\text{H}_2}} = K_c.$$

All pressure and concentration units cancel because $\Delta \nu_{\text{gas}} = 0$. Therefore

$$K_x = K_c = K_p = 0.703.$$

2.4 — Equilibrium composition

For ideal gases, volume fractions equal mole fractions. Initially there is no carbon dioxide, so the reaction proceeds in the reverse direction:



The total amount of gas remains constant. Let z be the equilibrium mole fraction of carbon dioxide. Stoichiometry then gives:

Gas	Initial mole fraction	Equilibrium mole fraction
CO ₂	0	z
H ₂	0.35	$0.35 + z$
CO	0.45	$0.45 - z$
H ₂ O	0.20	$0.20 - z$

The physically permitted interval is $0 < z < 0.20$. Substituting into the equilibrium expression for the reaction as originally written,

$$K_x = \frac{(0.45 - z)(0.20 - z)}{z(0.35 + z)} = 0.7029865.$$

Expansion gives

$$(1 - K_x)z^2 - (0.65 + 0.35K_x)z + 0.0900 = 0,$$

or

$$0.2970135z^2 - 0.8960453z + 0.0900 = 0.$$

The roots are approximately 0.1040285 and 2.91282. Only the first satisfies the physical bounds:

$$z = 0.1040285.$$

Thus the equilibrium composition is:

Gas	Equilibrium volume percentage
Hydrogen, H ₂	45.4%
Carbon monoxide, CO	34.6%
Water vapour, H ₂ O	9.6%
Carbon dioxide, CO ₂	10.4%

These percentages sum to 100.0%. Using the unrounded mole fractions also reproduces $K_x = 0.7029865$.

2.5 — Reaction enthalpy at 1400 K

Kirchhoff's law gives

$$\Delta H_{1400}^0 = \Delta H_{1000}^0 + \int_{1000 \text{ K}}^{1400 \text{ K}} \Delta c_p^0(T) dT,$$

where

$$\Delta c_p^0 = c_p^0(\text{CO}) + c_p^0(\text{H}_2\text{O}) - c_p^0(\text{CO}_2) - c_p^0(\text{H}_2).$$

The constant coefficient is

$$28.34 + 30.09 - 42.31 - 27.40 = -11.28,$$

and the coefficient of T is

$$(4.14 + 10.67 - 10.09 - 3.20) \times 10^{-3} = 1.52 \times 10^{-3}.$$

Therefore

$$\Delta c_p^0(T) = -11.28 \text{ J mol}^{-1} \text{ K}^{-1} + (1.52 \times 10^{-3} \text{ J mol}^{-1} \text{ K}^{-2})T.$$

With temperatures inserted numerically in kelvin,

$$\begin{aligned} \Delta H_{1400}^0 - \Delta H_{1000}^0 &= \left[-11.28(1400 - 1000) + \frac{1.52 \times 10^{-3}}{2}(1400^2 - 1000^2) \right] \text{ J mol}^{-1} \\ &= (-4512 + 729.6) \text{ J mol}^{-1} \\ &= -3782.4 \text{ J mol}^{-1}. \end{aligned}$$

Consequently,

$$\Delta H_{1400}^0 = 35040 - 3782.4 = 31257.6 \text{ J mol}^{-1},$$

so

$$\Delta H_{1400}^0 = +31.26 \text{ kJ mol}^{-1}.$$

2.6 — Effect of increasing temperature

The forward reaction is endothermic at both temperatures:

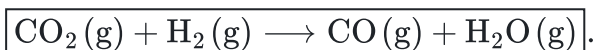
$$\Delta H_{1000}^0 = +35.040 \text{ kJ mol}^{-1}, \quad \Delta H_{1400}^0 = +31.26 \text{ kJ mol}^{-1}.$$

Moreover, $\Delta_c^0 < 0$ throughout 1000–1400 K, so the reaction enthalpy decreases continuously between these positive values and remains positive throughout that interval.

The van 't Hoff equation therefore gives

$$\frac{d \ln K_p}{dT} = \frac{\Delta H^0(T)}{RT^2} > 0.$$

Increasing temperature increases K_p and favours the endothermic forward reaction:



The equilibrium shifts towards carbon monoxide and water vapour.

The solution was checked against the official solution.

Problem 3: Chemistry of ions, stoichiometry, redox reactions: identification of a white crystalline compound A

(Chemistry of ions, stoichiometry, redox reactions)

A white crystalline solid compound **A** exhibits the following reactions:

- 1) The flame of a Bunsen burner is intensively yellow coloured.
- 2) An aqueous solution of **A** is neutral. Dropwise addition of sulphurous acid (an SO_2 solution) leads to a deep brown solution that is discoloured in the presence of excess of sulphurous acid.
- 3) If an AgNO_3 solution is added to the discoloured solution obtained by 2) and acidified with HNO_3 , a yellow precipitate is obtained that is insoluble on addition of NH_3 , but can be readily dissolved by adding CN^- or $\text{S}_2\text{O}_3^{2-}$.
- 4) If an aqueous solution of **A** is treated with KI and dilute H_2SO_4 a deep brown solution is formed that can be discoloured by addition of sulphurous acid or a $\text{Na}_2\text{S}_2\text{O}_3$ solution.
- 5) An amount of 0.1000 g of **A** is dissolved in water, then 0.5 g KI and a few cm^3 of dilute H_2SO_4 are added. The deep brown solution formed is titrated with 0.1000 M $\text{Na}_2\text{S}_2\text{O}_3$ solution until the solution is completely discoloured. The consumption is 37.40 cm^3 .

Problems:

3.1 What elements are contained in the compound **A**?

3.2 What compounds can be considered as present on the basis of reactions 1) to 4)? Calculate their molar masses.

3.3 Formulate the reactions corresponding to 2) to 4) for the compounds considered and write the corresponding equations in the ionic form.

3.4 Decide on the basis of 5) which compound is present.

Official English text of the problem.

Answers

- **3.1:** Sodium, iodine and oxygen.
- **3.2:** Sodium iodate, NaIO_3 , $[\text{Na}^+] \cdot [\text{O}^-] \text{I}(=\text{O})=\text{O}$, with $M = 197.9 \text{ g mol}^{-1}$; and sodium metaperiodate, NaIO_4 , $[\text{Na}^+] \cdot [\text{O}^-] \text{I}(=\text{O})(=\text{O})=\text{O}$, with $M = 213.9 \text{ g mol}^{-1}$.
- **3.3:** The brown product is iodine, I_2 , II , which is subsequently reduced to iodide, I^- , $[\text{I}^-]$. The yellow precipitate is silver iodide, AgI , $[\text{Ag}^+] \cdot [\text{I}^-]$, which dissolves through cyanide or thiosulfate complex formation. Acidified iodate and periodate produce respectively three and four iodine equivalents per formula unit. All balanced ionic equations are given below.
- **3.4: A is sodium metaperiodate, NaIO_4 .** Its eight-to-one thiosulfate stoichiometry gives an experimental molar mass of 213.9 g mol^{-1} .

Solution

3.1 — Elements present

The intense yellow flame identifies the sodium ion, Na^+ , $[\text{Na}^+]$.

The yellow silver precipitate, insoluble in ammonia but soluble in cyanide and thiosulfate, identifies **silver iodide**. Consequently, the colourless solution obtained after reduction contains iodide, and **A contains iodine**.

Sulphurous acid reduces the iodine-containing anion of **A** to brown iodine and subsequently to iodide. Conversely, **A** oxidizes added iodide to iodine. These observations identify an oxidizing iodine oxyanion, containing oxygen.

Thus the elements are **sodium, iodine and oxygen**.

3.2 — Possible compounds and their molar masses

The usual stable sodium iodine oxysalts consistent with these observations are:

Compound	Anion	Oxidation state of iodine
Sodium iodate, NaIO_3	Iodate, IO_3^-	+5
Sodium metaperiodate, NaIO_4	Metaperiodate, IO_4^-	+7

An iodide salt would not explain either the formation of iodine upon adding a reducing agent or the oxidation of added iodide.

No atomic masses are printed in the problem. Using the standard values

$$A_r(\text{Na}) = 22.99, \quad A_r(\text{I}) = 126.90, \quad A_r(\text{O}) = 16.00,$$

gives

$$M(\text{NaIO}_3) = 22.99 + 126.90 + 3(16.00) = 197.89 \text{ g mol}^{-1},$$

$$M(\text{NaIO}_4) = 22.99 + 126.90 + 4(16.00) = 213.89 \text{ g mol}^{-1}.$$

The salt SMILES in the answers describe their constituent ions, not their crystal lattices. Iodate is trigonal pyramidal; metaperiodate is tetrahedral. These geometries are not encoded by the SMILES.

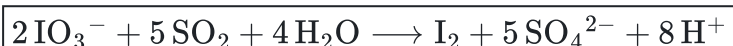
3.3 — Balanced ionic equations

Sulphurous acid is written below as aqueous SO_2 , as specified in the problem. Names and SMILES for the additional species are collected after the equations.

Reaction 2): reduction with sulphurous acid

With a limited quantity of sulphurous acid, iodine is formed. Sulfur is oxidized from +4 to +6.

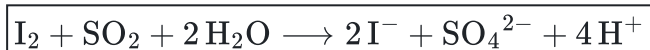
For iodate:



For periodate:



Excess sulphurous acid reduces the iodine to colourless iodide:

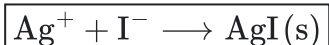


Thus the overall reactions with excess sulphurous acid are



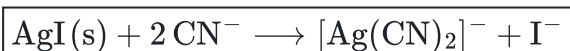
Reaction 3): precipitation and complex formation

Both candidates give iodide after complete reduction, so both give the same silver iodide precipitate:

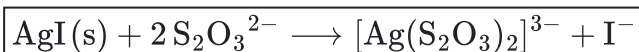


Ammonia does not produce appreciable dissolution under the stated test conditions.

Cyanide dissolves the precipitate by forming dicyanidoargentate(I):



Thiosulfate dissolves it by forming bis(thiosulfato)argentate(I):



Reaction 4): oxidation of iodide in acidic solution

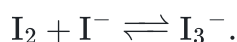
For iodate:



For periodate:

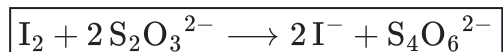


Where iodide is present, iodine also forms brown triiodide:



Decolourization by sulphurous acid follows the iodine-reduction equation already given under reaction 2).

With thiosulfate, iodine is reduced to iodide while thiosulfate is oxidized to tetrathionate:



Equivalently, for triiodide:



The additional molecular and ionic species used above have the following names and SMILES:

Species	Name	SMILES
IO_3^-	Iodate	<chem>[O-]I(=O)=O</chem>
IO_4^-	Metaperiodate	<chem>[O-]I(=O)(=O)=O</chem>
SO_2	Sulfur dioxide	<chem>O=S=O</chem>
H_2O	Water	<chem>O</chem>
H^+	Hydrogen ion, the aqueous proton shorthand	<chem>[H+]</chem>
SO_4^{2-}	Sulfate	<chem>[O-]S(=O)(=O)[O-]</chem>
Ag^+	Silver(I) ion	<chem>[Ag+]</chem>
NH_3	Ammonia	<chem>N</chem>
CN^-	Cyanide	<chem>[C-]#N</chem>
$\text{S}_2\text{O}_3^{2-}$	Thiosulfate	<chem>[O-]S(=O)(=O)[S-]</chem>
I_3^-	Triiodide	<chem>I[I-]I</chem>
$\text{S}_4\text{O}_6^{2-}$	Tetrathionate	<chem>[O-]S(=O)(=O)SSS(=O)(=O)[O-]</chem>
$[\text{Ag}(\text{CN})_2]^-$	Dicyanidoargentate(I)	<chem>[C-](#N)->[Ag+]<-[C-]#N</chem>
$[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$	Bis(thiosulfato)argentate(I)	<chem>[O-]S(=O)(=O)[S-]->[Ag+]<-[S-]S(=O)(=O)[O-]</chem>

The complex SMILES use dative-bond notation: cyanide coordinates through carbon, and thiosulfate through its terminal sulfur. Their simple two-coordinate representations have approximately linear donor–silver–donor arrangements. Triiodide is also linear; its delocalized bonding is not fully represented by the SMILES.

3.4 — Identification from the titration

The amount of thiosulfate consumed is

$$\begin{aligned} n(\text{S}_2\text{O}_3^{2-}) &= cV \\ &= (0.1000 \text{ mol L}^{-1})(37.40 \times 10^{-3} \text{ L}) \\ &= 3.740 \times 10^{-3} \text{ mol.} \end{aligned}$$

Since one mole of iodine consumes two moles of thiosulfate, the total iodine equivalent titrated is

$$n(\text{I}_2) = \frac{3.740 \times 10^{-3}}{2} = 1.870 \times 10^{-3} \text{ mol.}$$

The equations in 3.3 give the following relationships:

Candidate	Iodine equivalents per mole	Thiosulfate consumed per mole
NaIO_3	3	6

Candidate	Iodine equivalents per mole	Thiosulfate consumed per mole
NaIO ₄	4	8

For a 0.1000 g sample, the predicted titre is

$$V = \frac{r m}{Mc},$$

where r is the thiosulfate-to-compound mole ratio.

Thus

$$V_{\text{NaIO}_3} = \frac{6(0.1000)}{197.89(0.1000)} = 0.03032 \text{ L} = 30.32 \text{ cm}^3,$$

whereas

$$V_{\text{NaIO}_4} = \frac{8(0.1000)}{213.89(0.1000)} = 0.03740 \text{ L} = 37.40 \text{ cm}^3.$$

Only periodate matches the measured titre. Equivalently,

$$n(A) = \frac{3.740 \times 10^{-3}}{8} = 4.675 \times 10^{-4} \text{ mol},$$

and

$$M(A) = \frac{0.1000 \text{ g}}{4.675 \times 10^{-4} \text{ mol}} = 213.9 \text{ g mol}^{-1}.$$

Iodide is regenerated during titration. Combining iodine liberation and its reduction by thiosulfate gives



Consequently, the eight-to-one ratio remains valid when iodine continues to form during titration.

$$A = \text{NaIO}_4 \quad (\text{sodium metaperiodate})$$

The solution was checked against the official solution.

Problem 4: Organic chemistry, stereochemistry: an acid C₅H₈O₂, its hydrogenation and bromination

(Organic chemistry, stereochemistry)

Carboxylic acid **A** with an overall formula of C₅H₈O₂ yields two geometric isomers, cis (**A'**) and trans (**A''**). On hydrogenation with Pt/H₂ the same racemic carboxylic acid **B** is obtained from both stereoisomers that can be separated into enantiomers (+)-**B** and (-)-**B**.

A' and **A''** rapidly react with one mole of bromine in CCl₄ in the dark at 20 °C to yield **C**.

Problems:

4.1 What is the constitution of **A** and **B**?

4.2 Write the stereo formulae for **A'** and **A''** and the Fischer projection formulae for the enantiomer **B** (not considering the signs (+) or (-)).

4.3 How many stereo isomers of **C** are simultaneously formed when **A'** and **A''** are treated with bromine?

4.4 Briefly, give reasons for your answer to c).

4.5 Write the Fischer projection formulae and one Newman projection formula (conformation) for all the stereoisomers of **C**. Denote those that are mutually enantiomeric and diastereoisomeric.

Official English text of the problem.

Answers

For the A'/A'' labels below, **cis/trans** refers to the two methyl groups.

- **4.1:** **A** is **2-methylbut-2-enoic acid**, $\text{CC}=\text{C}(\text{C})\text{C}(=\text{O})\text{O}$. **B** is **2-methylbutanoic acid**, $\text{CCC}(\text{C})\text{C}(=\text{O})\text{O}$.
- **4.2:** A' is **(E)-2-methylbut-2-enoic acid**, $\text{O}=\text{C}(\text{O})/\text{C}(\text{C})=\text{C}/\text{C}$; A'' is **(Z)-2-methylbut-2-enoic acid**, $\text{O}=\text{C}(\text{O})/\text{C}(\text{C})=\text{C}\backslash\text{C}$. The enantiomers of **B** are **(R)-2-methylbutanoic acid**, $\text{O}=\text{C}(\text{O})[\text{C@H}](\text{C})\text{CC}$, and **(S)-2-methylbutanoic acid**, $\text{O}=\text{C}(\text{O})[\text{C@@H}](\text{C})\text{CC}$. Their projections are specified below.
- **4.3:** **Two enantiomers from each pure alkene; four stereoisomers altogether.** The *E* alkene gives $(2R, 3S)/(2S, 3R)$, and the *Z* alkene gives $(2R, 3R)/(2S, 3S)$.
- **4.4:** Bromination is stereospecific **anti addition**. The product has two stereogenic centers and no meso form; each alkene gives a racemic pair.
- **4.5:** The four products are stereoisomers of **2,3-dibromo-2-methylbutanoic acid**, $\text{O}=\text{C}(\text{O})\text{C}(\text{Br})(\text{C})\text{C}(\text{Br})\text{C}$. Their stereochemical SMILES, Fischer projections, and Newman conformations are tabulated below. The enantiomeric pairs are $(2R, 3S)/(2S, 3R)$ and $(2R, 3R)/(2S, 3S)$; every pairing between these two pairs is diastereomeric.

Solution

4.1 — Identification of A and B

The degree of unsaturation of **A** is

$$\text{DBE} = \frac{2(5) + 2 - 8}{2} = 2.$$

The carboxyl carbonyl accounts for one degree of unsaturation. The geometric isomerism and rapid bromine-addition reaction identify an alkene double bond as the other, in the intended alkene chemistry of this problem.

Hydrogenation gives a saturated acid of formula $\text{C}_5\text{H}_{10}\text{O}_2$. Its resolvability into enantiomers requires a stereogenic center. With only five carbon atoms, the required four different substituents are carboxyl, ethyl, methyl, and hydrogen. Thus **B** is **2-methylbutanoic acid**, $\text{CCC}(\text{C})\text{C}(=\text{O})\text{O}$:

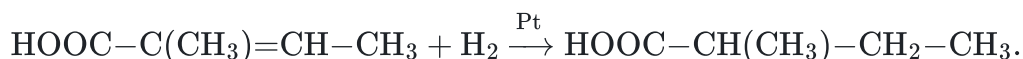


Restoring a double bond to this carbon skeleton must produce an alkene with two different substituents on each double-bond carbon. This places the double bond between C2 and C3:



Therefore **A** is **2-methylbut-2-enoic acid**, CC=C(C)C(=O)O.

Hydrogenation with molecular hydrogen, $[\text{H}][\text{H}]$, over platinum is balanced as



C3 becomes a methylene group, so the original geometric distinction disappears. C2 becomes stereogenic; hydrogenation in an achiral environment gives equal amounts of the two enantiomers of **B** from either alkene.

4.2 — Geometric structures of A and Fischer projections of B

Number the carboxyl carbon C1. To specify the alkene drawings, place **C2 on the left and C3 on the right**, joined by a horizontal double bond. Place the substituents above and below it as follows:

Form	Name and stereochemical SMILES	Above C2; above C3	Below C2; below C3
<i>A'</i> , methyl groups cis	(E)-2-methylbut-2-enoic acid , <chem>O=C(O)/C(C)=C/C</chem>	COOH; H	CH ₃ ; CH ₃
<i>A''</i> , methyl groups trans	(Z)-2-methylbut-2-enoic acid , <chem>O=C(O)/C(C)=C\C</chem>	COOH; CH ₃	CH ₃ ; H

For the *E/Z* assignments, the higher-priority substituent is COOH at C2 and CH₃ at C3.

Consequently, **cis methyl groups correspond to *E***, whereas **trans methyl groups correspond to *Z***.

For the Fischer projections of **B**, put COOH **at the top and CH₂CH₃ at the bottom**. Horizontal bonds point toward the viewer; vertical bonds point away.

Enantiomer	Left substituent	Right substituent	Stereochemical SMILES
(R)-2-methylbutanoic acid	H	CH ₃	<chem>O=C(O)[C@H](C)CC</chem>
(S)-2-methylbutanoic acid	CH ₃	H	<chem>O=C(O)[C@@H](C)CC</chem>

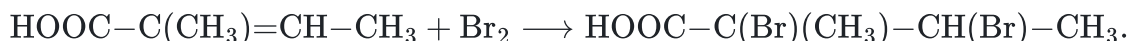
The priority order is



These projections are mirror images. Their *R/S* configurations do not determine which has positive or negative optical rotation.

4.3 — Number of bromination products

Bromine, Br₂, adds across the double bond in carbon tetrachloride, CCl₄, in the dark at 20 °C:



Thus one mole of **A** consumes one mole of bromine. The product **C** is **2,3-dibromo-2-methylbutanoic acid**, O=C(O)C(Br)(C)C(Br)C, with formula C₅H₈Br₂O₂.

Both C2 and C3 are stereogenic. The product has no internal symmetry that could produce a meso form, so its total number of stereoisomers is

$$2^2 = \boxed{4}.$$

Stereospecific anti addition gives:

Starting alkene	Products
A_E , here A'	$(2R, 3S)$ and $(2S, 3R)$, in equal amounts
A_Z , here A''	$(2R, 3R)$ and $(2S, 3S)$, in equal amounts

Therefore, **each separately brominated geometric isomer gives two stereoisomers**, while bromination of a mixture containing both gives **all four**. The relative amounts of the two racemic pairs depend on the starting mixture.

4.4 — Reasons for the stereochemical outcome

Under the stated conditions, electrophilic bromination is **anti addition**: the two new carbon–bromine bonds form on opposite faces of the original double bond.

For either planar alkene, the two mirror-related addition pathways are equally probable in the achiral reaction environment. They therefore give equal amounts of two enantiomers.

Changing the starting alkene from E to Z changes the relative configuration produced by anti addition, giving the other enantiomeric pair. No product is meso because the two stereogenic centers have different substituent sets: C2 bears a carboxyl group and a methyl group, whereas C3 bears a hydrogen and a methyl group.

4.5 — Fischer projections, Newman projections, and relationships

For every Fischer projection of **C**, draw the vertical backbone in this order:

COOH at the top, C2, C3, CH₃ at the bottom.

The table specifies every horizontal substituent. As usual, horizontal bonds point toward the viewer and vertical bonds point away.

Stereoisomer of 2,3-dibromo-2-methylbutanoic acid	C2: left / right	C3: left / right	Stereochemical SMILES
$(2R, 3S)$	Br / CH ₃	Br / H	<chem>O=C(O)[C@](Br)(C)[C@@H](Br)C</chem>
$(2S, 3R)$	CH ₃ / Br	H / Br	<chem>O=C(O)[C@@](Br)(C)[C@H](Br)C</chem>
$(2R, 3R)$	Br / CH ₃	H / Br	<chem>O=C(O)[C@](Br)(C)[C@H](Br)C</chem>
$(2S, 3S)$	CH ₃ / Br	Br / H	<chem>O=C(O)[C@@](Br)(C)[C@@H](Br)C</chem>

The configuration assignments use these priority orders:

C2 : Br > CH(Br)CH₃ > COOH > CH₃,
 C3 : Br > C(Br)(CH₃)COOH > CH₃ > H.

At C2, the neighboring brominated carbon outranks the carboxyl carbon because its attached-atom list begins with bromine, which outranks oxygen.

For the **Newman projections**, look **from C2 toward C3**, with C2 represented by the front dot and C3 by the rear circle. Use clock positions as seen by the viewer:

- Front bonds occupy **12, 4, and 8 o'clock**.

- Rear bonds occupy **2, 6, and 10 o'clock**.

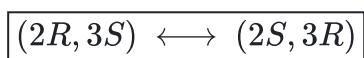
The following table specifies one staggered conformation for each stereoisomer:

Configuration	Front C2: 12 / 4 / 8 o'clock	Rear C3: 2 / 6 / 10 o'clock
(2 <i>R</i> , 3 <i>S</i>)	COOH / CH ₃ / Br	Br / CH ₃ / H
(2 <i>S</i> , 3 <i>R</i>)	COOH / Br / CH ₃	H / CH ₃ / Br
(2 <i>R</i> , 3 <i>R</i>)	COOH / CH ₃ / Br	H / CH ₃ / Br
(2 <i>S</i> , 3 <i>S</i>)	COOH / Br / CH ₃	Br / CH ₃ / H

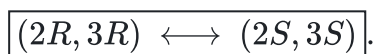
These clock positions specify conformations, which the stereochemical SMILES do not encode.

Rotation about the C2–C3 single bond changes the conformation without changing configuration; “anti addition” describes the reaction’s addition faces.

The **enantiomeric pairs** are



and



Each member of the first pair is **diastereomeric** with each member of the second pair.

The solution was checked against the official solution.

Problem 5: Inorganic chemistry: alkaline hydrolysis of a partially methylated disilane

(Inorganic chemistry)

From 20 mg of partially methylated disilane, $\text{Si}_2\text{H}_{6-x}(\text{CH}_3)_x$, 27.8 cm³ of hydrogen are evolved during alkaline hydrolysis at 294 K and 97400 Pa.

5.1 Why the Si-Si bond of the disilane reacts during hydrolysis?

5.2 Why the Si-H bonds of the disilane react during hydrolysis?

5.3 Calculate the degree of substitution x of the methylated disilane.

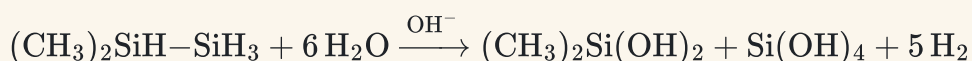
5.4 Write the complete reaction equation for the hydrolysis.

5.5 How many isomers can form the calculated compound? Give the structural formula for each isomer.

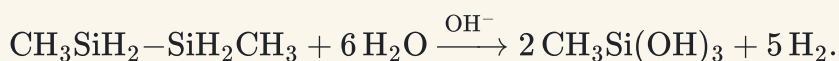
Official English text of the problem.

Answers

- **5.1:** Nucleophilic attack at silicon permits cleavage of the Si—Si bond, driven by formation of strong Si—O bonds. Replacing both ends of this bond with hydroxyl groups produces **one equivalent of hydrogen**.
- **5.2:** The Si—H bonds are polarized toward hydrogen. Their hydrogen has hydride character and combines with protonic hydrogen from water, producing **one equivalent of hydrogen per Si—H bond**.
- **5.3:** $x = 2$. The compound is dimethyldisilane, $\text{Si}_2\text{H}_4(\text{CH}_3)_2$, with molecular formula $\text{C}_2\text{H}_{10}\text{Si}_2$.
- **5.4:** Written with the primary, uncondensed silanol products, the equations for the two possible isomers are



and



Their alkaline ionic forms are discussed below.

- **5.5:** There are **two constitutional isomers** within the specified methylated-disilane family:
- **1,1-Dimethyldisilane:** $(\text{CH}_3)_2\text{SiH}-\text{SiH}_3$, $\text{C}[\text{SiH}](\text{C})[\text{SiH}_3]$.
- **1,2-Dimethyldisilane:** $\text{CH}_3\text{SiH}_2-\text{SiH}_2\text{CH}_3$, $\text{C}[\text{SiH}_2][\text{SiH}_2]\text{C}$.

Solution

5.1 — Hydrolysis of the silicon–silicon bond

The parent compound is disilane, Si_2H_6 , $[\text{SiH}_3][\text{SiH}_3]$. The small species involved are water, H_2O , O ; hydroxide ion, OH^- , $[\text{OH}-]$; and dihydrogen, H_2 , $[\text{H}][\text{H}]$.

Silicon can undergo nucleophilic attack by hydroxide through an increase in its coordination number. This facilitates cleavage of the relatively weak Si—Si bond. Formation of strong Si—O bonds makes the overall transformation favourable; the starting Si—Si bond does not have to be polar.

For hydrogen accounting, cleavage replaces the Si—Si bond with one hydroxyl group on each silicon. Two water molecules supply these hydroxyl groups, leaving two hydrogen atoms that form one molecule of dihydrogen.

Thus,

one Si—Si bond contributes one H_2 .

This also agrees with oxidation-state accounting: each silicon changes from +III to +IV, supplying two electrons in total to reduce water-derived hydrogen.

5.2 — Hydrolysis of the silicon–hydrogen bonds

Silicon is less electronegative than hydrogen, so a Si—H bond has partially positive silicon and partially negative, hydridic hydrogen.

During hydrolysis, a hydroxyl group replaces the silicon-bound hydrogen. That hydrogen combines with a protonic hydrogen from water to form dihydrogen. Consequently, replacing each Si–H bond with a Si–OH group consumes one water molecule and releases one hydrogen molecule.

The methyl groups remain attached through their Si–C bonds. Therefore, a molecule containing $6 - x$ silicon-bound hydrogen atoms and one Si–Si bond gives

$$n(\text{H}_2) = (7 - x) n(\text{methylated disilane}).$$

5.3 — Calculation of x

Treating the hydrogen as an ideal gas, with

$$V = 27.8 \times 10^{-6} \text{ m}^3$$

and $R = 8.314 \text{ Pa m}^3 \text{ mol}^{-1} \text{ K}^{-1}$,

$$\begin{aligned} n(\text{H}_2) &= \frac{PV}{RT} \\ &= \frac{(97400 \text{ Pa})(27.8 \times 10^{-6} \text{ m}^3)}{(8.314 \text{ Pa m}^3 \text{ mol}^{-1} \text{ K}^{-1})(294 \text{ K})} \\ &= 1.108 \times 10^{-3} \text{ mol}. \end{aligned}$$

Using standard atomic molar masses 28.085 , 12.011 , and 1.008 g mol^{-1} for silicon, carbon, and hydrogen, respectively,

$$\begin{aligned} M(x) &= 2(28.085) + (6 - x)(1.008) + x(12.011 + 3(1.008)) \\ &= (62.218 + 14.027x) \text{ g mol}^{-1}. \end{aligned}$$

The sample mass is 0.020 g , so

$$1.108 \times 10^{-3} \text{ mol} = (7 - x) \frac{0.020 \text{ g}}{(62.218 + 14.027x) \text{ g mol}^{-1}}.$$

Solving with unrounded intermediate values gives $x \approx 2.00$. Since x counts methyl substituents,

$$x = 2.$$

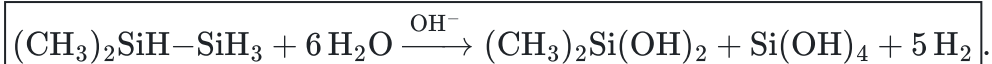
As a check, the molar mass is 90.27 g mol^{-1} , giving approximately $2.22 \times 10^{-4} \text{ mol}$ of compound. Its four Si–H bonds and one Si–Si bond yield five equivalents of hydrogen, consistent with the measured volume.

5.4 — Complete hydrolysis equations

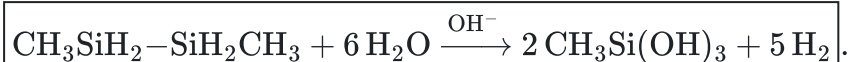
Each silicon acquires an hydroxyl group for every Si–H bond and for its end of the Si–Si bond. The primary products are:

Product	Name	SMILES
$(\text{CH}_3)_2\text{Si}(\text{OH})_2$	Dimethylsilanediol	<chem>C[Si](C)(O)O</chem>
$\text{Si}(\text{OH})_4$	Orthosilicic acid	<chem>O[Si](O)(O)O</chem>
$\text{CH}_3\text{Si}(\text{OH})_3$	Methylsilanetriol	<chem>C[Si](O)(O)O</chem>

For **1,1-dimethyldisilane**, the silicon bearing two methyl groups acquires two hydroxyl groups; the other silicon acquires four:



For **1,2-dimethyldisilane**, each silicon acquires three hydroxyl groups:



These equations express complete cleavage of the hydrolysable bonds. In alkaline solution, the hydroxylated products undergo acid–base equilibration. For example, **with one hydroxyl group deprotonated on each silicon**, the corresponding balanced net ionic equations are



and



The ions in these representations are:

Ion	Name	SMILES
$[(\text{CH}_3)_2\text{Si}(\text{OH})\text{O}]^-$	Hydroxy(dimethyl)silanolate	<chem>C[Si](C)(O)[O-]</chem>
$[\text{Si}(\text{OH})_3\text{O}]^-$	Trihydrogen orthosilicate	<chem>O[Si](O)(O)[O-]</chem>
$[\text{CH}_3\text{Si}(\text{OH})_2\text{O}]^-$	Dihydroxy(methyl)silanolate	<chem>C[Si](O)(O)[O-]</chem>

Further deprotonation or condensation depends on solution conditions and does not change the five-equivalent hydrogen yield.

5.5 — Isomer enumeration

Distribute the two methyl groups between the two equivalent silicon atoms. The distinct distributions are

$$(2, 0) \quad \text{and} \quad (1, 1).$$

The distribution (0, 2) is identical to (2, 0) after exchanging the silicon atoms.

Isomer	Structural formula	SMILES
1,1-Dimethyldisilane	$(\text{CH}_3)_2\text{SiH}-\text{SiH}_3$	<chem>C[SiH](C)[SiH3]</chem>
1,2-Dimethyldisilane	$\text{CH}_3\text{SiH}_2-\text{SiH}_2\text{CH}_3$	<chem>C[SiH2][SiH2]C</chem>

Neither structure has a stereogenic silicon centre: each silicon has at least two identical substituents. Rotation about the single Si–Si bond gives conformations, not additional constitutional isomers.

Thus, the requested number is 2.

The solution was checked against the official solution.

Problem 6: Organic chemistry, syntheses: products from benzaldehyde and malonic acid

(Organic chemistry, syntheses)

Benzaldehyde and malonic acid reacted in pyridine at 80 °C yielding (among others) CO₂ and compound **A** in a yield of ca. 80 % of the theoretical value. Catalytic hydrogenation of 1.48 g **A** on Pt at room temperature and normal pressure yielded **B** with a consumption of 0.25 litre of hydrogen. On reaction of **B** with a polyphosphoric acid (the Friedel-Crafts' conditions) compound **C** can be isolated accompanied by two acidic, isomeric side products. The side products **Da** and **Db** can be formed in a greater amount at a high concentration of **B** in the reaction medium, and can be suppressed by dilution.

The elemental analysis of **C** yields 81.8 % of carbon and 6.1 % of hydrogen. The corresponding values for **Da** and **Db**, identical within the experimental error, are 76.6 % and 6.4 %, respectively. An amount of 2.82 g **Da**, as well as **Db** requires ca. 100 cm³ 0.1 N potassium hydroxide solution for its neutralization. **C** can be purified by distillation (b. p. 243 – 245 °C) and then exhibits a melting point of 40 °C and density of 1.09 g/cm³. The relative molecular mass can be obtained by mass spectrometry and its value is 132.

Using this information solve the following problems:

6.1 The structural formula of **A**.

6.2 The structural formula of **B**.

6.3 The structural formula of **C**.

6.4 The structural formulae of **Da** and **Db**.

6.5 Give an alternative pathway for the synthesis of **A** using the simplest possible starting materials and forming at least one C–C bond.

6.6 Give an alternative pathway for the synthesis of **B** using the simplest possible starting materials and forming at least one C–C bond.

6.7 Give structural formulae for the products of the following reactions:

- a) **C** + hydroxylamine (with acid catalysis) →
- b) **C** + phenylmagnesium bromide (C₆H₅MgBr) and subsequent treatment under acidic conditions →
- c) **C** + benzaldehyde + C₂H₅O[−] Na⁺ →

Official English text of the problem.

Answers

- **6.1 — A:** Cinnamic acid, normally predominantly the *E* isomer: O=C(O)/C=C/c1ccccc1.
- **6.2 — B:** 3-Phenylpropanoic acid (hydrocinnamic acid): O=C(O)CCc1ccccc1.
- **6.3 — C:** Indan-1-one: O=C1CCc2ccccc21.
- **6.4 — Da and Db:** Assigning the labels arbitrarily:
- **Da:** 3-[2-(3-Phenylpropanoyl)phenyl]propanoic acid, the ortho isomer: O=C(O)CCc1ccccc1C(=O)CCc1ccccc1.

- **Db:** 3-[4-(3-Phenylpropanoyl)phenyl]propanoic acid, the para isomer:
O=C(O)CCc1ccc(C(=O)CCc2ccccc2)cc1.
- **6.5:** Perkin synthesis of **A** from benzaldehyde and acetic anhydride, using sodium acetate and heat, followed by hydrolysis.
- **6.6:** Malonic ester synthesis of **B**: benzylate diethyl malonate, then hydrolyze and decarboxylate.
- **6.7(a):** Indan-1-one oxime: ON=C1CCc2ccccc21; its *E/Z* composition is unspecified.
- **6.7(b):** 3-Phenyl-1H-indene: c1ccc(C2=CCc3ccccc32)cc1, formed by acid-catalyzed dehydration of the initially produced tertiary alcohol.
- **6.7(c):** 2-Benzylideneindan-1-one, normally predominantly *E*:
O=C1/C(=C/c2ccccc2)Cc2ccccc21.

Solution

6.1 — Identification of A

Benzaldehyde O=Cc1ccccc1 and malonic acid O=C(O)CC(=O)O undergo a Knoevenagel–Doebner condensation in pyridine c1ccncc1.

Condensation first gives benzylidenemalonic acid O=C(O)C(=Cc1ccccc1)C(=O)O:



Decarboxylation then gives cinnamic acid:



The by-products are water O and carbon dioxide O=C=O. The overall balanced reaction is therefore



Thus **A** is cinnamic acid, C9H8O2, with molar mass

$$M_A = 9(12) + 8(1) + 2(16) = 148 \text{ g mol}^{-1}.$$

The usual major product is the more stable *E* isomer.

6.2 — Identification of B

The amount of **A** hydrogenated is

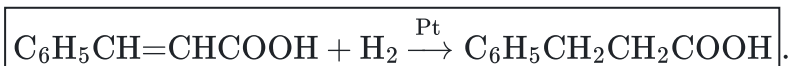
$$n_A = \frac{1.48 \text{ g}}{148 \text{ g mol}^{-1}} = 0.0100 \text{ mol}.$$

If one mole of molecular hydrogen, [H][H], reacts per mole of **A**, the observed volume corresponds to

$$V_m = \frac{0.25 \text{ L}}{0.0100 \text{ mol}} = 25 \text{ L mol}^{-1},$$

consistent, at the precision of the problem, with a gas at room temperature and normal pressure. Thus approximately one equivalent of hydrogen is consumed.

Hydrogenation reduces the side-chain double bond:



Therefore **B** is 3-phenylpropanoic acid, C9H10O2, with $M_B = 150 \text{ g mol}^{-1}$.

6.3 — Identification of C

The oxygen percentage is

$$100 - 81.8 - 6.1 = 12.1\%.$$

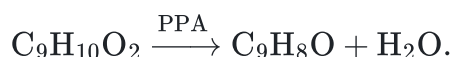
Using $M_C = 132 \text{ g mol}^{-1}$ and the usual integer atomic masses gives the numbers of atoms per molecule:

$$N_C = \frac{0.818(132)}{12} = 9.00, \quad N_H = \frac{0.061(132)}{1} = 8.05, \quad N_O = \frac{0.121(132)}{16} = 1.00.$$

Hence the molecular formula is



This differs from **B**, $\text{C}_9\text{H}_{10}\text{O}_2$, by one molecule of water:



Polyphosphoric acid activates the carboxyl group for an intramolecular Friedel–Crafts acylation. An ortho carbon of the aromatic ring bonds to the carboxyl carbon, closing a five-membered ring.

Consequently, **C** is **indan-1-one**. Its five-membered ring contains the carbonyl carbon and two methylene groups, and shares an edge with the benzene ring. Its formula also gives six degrees of unsaturation:

$$\text{DBE} = \frac{2(9) + 2 - 8}{2} = 6,$$

accounted for by the benzene ring, the additional ring, and the carbonyl bond.

6.4 — Identification of Da and Db

Potassium hydroxide $[\text{K}^+] \cdot [\text{OH}^-]$ is monobasic. The quantity used in the titration is

$$n_{\text{eq}} = (0.100 \text{ L})(0.1 \text{ eq L}^{-1}) \simeq 0.010 \text{ eq}.$$

Thus each side product has equivalent mass

$$E = \frac{2.82 \text{ g}}{0.010 \text{ eq}} \simeq 282 \text{ g eq}^{-1}.$$

The concentration dependence suggests an **intermolecular** reaction involving two molecules of **B**. If the activated carboxyl group of one molecule acylates the aromatic ring of another, the resulting product retains one carboxyl group:



The predicted molecular formula and molar mass are

$$2 \text{ C}_9\text{H}_{10}\text{O}_2 - \text{H}_2\text{O} = \text{C}_{18}\text{H}_{18}\text{O}_3, \\ M_D = 2(150) - 18 = 282 \text{ g mol}^{-1}.$$

Because this product has one carboxyl group, its equivalent mass is also 282 g eq^{-1} , matching the titration. Its calculated elemental composition is

$$w_C = \frac{18(12)}{282} \times 100 = 76.6\%, \\ w_H = \frac{18(1)}{282} \times 100 = 6.38\% \approx 6.4\%.$$

Both agree with the measured values.

The existing $-\text{CH}_2\text{CH}_2\text{COOH}$ substituent is attached to the aromatic ring through an alkyl carbon and directs electrophilic substitution principally **ortho and para**. The incoming group is $-\text{COCH}_2\text{CH}_2\text{C}_6\text{H}_5$. This gives the two structures listed as **Da** and **Db**.

Dilution suppresses these products because intermolecular acylation requires a second molecule of **B**, whereas formation of **C** closes a ring within one molecule. The labels **Da** and **Db** may be interchanged.

6.5 — Alternative synthesis of A

A suitable alternative is the **Perkin reaction**.

Heat benzaldehyde with acetic anhydride $\text{CC}(=\text{O})\text{OC}(\text{C})=\text{O}$ in the presence of sodium acetate $\text{CC}(=\text{O})[\text{O}-] \cdot [\text{Na}+]$, then perform an aqueous work-up. The overall balanced equation is



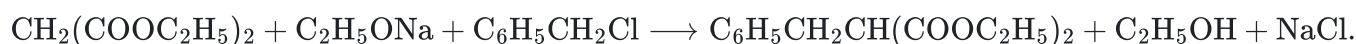
The other organic product is acetic acid $\text{CC}(=\text{O})\text{O}$.

The new C–C bond joins the original aldehyde carbon to a methyl carbon supplied by acetic anhydride. Condensation and subsequent hydrolysis yield **A**, normally predominantly *E*-cinnamic acid.

6.6 — Alternative synthesis of B

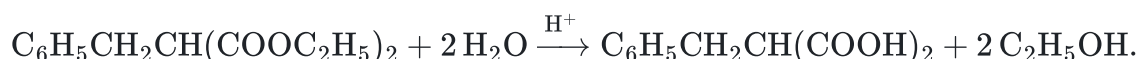
A standard alternative is the **malonic ester synthesis**, using diethyl malonate $\text{CCOC}(=\text{O})\text{CC}(=\text{O})\text{OCC}$ and benzyl chloride $\text{ClC}(\text{c}1\text{ccccc}1)$.

First, sodium ethoxide $\text{CC}[\text{O}-] \cdot [\text{Na}+]$ removes a proton from diethyl malonate. The resulting malonate anion, $\text{CCOC}(=\text{O})[\text{CH}-]\text{C}(=\text{O})\text{OCC}$, attacks benzyl chloride in an $\text{S}_{\text{N}}2$ reaction. The combined balanced equation is

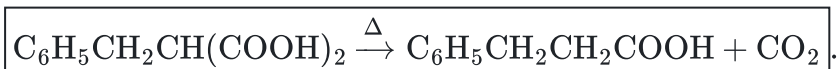


The organic product is diethyl benzylmalonate $\text{CCOC}(=\text{O})\text{C}(\text{Cc}1\text{ccccc}1)\text{C}(=\text{O})\text{OCC}$. The coproducts are ethanol CCO and sodium chloride $[\text{Na}+] \cdot [\text{Cl}-]$.

Hydrolysis of both ester groups gives benzylmalonic acid $\text{O}=\text{C}(\text{O})\text{C}(\text{Cc}1\text{ccccc}1)\text{C}(=\text{O})\text{O}$:



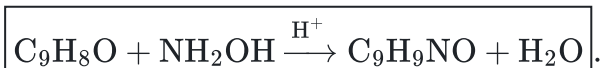
Heating then causes decarboxylation:



The product is **B**. The required new C–C bond is formed between the benzyl carbon and the central carbon of malonate.

6.7(a) — Reaction with hydroxylamine

Hydroxylamine **NO** condenses with the ketone carbonyl group under acid catalysis, producing **indan-1-one oxime**:



The original $\text{C}=\text{O}$ group becomes $\text{C}=\text{N}-\text{OH}$.

The connectivity is ON=C1CCc2ccccc21. Because the two ring paths attached to the imine carbon differ, geometrical isomers are possible:

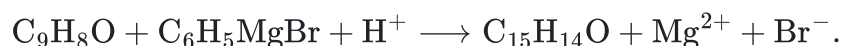
- (*E*)-Indan-1-one oxime: O/N=C1\CCc2ccccc21.
- (*Z*)-Indan-1-one oxime: O/N=C1/CCc2ccccc21.

The problem does not establish their proportions.

6.7(b) — Grignard addition and subsequent acidic treatment

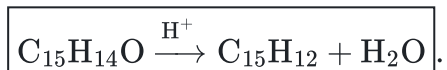
Phenylmagnesium bromide Br[Mg]c1ccccc1 adds a phenyl group to the carbonyl carbon. This SMILES represents formal connectivity; it omits solvent coordination and aggregation.

Protonation initially gives **1-phenylindan-1-ol**, OC1(c2ccccc2)CCc2ccccc21, formed as a racemate. A balanced equation for addition and acidic work-up is



Here the work-up ions are hydrogen ion [H+], magnesium(II) ion [Mg+2], and bromide [Br-].

The tertiary benzylic alcohol then undergoes **acid-catalyzed dehydration**:

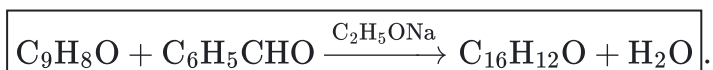


Protonation of the hydroxyl group permits loss of water. Removal of a proton from the adjacent methylene group forms a double bond between that carbon and the former carbonyl carbon.

The final product is therefore **3-phenyl-1H-indene**, c1ccc(C2=CCc3ccccc32)cc1. In the original indanone numbering, the phenyl group remains at C1 and the new double bond lies between C1 and C2; renumbering the indene gives the name above.

6.7(c) — Reaction with benzaldehyde and sodium ethoxide

Ethoxide removes an α -hydrogen from C2 of indan-1-one. The resulting enolate attacks benzaldehyde, and the aldol addition product loses water to form a conjugated enone. This is a Claisen–Schmidt condensation:



The product is **2-benzylideneindan-1-one**. The original ketone carbonyl remains, and C2 bears an exocyclic =CHC_6H_5 group.

The normally favored *E* product is O=C1/C(=C/c2ccccc2)Cc2ccccc21; the phenyl group and the carbonyl-bearing side of the ring lie on opposite sides of the exocyclic double bond.

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.