

IChO 1992

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Problem 1: Diatoms, whales and the carbon cycle

Diatoms, microscopic organisms, are an abundant food source in the oceans producing carbohydrates from carbon dioxide and water by photosynthesis:



1.1 During the first five years of life blue whales gain 75 kg of mass per day by feeding on krill. The whale must consume ten times this mass of krill each day. The krill must consume 10.0 kg of diatoms to produce 1.0 kg of krill. Assuming that the mass gain in the first years of a whale's life is due to the consumption of carbohydrates ($\text{C}_6\text{H}_{12}\text{O}_6$), calculate the volume of CO_2 at STP (0 °C, 101 kPa) that must be used by the diatoms to produce the carbohydrates consumed by a blue whale in its first five years of life.

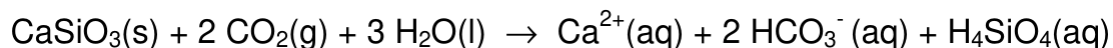
1.2 There is 0.23 cm³ of dissolved CO_2 per one litre sea water (at 24 °C and 101 kPa).

i) If diatoms can completely remove carbon dioxide from the water they process, what volume of water would they process to produce the carbohydrates required by a blue whale during the first five years of life?

ii) What fraction of the total volume of the oceans will be needed to supply the carbon dioxide for the first five years of growth of 1000 blue whales? The volume of the oceans is $1.37 \times 10^{18} \text{ m}^3$.

1.3 Three percent of the mass of a $9.1 \times 10^4 \text{ kg}$ adult whale is nitrogen. When a $9.1 \times 10^4 \text{ kg}$ blue whale dies, what is the maximum mass of NH_4^+ that can become available for other marine organisms?

1.4 Eighteen percent of a $9.1 \times 10^4 \text{ kg}$ whale's mass is carbon. Carbon can be returned to the atmosphere as CO_2 and then removed from the atmosphere by weathering of rocks containing calcium silicate.



What are the maximum number of grams of CaSiO_3 that can be weathered by the carbon dioxide produced from the decomposition of 1000 blue whales, the number estimated to die annually?

Official English text of the problem.

Answers

- 1.1: $1.0 \times 10^7 \text{ m}^3$ of carbon dioxide at STP, equivalent to $1.0 \times 10^{10} \text{ L}$.
- 1.2 i): $4.9 \times 10^{10} \text{ m}^3$ of seawater, equivalent to $4.9 \times 10^{13} \text{ L}$.
- 1.2 ii): 3.5×10^{-5} of the ocean volume, or approximately 0.0035%.
- 1.3: $3.5 \times 10^3 \text{ kg}$ of ammonium ions, NH_4^+ .
- 1.4: $7.9 \times 10^{10} \text{ g}$ of calcium silicate, CaSiO_3 .

Solution

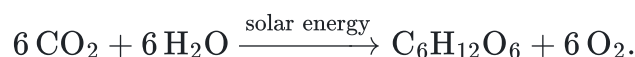
Take one year as 365 days, neglecting leap days. Use the ideal-gas law with

$$R = 8.314 \text{ L kPa mol}^{-1} \text{ K}^{-1}.$$

Intermediate values retain extra digits; final results are rounded to approximately two significant figures.

1.1 — Carbon dioxide required for photosynthesis

The balanced photosynthesis equation is



The species are carbon dioxide ($\text{O}=\text{C}=\text{O}$), water (O), a hexose carbohydrate such as glucose (open-chain connectivity SMILES $\text{O}=\text{CC}(\text{O})\text{C}(\text{O})\text{C}(\text{O})\text{C}(\text{O})\text{CO}$), and dioxygen ($\text{O}=\text{O}$). The carbohydrate's stereochemistry is unspecified and does not affect this calculation.

The whale's daily krill consumption is

$$10(75 \text{ kg d}^{-1}) = 750 \text{ kg d}^{-1}.$$

Producing this krill requires

$$750 \text{ kg d}^{-1} \times \frac{10.0 \text{ kg diatoms}}{1.0 \text{ kg krill}} = 7500 \text{ kg diatoms d}^{-1}.$$

Under the problem's carbohydrate mass-accounting assumption, the required carbohydrate mass over five years is therefore

$$m(\text{C}_6\text{H}_{12}\text{O}_6) = (7500 \text{ kg d}^{-1})(5 \times 365 \text{ d}) = 1.36875 \times 10^7 \text{ kg}.$$

Using $M(\text{C}_6\text{H}_{12}\text{O}_6) = 180 \text{ g mol}^{-1}$, and six moles of carbon dioxide per mole of carbohydrate,

$$n(\text{CO}_2) = 6 \left(\frac{1.36875 \times 10^{10} \text{ g}}{180 \text{ g mol}^{-1}} \right) = 4.5625 \times 10^8 \text{ mol}.$$

At $T = 273.15 \text{ K}$ and $P = 101 \text{ kPa}$,

$$\begin{aligned} V_0(\text{CO}_2) &= \frac{nRT}{P} \\ &= \frac{(4.5625 \times 10^8)(8.314)(273.15)}{101} \text{ L} \\ &= 1.02587 \times 10^{10} \text{ L}. \end{aligned}$$

Thus

$$\boxed{V_0(\text{CO}_2) \approx 1.0 \times 10^7 \text{ m}^3}.$$

1.2 i) — Seawater processed

The dissolved carbon dioxide content is expressed as a gas volume at 24 °C, so the required carbon dioxide volume must first be converted to that temperature. At unchanged pressure,

$$\frac{V_{24}}{V_0} = \frac{297.15}{273.15}.$$

Hence

$$V_{24} = (1.02587 \times 10^{10} \text{ L}) \frac{297.15}{273.15} = 1.11601 \times 10^{10} \text{ L} = 1.11601 \times 10^{13} \text{ cm}^3.$$

Each litre of seawater supplies 0.23 cm³ of carbon dioxide at these conditions. Complete extraction therefore requires

$$\begin{aligned} V_{\text{seawater}} &= \frac{1.11601 \times 10^{13} \text{ cm}^3}{0.23 \text{ cm}^3 \text{ L}^{-1}} \\ &= 4.85221 \times 10^{13} \text{ L} \\ &= 4.85221 \times 10^{10} \text{ m}^3. \end{aligned}$$

Thus

$$\boxed{V_{\text{seawater}} \approx 4.9 \times 10^{10} \text{ m}^3}.$$

1.2 ii) — Fraction of the oceans for 1000 whales

Using the unrounded water volume from part i),

$$f = \frac{1000(4.85221 \times 10^{10} \text{ m}^3)}{1.37 \times 10^{18} \text{ m}^3} = 3.54176 \times 10^{-5}.$$

Therefore

$$\boxed{f \approx 3.5 \times 10^{-5}},$$

equivalent to approximately 0.0035% of the ocean volume.

1.3 — Maximum ammonium mass

The ammonium ion is NH_4^+ , SMILES `[NH4+]`.

The whale contains

$$m(\text{N}) = 0.03(9.1 \times 10^4 \text{ kg}) = 2.73 \times 10^3 \text{ kg}$$

of nitrogen.

The maximum occurs when all this nitrogen becomes ammonium. Each ammonium ion contains one nitrogen atom, so

$$n(\text{NH}_4^+) = n(\text{N}).$$

Using $M(\text{N}) = 14 \text{ g mol}^{-1}$ and $M(\text{NH}_4^+) = 18 \text{ g mol}^{-1}$,

$$m(\text{NH}_4^+) = (2.73 \times 10^3 \text{ kg}) \frac{18}{14} = 3.510 \times 10^3 \text{ kg}.$$

The hydrogen incorporated into ammonium supplies the additional mass. Thus

$$m_{\max}(\text{NH}_4^+) \approx 3.5 \times 10^3 \text{ kg}.$$

1.4 — Maximum calcium silicate weathered

The balanced weathering reaction is



The aqueous products are calcium(II) ions ($[\text{Ca}+2]$), hydrogen carbonate or bicarbonate ions ($\text{O}=\text{C}(\text{O})[\text{O}-]$), and orthosilicic acid ($\text{O}[\text{Si}](\text{O})(\text{O})\text{O}$). Calcium silicate has the formal formula-unit SMILES $[\text{Ca}+2].[\text{O}-][\text{Si}](=\text{O})[\text{O}-]$; this represents its composition, not its extended crystal lattice or coordination geometry.

The carbon mass in 1000 whales is

$$\begin{aligned} m(\text{C}) &= 1000(9.1 \times 10^4 \text{ kg})(0.18) \\ &= 1.638 \times 10^7 \text{ kg} = 1.638 \times 10^{10} \text{ g}. \end{aligned}$$

For the maximum, all whale carbon becomes carbon dioxide. Each mole of carbon supplies one mole of carbon dioxide:

$$n(\text{CO}_2) = \frac{1.638 \times 10^{10} \text{ g}}{12 \text{ g mol}^{-1}} = 1.365 \times 10^9 \text{ mol}.$$

The weathering equation consumes two moles of carbon dioxide per mole of calcium silicate:

$$n(\text{CaSiO}_3) = \frac{1.365 \times 10^9}{2} = 6.825 \times 10^8 \text{ mol}.$$

With

$$M(\text{CaSiO}_3) = 40 + 28 + 3(16) = 116 \text{ g mol}^{-1},$$

the maximum mass weathered is

$$\begin{aligned} m(\text{CaSiO}_3) &= (6.825 \times 10^8 \text{ mol})(116 \text{ g mol}^{-1}) \\ &= 7.917 \times 10^{10} \text{ g}. \end{aligned}$$

Therefore

$$m_{\max}(\text{CaSiO}_3) \approx 7.9 \times 10^{10} \text{ g}.$$

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: Acid mine drainage: oxidation of pyrite

Many streams drain in areas where coal or metallic ores are mined. These streams have become acidic and contain high concentrations of dissolved iron and sulphate, due to sulphur-containing ores being exposed to the atmosphere or to oxygenated waters. The most common sulphur-containing mineral is pyrite, FeS_2 , in which the oxidation state of iron is +2. As the iron-rich streams mix with other waters, the dissolved iron precipitates as goethite, $\text{FeO}(\text{OH})$, which coats the stream bottom while the water remains acidic.

2.1 Draw the electron dot structure that illustrates the bonding in the ion S_2^{2-} , showing all valence electrons.

2.2 Write a balanced chemical equation to show how hydrogen ions (H^+) are generated during the oxidation of pyrite to form a solution of iron(II) and sulphate ions.

2.3 Write a balanced equation to show how many additional moles of hydrogen are generated when iron(II) ions are oxidized to form the mineral goethite, $\text{FeO}(\text{OH})$.

2.4 Calculate how many moles of pyrite would be required to bring 1.0 dm^3 of pure water to a pH of 3.0 if the pyrite was completely converted into $\text{FeO}(\text{OH})$ and H^+ ions. Neglect the formation of HSO_4^- .

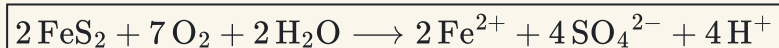
2.5 The concentration of iron as $\text{Fe}(\text{II})$ in a stream is 0.00835 M. At a very narrow point in the stream it empties into a large pond, with a flow rate of 20.0 l each minute. The water in this stream is sufficiently aerated that 75 % of the $\text{Fe}(\text{II})$ is oxidized to $\text{Fe}(\text{III})$. The pH of the pond is high enough (> 7) that the iron(III) precipitates immediately as $\text{Fe}(\text{OH})_3$ which on aging becomes Fe_2O_3 . What mass of Fe_2O_3 will be deposited on the bottom of the pond in two years?

Official English text of the problem.

Answers

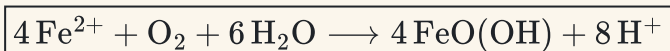
- **2.1** The **disulfide ion**, $[\text{S}^-][\text{S}^-]$, has one single bond between the sulfur atoms and **three lone pairs on each sulfur**. Each sulfur has formal charge -1 ; there are **14 valence electrons** in total.

- **2.2**



This generates **2 mol of hydrogen ions per mole of pyrite**.

- **2.3**



This generates **2 additional mol of hydrogen ions per mole of iron(II)**.

- **2.4**

$$n(\text{FeS}_2) = 2.5 \times 10^{-4} \text{ mol}$$

- **2.5** Approximately

$$m(\text{Fe}_2\text{O}_3) = 1.05 \times 10^4 \text{ kg} = 10.5 \text{ t}$$

or 11 t when rounded to two significant figures.

Solution

The following names and SMILES identify the species used below. For the extended solids, the disconnected SMILES describe **ionic formula units only**; they do not represent the crystal lattices or iron coordination geometries.

Species	SMILES
Disulfide ion, S_2^{2-}	[S-][S-]
Dioxygen, O_2	O=O
Water, H_2O	O
Hydrogen ion (proton), H^+	[H+]
Iron(II) ion, Fe^{2+}	[Fe+2]
Iron(III) ion, Fe^{3+}	[Fe+3]
Sulphate ion, SO_4^{2-}	[O-]S(=O)(=O)[O-]
Hydroxide ion, OH^-	[OH-]
Pyrite, FeS_2	[Fe+2].[S-][S-]
Goethite, $\text{FeO}(\text{OH})$	[Fe+3].[O-2].[OH-]
Iron(III) hydroxide, $\text{Fe}(\text{OH})_3$	[Fe+3].[OH-].[OH-].[OH-]
Iron(III) oxide, Fe_2O_3	[Fe+3].[Fe+3].[O-2].[O-2].[O-2]

2.1

Each sulfur atom contributes six valence electrons, and the dianionic charge supplies two more:

$$N_{\text{valence}} = 2(6) + 2 = 14.$$

A single bond uses two electrons. The remaining twelve electrons form six lone pairs, three on each sulfur, giving both atoms complete octets.

The formal charge on each sulfur is

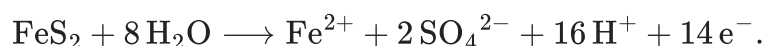
$$\text{FC} = 6 - \left(6 + \frac{2}{2}\right) = -1.$$

To draw the electron-dot structure, place two sulfur symbols side by side with **one shared pair of dots between them**. Place three lone pairs around each sulfur: one above, one below, and one on its outer side. Enclose the whole structure in brackets labelled $2-$. The SMILES records the bond and charges; the lone pairs must be shown explicitly in the drawing.

2.2

Because iron in pyrite is $+2$, the sulfur pair has total oxidation state -2 , so each sulfur is at -1 . In sulphate, sulfur is at $+6$. Thus each sulfur loses seven electrons, and each formula unit of pyrite releases fourteen electrons. Iron remains at $+2$.

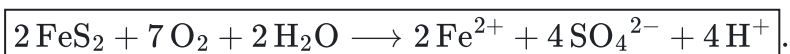
The oxidation half-equation is



Oxygen is reduced according to



Multiplying the first half-equation by 2 and the second by 7, then adding and cancelling, gives



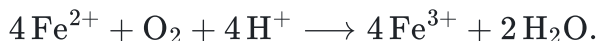
Therefore,

$$\frac{n(\text{H}^+)}{n(\text{FeS}_2)} = 2.$$

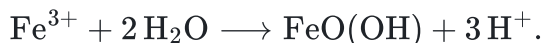
2.3

Goethite contains one oxide ion and one hydroxide ion per iron, so its iron has oxidation state +3.

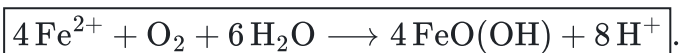
Oxidation of iron(II) by oxygen is



Formation of goethite from iron(III) releases hydrogen ions:



Multiplying the second equation by 4 and combining gives



Oxidation consumes one hydrogen ion per iron, whereas goethite formation releases three. The net production is therefore **two additional hydrogen ions per iron**, or 2 mol per mole of original pyrite.

2.4

Combining the reactions from 2.2 and 2.3 gives the overall conversion:



Thus complete conversion generates **four moles of hydrogen ions per mole of pyrite**.

Using the dilute-solution approximation,

$$[\text{H}^+] = 10^{-\text{pH}} = 10^{-3.0} \text{ mol dm}^{-3}.$$

In 1.0 dm^3 , the required amount is

$$n(\text{H}^+) = (10^{-3.0} \text{ mol dm}^{-3})(1.0 \text{ dm}^3) = 1.0 \times 10^{-3} \text{ mol}.$$

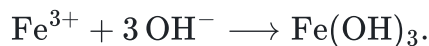
Water autoionization is negligible at this pH, and sulphate protonation is neglected as instructed.

Hence

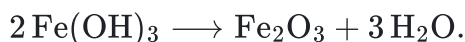
$$n(\text{FeS}_2) = \frac{1.0 \times 10^{-3}}{4} = 2.5 \times 10^{-4} \text{ mol}.$$

2.5

The oxidized iron precipitates as iron(III) hydroxide:



On aging,



Consequently, every two moles of precipitated iron produce one mole of iron(III) oxide.

Taking one year as 365 days, the elapsed time is

$$t = 2(365)(24)(60) = 1\,051\,200 \text{ min}.$$

The amount of iron entering the pond is

$$\begin{aligned} n_{\text{Fe, in}} &= (0.00835 \text{ mol L}^{-1})(20.0 \text{ L min}^{-1})(1\,051\,200 \text{ min}) \\ &= 175\,550.4 \text{ mol}. \end{aligned}$$

Only 75% is oxidized and precipitated, so

$$n(\text{Fe}_2\text{O}_3) = \frac{0.75}{2} n_{\text{Fe, in}} = 65\,831.4 \text{ mol.}$$

Using standard atomic molar masses of 55.85 g mol^{-1} for iron and 16.00 g mol^{-1} for oxygen,

$$M(\text{Fe}_2\text{O}_3) = 2(55.85) + 3(16.00) = 159.70 \text{ g mol}^{-1}.$$

Therefore,

$$\begin{aligned} m(\text{Fe}_2\text{O}_3) &= (65\,831.4 \text{ mol})(159.70 \text{ g mol}^{-1}) \\ &= 1.051327 \times 10^7 \text{ g} \\ &\approx \boxed{1.05 \times 10^4 \text{ kg} = 10.5 \text{ t}}. \end{aligned}$$

Rounding to the two significant figures of the stated 75% gives $1.1 \times 10^4 \text{ kg}$, or 11 t.

The solution was checked against the official solution.

Problem 3: Coniferyl alcohol: structure and stereoisomers of its dibromide

Coniferyl alcohol has the molecular formula $\text{C}_{10}\text{H}_{12}\text{O}_3$. It is isolated from pine trees. Coniferyl alcohol is not soluble in water or aqueous NaHCO_3 . A solution of Br_2 in CCl_4 is decolorized when added to coniferyl alcohol forming **A** ($\text{C}_{10}\text{H}_{12}\text{O}_3\text{Br}_2$). Upon reductive ozonolysis coniferyl alcohol produces vanillin (4-hydroxy-3-methoxybenzaldehyd) and **B** ($\text{C}_2\text{H}_4\text{O}_2$). Coniferyl alcohol reacts with benzoyl chloride ($\text{C}_6\text{H}_5\text{COCl}$) in the presence of a base to form **C** ($\text{C}_{24}\text{H}_{20}\text{O}_5$). This product rapidly decolorizes KMnO_4 (aq) and is insoluble in dilute NaOH .

Coniferyl alcohol reacts with cold HBr to form **D** ($\text{C}_{10}\text{H}_{11}\text{O}_2\text{Br}$). Hot HI converts ArOR to ArOH and RI . Coniferyl alcohol reacts with excess hot HI to give **E** ($\text{C}_9\text{H}_9\text{O}_2\text{I}$) and CH_3I . CH_3I in aqueous base reacts with coniferyl alcohol to form **F** ($\text{C}_{11}\text{H}_{14}\text{O}_3$), which is not soluble in a strong base, but decolorizes Br_2/CCl_4 -solution.

3.1 Draw the structures of coniferyl alcohol and compounds **A** - **F**.

3.2 There are a number of stereoisomers of compound **A**. Draw structure of compound **A**. Label each chiral centre in compound **A** with an asterisk (*). For all stereoisomers draw Fischer projections and label each chiral center with the proper *R* or *S* designation giving the absolute configuration about the chiral centre.

Official English text of the problem.

Answers

- 3.1.** The structures are as follows. Alkene geometry is left unspecified because the stated experiments do not determine it.

Compound	Name	SMILES
Coniferyl alcohol	3-(4-Hydroxy-3-methoxyphenyl)prop-2-en-1-ol	<chem>OCC=Cc1cc(OC)c(O)cc1</chem>
A	2,3-Dibromo-3-(4-hydroxy-3-methoxyphenyl)propan-1-ol	<chem>OCC(Br)C(Br)c1cc(OC)c(O)cc1</chem>
B	2-Hydroxyethanal, also called glycolaldehyde	<chem>O=CCO</chem>
C	Coniferyl alcohol dibenzoate: 3-[4-(benzoyloxy)-3-methoxyphenyl]prop-2-en-1-yl benzoate	<chem>O=C(OCC=Cc1cc(OC)c(OC(=O)c2ccccc2)cc1)c1ccccc1</chem>
D	4-(3-Bromoprop-1-en-1-yl)-2-methoxyphenol	<chem>BrCC=Cc1cc(OC)c(O)cc1</chem>
E	4-(3-Iodoprop-1-en-1-yl)benzene-1,2-diol	<chem>ICC=Cc1cc(O)c(O)cc1</chem>
F	3-(3,4-Dimethoxyphenyl)prop-2-en-1-ol	<chem>OCC=Cc1cc(OC)c(OC)cc1</chem>

- **3.2.** Number the side chain from the alcohol end: C1 is the hydroxymethyl carbon, C2 is the middle carbon, and C3 is attached to the aromatic ring. **C2 and C3 are the two chiral centres. There are four stereoisomers and no meso form.**

The following table precisely specifies their Fischer projections. Put the **4-hydroxy-3-methoxyphenyl group at the top**, then **C3**, then **C2**, and finally **CH₂OH** at the bottom. Horizontal bonds point toward the viewer; vertical bonds point away.

Stereoisomer of A	C3: left / right	C2: left / right	Isomeric SMILES
(2 <i>R</i> , 3 <i>R</i>)	Br / H	H / Br	<chem>OC[C@H](Br)[C@H](Br)c1cc(OC)c(O)cc1</chem>
(2 <i>S</i> , 3 <i>S</i>)	H / Br	Br / H	<chem>OC[C@H](Br)[C@H](Br)c1cc(OC)c(O)cc1</chem>
(2 <i>R</i> , 3 <i>S</i>)	H / Br	H / Br	<chem>OC[C@@H](Br)[C@@H](Br)c1cc(OC)c(O)cc1</chem>
(2 <i>S</i> , 3 <i>R</i>)	Br / H	Br / H	<chem>OC[C@H](Br)[C@H](Br)c1cc(OC)c(O)cc1</chem>

Solution

3.1. Identification of coniferyl alcohol and A–F

The degree of unsaturation of coniferyl alcohol is

$$\text{DBE} = \frac{2(10) + 2 - 12}{2} = 5.$$

A benzene ring accounts for four degrees of unsaturation, leaving one additional double bond.

Vanillin is **4-hydroxy-3-methoxybenzaldehyde**, O=Cc1cc(OC)c(O)cc1. Its formation by reductive ozonolysis establishes an aromatic fragment bearing hydroxy and methoxy groups at positions 4 and 3 relative to the side chain. The original side chain therefore contains an $\text{Ar}-\text{CH}=\text{CH}-$ unit, where Ar denotes the 4-hydroxy-3-methoxyphenyl group.

Benzoylation provides the other essential constraint. Replacing an $\text{O}-\text{H}$ hydrogen by a benzoyl group adds the net composition $\text{C}_7\text{H}_4\text{O}$. The observed formula change is

$$\Delta = \text{C}_{14}\text{H}_8\text{O}_2 = 2 \times \text{C}_7\text{H}_4\text{O}.$$

Thus **two hydroxyl groups are benzoylated**. One is the phenolic hydroxyl identified through vanillin; the other must be an alcoholic hydroxyl. Together with the two-carbon ozonolysis fragment, this establishes the parent structure:



The lack of bicarbonate solubility is consistent with a phenol, whose acidity is insufficient for the usual bicarbonate reaction of carboxylic acids.

Formation of A: bromine addition.

Bromine adds across the side-chain double bond:



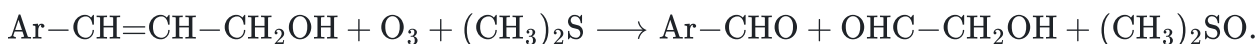
This gives **A**, retaining all twelve hydrogen atoms and adding two bromine atoms, exactly as required by $\text{C}_{10}\text{H}_{12}\text{O}_3\text{Br}_2$.

Formation of B: reductive ozonolysis.

Cleavage of the double bond gives vanillin from the aromatic end and glycolaldehyde from the alcohol end:



For an explicitly balanced net equation, dimethyl sulfide, $\text{CS}(\text{C})$, can be chosen as the reductive work-up reagent; its oxidation product is dimethyl sulfoxide, $\text{CS}(\text{C})=\text{O}$:



The second organic product is therefore **B**, glycolaldehyde, $\text{C}_2\text{H}_4\text{O}_2$.

Formation of C: benzoylation of both hydroxyl groups.

The phenolic and primary-alcohol hydroxyl groups both form benzoate esters. Writing sodium hydroxide as the base gives the balanced equation



In **C**, the ring substituent $-\text{OH}$ has become $-\text{OCOC}_6\text{H}_5$, and the side-chain terminus $-\text{CH}_2\text{OH}$ has become $-\text{CH}_2\text{OCOC}_6\text{H}_5$. The methoxy group and alkene remain intact.

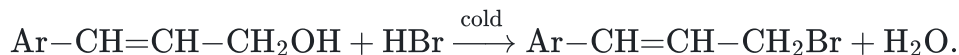
The absence of a free phenolic hydroxyl explains insolubility in dilute sodium hydroxide. The retained alkene explains rapid permanganate decolorization. Under the usual mild alkaline test conditions, a balanced representative reaction is



Here the organic product is **2,3-dihydroxy-3-[4-(benzoyloxy)-3-methoxyphenyl]propyl benzoate**, O=C(OCC(O)C(O)c1cc(OC)c(OC(=O)c2ccccc2)cc1)c1ccccc1. The problem gives only the decolorization observation, so a particular isolated oxidation product is not needed for identifying **C**.

Formation of **D**: replacement of the alcoholic hydroxyl by bromine.

The formula change corresponds to loss of OH and introduction of Br:



Thus **D** is the allylic bromide. Simple addition of hydrogen bromide across the alkene would retain all three oxygen atoms and would not match the stated formula.

Formation of **E**: ether cleavage and alcohol substitution.

Excess hot hydrogen iodide causes two transformations:

1. The aromatic methoxy group becomes a hydroxyl group, releasing **iodomethane (methyl iodide)**, CI.
2. The side-chain alcoholic hydroxyl is replaced by iodine.

The balanced overall equation is



Hence **E** has adjacent phenolic hydroxyl groups and the side chain $-\text{CH}=\text{CH}-\text{CH}_2\text{I}$. Its formula requires retention of the alkene.

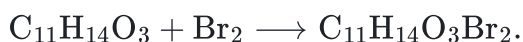
Formation of **F**: methylation of the phenolic hydroxyl.

In aqueous base, the phenolic hydroxyl is preferentially deprotonated and methylated. The balanced net equation is



The product **F** therefore has two aromatic methoxy groups and retains its primary-alcohol group. With no free phenolic hydroxyl, it does not acquire the usual phenolate-mediated solubility in aqueous strong base.

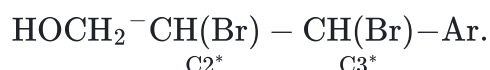
Its remaining double bond consumes bromine:



The addition product is **2,3-dibromo-3-(3,4-dimethoxyphenyl)propan-1-ol**, OCC(Br)C(Br)c1cc(OC)c(OC)cc1.

3.2. Chiral centres, Fischer projections, and absolute configurations

The starred carbon atoms in **A** are



Each has four different substituents. The hydroxymethyl carbon is not chiral because it bears two hydrogen atoms.

The Cahn–Ingold–Prelog priorities are:

- **At C2:**



The two carbon ligands are distinguished by their next attached atoms: (Br, C, H) outranks (O, H, H).

- **At C3:**



The side-chain carbon has bromine in its next comparison sphere and therefore outranks the aromatic carbon.

These priorities give the Fischer projections specified in the Answers table. In every listed projection, hydrogen lies on a horizontal bond and points toward the viewer, so the apparent clockwise or counterclockwise $1 \rightarrow 2 \rightarrow 3$ order must be reversed.

There are

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

configurational stereoisomers. The different aromatic and hydroxymethyl ends prevent an internal symmetry element from producing a meso form. The enantiomeric pairs are



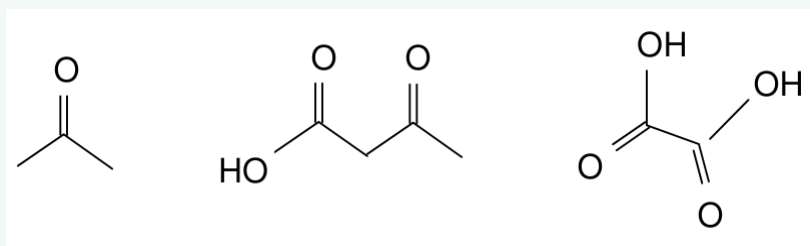
Members of different pairs are diastereomers. Anti bromination of a single alkene geometrical isomer ordinarily produces one enantiomeric pair; the question asks for **all** stereoisomers of the dibromide.

The solution was checked against the official solution.

Problem 4: Geraniol from rose oil

Rose oil is an essential oil obtained from the steam distillation of plant material from roses. It contains a number of terpenes, one of which is geraniol, $\text{C}_{10}\text{H}_{18}\text{O}$ (**A**). Upon oxidation, geraniol can either give a ten-carbon aldehyde or a ten-carbon carboxylic acid. Reaction with two moles of bromine gives a tetrabromide ($\text{C}_{10}\text{H}_{18}\text{OBr}_4$) (**B**). Geraniol reacts with HBr to give two bromides of formula $\text{C}_{10}\text{H}_{17}\text{Br}$.

When geraniol is vigorously oxidized, three products are obtained:



4.1 Give the structure of geraniol **A**.

4.2 Give the structure of compound **B**.

4.3 Give the structures of the two bromides of formula $\text{C}_{10}\text{H}_{17}\text{Br}$.

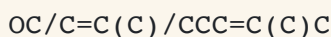
4.4 Indicate which of the two bromides is formed in greater proportions.

Official English text of the problem.

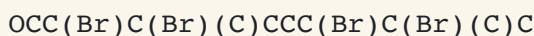
Answers

The following are the intended answers for geraniol. **The middle oxidation-product drawing contains a carbon-count discrepancy**, explained below.

- **4.1 Geraniol**, (2*E*)-3,7-dimethylocta-2,6-dien-1-ol:



- **4.2 B**, 2,3,6,7-tetrabromo-3,7-dimethyloctan-1-ol:



This connectivity represents a mixture of stereoisomers.



- **4.3** The two constitutional substitution products are:
- **Geranyl bromide**, (2*E*)-1-bromo-3,7-dimethylocta-2,6-diene:

$$\text{BrC/C=C(C)/CCC=C(C)C}$$
- **Linalyl bromide**, racemic 3-bromo-3,7-dimethylocta-1,6-diene:

$$\text{C=CC(Br)(C)CCC=C(C)C}$$
- **4.4 Linalyl bromide** is the expected major product under the allylic-carbocation model intended by the question.

Solution

4.1 — Identification of geraniol

The degree of unsaturation is

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

Addition of two equivalents of bromine accounts for two carbon–carbon double bonds, using both degrees of unsaturation.

Oxidation to either an aldehyde or a carboxylic acid, retaining all ten carbons, identifies a **primary alcohol**, —CH₂OH.

There is a problem with the printed degradation diagram:

Position in the figure	Product actually drawn	SMILES	Carbon atoms
Left	Propan-2-one, acetone	CC(=O)C	3
Middle	3-Oxobutanoic acid, acetoacetic acid	CC(=O)CC(=O)O	4
Right	Ethanedioic acid, oxalic acid	O=C(O)C(=O)O	2

These fragments contain $3 + 4 + 2 = 9$ carbons. For the ordinary oxidative cleavage of ten-carbon geraniol, the middle product must instead be **4-oxopentanoic acid, levulinic acid**, CC(=O)CCC(=O)O . Its structure contains an additional CH₂ group.

Using that explicit correction, the fragments reconstruct the molecule:

- **Acetone** identifies an alkene end of the form $=C(CH_3)_2$: an alkene carbon without hydrogen gives a ketone.
- **Oxalic acid** identifies the alcohol-containing end $HOCH_2-CH=$. The primary alcohol becomes one carboxyl group, while oxidative cleavage of the alkene carbon bearing hydrogen produces the other.
- **Levulinic acid**, $CH_3COCH_2CH_2COOH$, identifies the intervening portion $=C(CH_3)-CH_2-CH_2-CH=$.

Joining these pieces gives

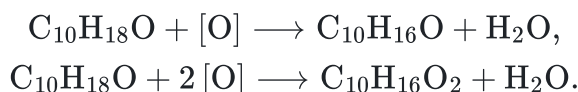


The name **geraniol** specifies the *E* configuration at the C2=C3 double bond. Thus the CH_2OH group and the continuing carbon chain lie on opposite sides of that double bond. The C6=C7 bond has no *E/Z* configuration because C7 bears two identical methyl groups.

The mild oxidation products are:

- **Geranial**, (*2E*)-3,7-dimethylocta-2,6-dienal:
 $O=C/C=C(C)/CCC=C(C)C$
- **Geranic acid**, (*2E*)-3,7-dimethylocta-2,6-dienoic acid:
 $O=C(O)/C=C(C)/CCC=C(C)C$

Writing [O] for one oxygen-atom equivalent supplied by the unspecified oxidant, the balanced equations are



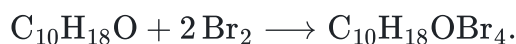
Here water has SMILES O.

The balanced vigorous-oxidation equation, **with the corrected middle product**, is

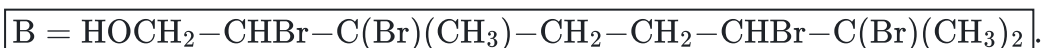


4.2 — Formation of the tetrabromide

Bromine, $BrBr$, adds across each double bond, placing one bromine atom on each former alkene carbon:



Consequently,



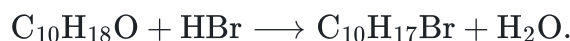
Ordinary electrophilic bromination proceeds through bromonium ions, followed by attack of bromide ion, $[Br^-]$, from the opposite face. Addition is therefore **anti**.

The product has stereogenic centers at C2, C3 and C6; C7 is not stereogenic because it bears two methyl groups. One permitted stereoisomer of **B** is represented by
 $OC[C@H](Br)[C@@](Br)(C)CC[C@H](Br)C(Br)(C)C.$

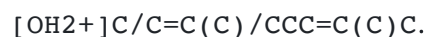
Its mirror image and the corresponding C6 epimers give four possible stereoisomers, arranged in two enantiomeric pairs. The problem does not specify their relative proportions.

4.3 — Formation of the two bromides

The product formula indicates substitution of the hydroxyl group by bromine, with loss of water. For either constitutional product, the balanced net equation with hydrogen bromide, $[H]Br$, is



Protonation gives **protonated geraniol**,



The C–O bonding electron pair then leaves with water, generating an allylic carbocation. Its two resonance contributors are represented by:

- **Geranyl-cation contributor**, with charge at C1:
 $[CH_2^+]C/C=C(C)/CCC=C(C)C$
- **Linalyl-cation contributor**, with charge at C3:
 $C=C[C^+](C)CCC=C(C)C$

These are two representations of the same delocalized ion. Moving the C2=C3 π -electron pair toward C1 forms C1=C2 and shifts the positive charge to C3.

A lone pair on bromide can attack either end of this allylic system:

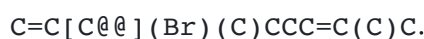
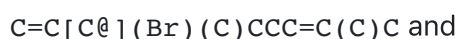
1. **Attack at C1** gives **geranyl bromide**:



2. **Attack at C3** gives **linalyl bromide**, with the first double bond shifted to C1=C2:



Attack at the planar C3 center can occur from either face. In an achiral medium, linalyl bromide is therefore racemic; its two enantiomeric SMILES are



4.4 — Major bromide

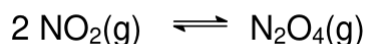
The contributor with positive charge at C3 places the charge on a **tertiary** carbon; the C1 contributor places it on a **primary** carbon. The tertiary contributor is better stabilized by the surrounding alkyl groups.

The intended qualitative argument therefore predicts preferential bromide capture at C3, giving **linalyl bromide as the major product**. No numerical product ratio can be obtained from the supplied information.

The solution was checked against the official solution.

Problem 5: Nitrogen dioxide - dinitrogen tetroxide equilibrium and kinetics

Nitrogen dioxide NO_2 is one of a number of oxides of nitrogen found in our atmosphere. It can dimerize to give $N_2O_4(g)$:

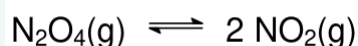


5.1 With a diagram, show the bonds present in $\text{NO}_2(\text{g})$ using the concept of resonance if necessary. Nitrogen dioxide, NO_2 , is paramagnetic.

5.2 Show, with bonding diagrams, how two molecules of $\text{NO}_2(\text{g})$ combine to give a molecule of $\text{N}_2\text{O}_4(\text{g})$ which is not paramagnetic.

5.3 At 298 K, the ΔG° of formation for $\text{N}_2\text{O}_4(\text{g})$ is 98.28 kJ, whereas for $\text{NO}_2(\text{g})$ is 51.84 kJ. Starting with one mole of $\text{N}_2\text{O}_4(\text{g})$ at 1.0 atm and 298 K, calculate what fraction will be decomposed if the total pressure is kept constant at 1.0 atm and the temperature is maintained at 298 K.

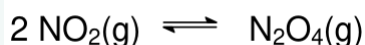
5.4 If ΔH° for the reaction



is 58.03 kJ, at what temperature would the fraction of N_2O_4 decomposed be double that calculated in part 5.3?

5.5 The dissociation of $\text{N}_2\text{O}_4(\text{g})$ to give $\text{NO}_2(\text{g})$ is a first order process with a specific rate constant of $5.3 \times 10^4 \text{ s}^{-1}$ at 298 K. Starting with an initial concentration of 0.10 M, how many seconds would it take for 20 % of the original N_2O_4 to decompose?

5.6 The association of $\text{NO}_2(\text{g})$ to give $\text{N}_2\text{O}_4(\text{g})$ is a second-order process with a specific rate constant of $9.8 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 298 K. Calculate the concentration equilibrium constant, K_c , at 298 K for the reaction



Official English text of the problem.

Answers

- 5.1** Nitrogen dioxide, $[\text{O}-][\text{N}^+]=\text{O}$, is a bent radical with one unpaired electron. Two equivalent resonance contributors give equivalent $\text{N}-\text{O}$ bonds, with formal mean bond order 1.5.
- 5.2** Dinitrogen tetroxide, $[\text{O}-][\text{N}^+](=\text{O})[\text{N}^+](=\text{O})[\text{O}-]$, forms an $\text{N}-\text{N}$ single bond by pairing the two radicals' unpaired electrons. All electrons are paired, so it is diamagnetic.
- 5.3** The fraction decomposed is 0.166 , approximately 16.6% .
- 5.4** $T \approx 318 \text{ K}$, with the pressure maintained at 1.0 atm.
- 5.5** $t = 4.2 \times 10^{-6} \text{ s}$, using the first-order dissociation law and neglecting reassociation.
- 5.6** $K_c \approx 1.8 \times 10^2 \text{ dm}^3 \text{ mol}^{-1}$ to two significant figures; the calculated value is $184.9 \text{ dm}^3 \text{ mol}^{-1}$.

Solution

5.1

Nitrogen dioxide has

$$5 + 2(6) = 17$$

valence electrons. The odd electron count requires an unpaired electron, explaining its paramagnetism.

The two principal Lewis resonance contributors are



To draw them precisely:

- Draw a bent O—N—O skeleton.
- In the first contributor, draw one N=O double bond and one N—O[−] single bond. Put a positive formal charge and one unpaired-electron dot on nitrogen.
- Give the doubly bonded oxygen two lone pairs and the singly bonded oxygen three lone pairs.
- In the second contributor, interchange the single and double bonds and the corresponding oxygen formal charges.

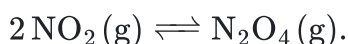
The actual molecule is a resonance hybrid: its two N—O bonds are equivalent, with formal mean bond order

$$\frac{2 + 1}{2} = 1.5.$$

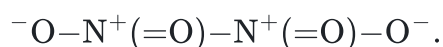
The SMILES [O-] [N+] =O represents one charge-separated bonding contributor. It does not depict the bent geometry or the resonance-delocalized electron distribution.

5.2

The balanced dimerization reaction is



Each radical supplies its unpaired electron to a new two-electron N—N sigma bond. One Lewis contributor of the product is



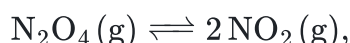
For the bonding diagram, draw a central N—N single bond. Attach two oxygens to each nitrogen, one through a double bond and one through a single bond. Each nitrogen has formal charge +1, and each singly bonded oxygen has formal charge −1. Each nitrogen now has an octet.

Interchanging the single and double N—O bonds within either group generates four resonance contributors in total. All electrons are paired, making the product diamagnetic.

Dinitrogen tetroxide has a planar equilibrium structure with approximately trigonal-planar coordination around each nitrogen. Its SMILES, [O-] [N+] (=O) [N+] (=O) [O-], does not specify that conformation.

5.3

For dissociation,



the standard reaction Gibbs energy is

$$\begin{aligned}\Delta_r G^\circ &= 2\Delta_f G^\circ(\text{NO}_2) - \Delta_f G^\circ(\text{N}_2\text{O}_4) \\ &= 2(51.84) - 98.28 \\ &= 5.40 \text{ kJ mol}^{-1}.\end{aligned}$$

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

$$K_p = \exp\left(-\frac{\Delta_r G^\circ}{RT}\right) = \exp\left(-\frac{5400}{8.314(298)}\right) = 0.11309.$$

Let α be the fraction of the initial mole that dissociates. At equilibrium,

$$n(\text{N}_2\text{O}_4) = (1 - \alpha) \text{ mol}, \quad n(\text{NO}_2) = 2\alpha \text{ mol},$$

so

$$n_{\text{tot}} = (1 + \alpha) \text{ mol}.$$

At total pressure P ,

$$p_{\text{NO}_2} = \frac{2\alpha}{1 + \alpha}P, \quad p_{\text{N}_2\text{O}_4} = \frac{1 - \alpha}{1 + \alpha}P.$$

Taking the standard pressure as $p^\circ = 1 \text{ atm}$,

$$K_p = \frac{(p_{\text{NO}_2}/p^\circ)^2}{p_{\text{N}_2\text{O}_4}/p^\circ} = \frac{4\alpha^2}{1 - \alpha^2} \frac{P}{p^\circ}.$$

Here $P/p^\circ = 1$, hence

$$\alpha = \sqrt{\frac{K_p}{4 + K_p}} = \sqrt{\frac{0.11309}{4.11309}} = 0.16582.$$

Thus

$\alpha \approx 0.166, \quad 16.6\% \text{ decomposed.}$
--

5.4

Assume that the total pressure remains 1.0 atm and that $\Delta_r H^\circ$ is constant over the temperature interval.

The required dissociation fraction is

$$\alpha_2 = 2\alpha_1 = 0.33164.$$

Therefore, the required equilibrium constant is

$$K_{p,2} = \frac{4\alpha_2^2}{1 - \alpha_2^2} = \frac{4(0.33164)^2}{1 - (0.33164)^2} = 0.49429.$$

The integrated van 't Hoff equation gives

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

Substitution yields

$$\frac{1}{T_2} = \frac{1}{298} - \frac{8.314}{58030} \ln\left(\frac{0.49429}{0.11309}\right),$$

and hence

$$T_2 = 318.03 \text{ K} \approx 318 \text{ K}.$$

The increase in temperature is consistent with dissociation being endothermic.

5.5

For the stated first-order dissociation calculation,

$$-\frac{d[\text{N}_2\text{O}_4]}{dt} = k_d[\text{N}_2\text{O}_4],$$

whose integrated form is

$$\ln \left(\frac{[\text{N}_2\text{O}_4]_0}{[\text{N}_2\text{O}_4]_t} \right) = k_d t.$$

After 20% decomposition,

$$[\text{N}_2\text{O}_4]_t = 0.80(0.10) = 0.080 \text{ mol dm}^{-3}.$$

Thus

$$t = \frac{\ln(0.10/0.080)}{5.3 \times 10^4 \text{ s}^{-1}} = 4.2103 \times 10^{-6} \text{ s}.$$

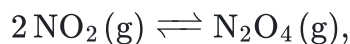
Therefore,

$$t = 4.2 \times 10^{-6} \text{ s} = 4.2 \mu\text{s}.$$

The initial concentration cancels because a fixed fractional conversion in a first-order process depends only on k_d .

5.6

For association,



use the reaction rates

$$r_a = k_a[\text{NO}_2]^2, \quad r_d = k_d[\text{N}_2\text{O}_4].$$

At equilibrium, formation and dissociation of the dimer balance:

$$k_a[\text{NO}_2]_{\text{eq}}^2 = k_d[\text{N}_2\text{O}_4]_{\text{eq}}.$$

Consequently,

$$\begin{aligned} K_c &= \frac{[\text{N}_2\text{O}_4]_{\text{eq}}}{[\text{NO}_2]_{\text{eq}}^2} \\ &= \frac{k_a}{k_d} \\ &= \frac{9.8 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}}{5.3 \times 10^4 \text{ s}^{-1}} \\ &= 184.9 \text{ dm}^3 \text{ mol}^{-1}. \end{aligned}$$

Thus, to two significant figures,

$$K_c \approx 1.8 \times 10^2 \text{ dm}^3 \text{ mol}^{-1}.$$

There is no additional factor of two: r_a counts dimer formation. The corresponding monomer consumption rate is $2r_a$.

The solution was checked against the official solution.

Problem 6: Carbon dioxide in the atmosphere and in water

The concentration of carbon dioxide in the atmosphere has increased substantially during this century and is predicted to continue to increase. The $[\text{CO}_2]$ is expected to be about 440 ppm ($440 \times 10^{-6} \text{ atm}$) in the year 2020.

6.1 Calculate the concentration (in mol dm^{-3}) of CO_2 dissolved in distilled water equilibrated with the atmosphere in the year 2020.

6.2 Calculate the pH -value of the solution in 6.1.

6.3 Calculate the enthalpy of reaction between $\text{CO}_2(\text{aq})$ and H_2O .

6.4 If the temperature of an equilibrated solution of CO_2 is increased and the concentration of dissolved carbon dioxide is maintained constant, the pH of the solution may change. Predict whether the pH will increase or decrease.

Data:

Henry's Law constant for CO_2 at 298 K: $0.0343 \text{ dm}^3 \text{ mol}^{-1} \text{ atm}^{-1}$

Thermodynamic values, in kJ/mol at 298 K are:

	$\Delta_f G^0$	$\Delta_f H^0$
$\text{CO}_2(\text{aq})$	-386.2	-412.9
$\text{H}_2\text{O}(\text{l})$	-237.2	-285.8
$\text{HCO}_3^-(\text{aq})$	-587.1	-691.2
$\text{H}^+(\text{aq})$	0.00	0.00

Official English text of the problem.

Answers

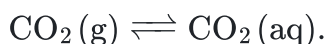
- 6.1:** $[\text{CO}_2(\text{aq})] = 1.51 \times 10^{-5} \text{ mol dm}^{-3}$ at 298 K.
- 6.2:** $pH = 5.59$.
- 6.3:** $\Delta_r H^\circ = +7.5 \text{ kJ mol}^{-1}$ for $\text{CO}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{HCO}_3^-(\text{aq})$; the reaction is endothermic.
- 6.4:** The pH decreases.

Solution

The species involved are carbon dioxide, CO_2 , $\text{O}=\text{C}=\text{O}$; water, H_2O , O ; hydrogen carbonate (bicarbonate), HCO_3^- , $\text{O}=\text{C}(\text{O})[\text{O}-]$; and the hydrogen ion, H^+ , $[\text{H}^+]$. In water, the hydrogen ion is solvated; its hydration is not represented by $[\text{H}^+]$.

6.1

The dissolution equilibrium is



Henry's law gives

$$[\text{CO}_2(\text{aq})] = k_H p_{\text{CO}_2}.$$

For this equation, the given numerical constant is interpreted as $k_H = 0.0343 \text{ mol dm}^{-3} \text{ atm}^{-1}$. Thus,

$$\begin{aligned} &= (0.0343 \text{ mol dm}^{-3} \text{ atm}^{-1})(440 \times 10^{-6} \text{ atm}) \\ &= 1.5092 \times 10^{-5} \text{ mol dm}^{-3} \\ &\approx \boxed{1.51 \times 10^{-5} \text{ mol dm}^{-3}}. \end{aligned}$$

This is the concentration of molecular dissolved carbon dioxide. Equilibration with the atmosphere maintains this concentration while some dissolved carbon dioxide reacts with water.

6.2

The supplied thermodynamic data describe the net acid dissociation:



Its standard Gibbs energy change is

$$\begin{aligned} \Delta_r G^\circ &= \sum \Delta_f G^\circ(\text{products}) - \sum \Delta_f G^\circ(\text{reactants}) \\ &= [0.00 + (-587.1)] - [(-386.2) + (-237.2)] \\ &= +36.3 \text{ kJ mol}^{-1}. \end{aligned}$$

Using $\Delta_r G^\circ = -RT \ln K$, with $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$,

$$K = \exp\left(-\frac{36.3 \times 10^3}{8.314 \times 298}\right) = 4.33 \times 10^{-7}.$$

Taking the activity of water as unity and treating the solution as ideal,

$$K \simeq \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2]c^\circ}, \quad c^\circ = 1 \text{ mol dm}^{-3}.$$

Neglecting water's autoionization and further dissociation of hydrogen carbonate, electroneutrality gives

$$[\text{H}^+] \simeq [\text{HCO}_3^-] = x.$$

Therefore,

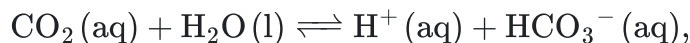
$$\begin{aligned} x &= \sqrt{K[\text{CO}_2]c^\circ} \\ &= \sqrt{(4.33 \times 10^{-7})(1.5092 \times 10^{-5} \text{ mol dm}^{-3})(1 \text{ mol dm}^{-3})} \\ &= 2.56 \times 10^{-6} \text{ mol dm}^{-3}. \end{aligned}$$

Hence,

$$\text{pH} = -\log_{10}\left(\frac{[\text{H}^+]}{c^\circ}\right) = 5.59.$$

6.3

For the same balanced reaction,



Hess's law gives

$$\begin{aligned}\Delta_r H^\circ &= \sum \Delta_f H^\circ(\text{products}) - \sum \Delta_f H^\circ(\text{reactants}) \\ &= [0.00 + (-691.2)] - [(-412.9) + (-285.8)] \\ &= \boxed{+7.5 \text{ kJ mol}^{-1}}.\end{aligned}$$

The formation of hydrogen ions and hydrogen carbonate from dissolved carbon dioxide and water is therefore **endothermic**.

6.4

The van 't Hoff equation gives

$$\frac{d \ln K}{dT} = \frac{\Delta_r H^\circ}{RT^2} > 0.$$

Thus, increasing temperature increases the equilibrium constant for the endothermic reaction. Since the dissolved carbon dioxide concentration is maintained constant,

$$[\text{H}^+] \simeq \sqrt{K[\text{CO}_2]c^\circ}$$

increases as K increases. Consequently, the **pH decreases**.

The solution was checked against the official solution.

Problem 7: Determination of chloride in Chesapeake Bay water

When the fresh-water rivers that run into the Chesapeake Bay flood after heavy rains in the spring, the increase in fresh water in the Bay causes a decrease in the salinity in the areas where oysters grow. The minimum concentration of chloride ions needed in oyster beds for normal growth is 8 ppm (8 mg dm^{-3}).

After one week of heavy rain, the following analysis is done on water from the bay. To a 50.00 cm^3 sample of bay water a few drops of a K_2CrO_4 solution are added. The sample is then titrated with 16.16 cm^3 of a 0.00164 M AgNO_3 solution. After AgNO_3 solution has been added to the sample a bright red-orange precipitate forms.

7.1 What is the molar concentration of chloride in the sample?

7.2 Does the water contain sufficient chloride for the normal growth of oysters? Show your calculation.

7.3 Write a balanced equation for the reaction of the analyte with the titrant.

7.4 Write a balanced net-ionic equation that describes the reaction responsible for the colour change at the endpoint of the titration. Which compound produces the brick-red colour?

7.5 The concentration of chromate at the endpoint is 0.020 M. Calculate the concentration of chloride ions in the solution when the red precipitate forms.

7.6 For this titration to work most effectively, the solution being titrated must be neutral or slightly basic. Write a balanced equation for the competing reaction that would occur in acidic medium that would influence the observed endpoint of this titration.

Typically, a buffer is added to the solution being titrated to control the pH if the initial sample is acidic. Suppose the pH of the sample of bay water was 5.10, thus too acidic to perform the analysis accurately.

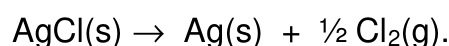
7.7 Select a buffer from the list that would enable you to establish and maintain a pH of 7.20 in aqueous medium. Show the calculations which lead to your choice.

	Buffer systems	K_a of weak acid
1.	0.10 M lactic acid / 0.10 M sodium lactate	1.4×10^{-4}
2.	0.10 M acetic acid / 0.10 M sodium acetate	1.8×10^{-5}
3.	0.10 M sodium dihydrogen phosphate / / 0.10 M sodium hydrogen phosphate	6.2×10^{-8}
4.	0.10 M ammonium chloride / 0.10 M ammonia	5.6×10^{-10}

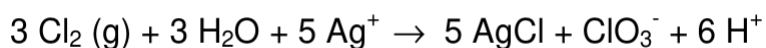
7.8 Using the selected buffer system, calculate the mass (in g) of weak acid and of conjugated base you would need to dissolve in distilled water to prepare 500 cm³ of a stock solution buffered at a pH of 7.2.

7.9 The chloride concentration in another 50.00 cm³ sample of bay water was determined by the Volhard method. In this method an excess of AgNO₃ is added to the sample. The excess Ag⁺ is titrated with standardized KSCN, forming a precipitate of AgSCN. The endpoint is signalled by the formation of the reddish-brown FeSCN²⁺ complex that forms when Ag⁺ is depleted. If the excess Ag⁺ from the addition of 50.00 cm³ of 0.00129 M AgNO₃ to the water sample required 27.46 cm³ of 1.41 10⁻³ M KSCN for titration, calculate the concentration of chloride in the bay water sample.

In natural waters with much higher concentration of Cl⁻, the Cl⁻ can be determined gravimetrically by precipitating the Cl⁻ as AgCl. A complicating feature of this method is the fact that AgCl is susceptible to photodecomposition as shown by the reaction:



Furthermore, if this photodecomposition occurs in the presence of excess Ag⁺, the following additional reaction occurs:



If 0.010 g of a 3.000 g sample of AgCl contaminated with excess Ag⁺ undergoes photodecomposition by the above equations

7.10 Will the apparent weight of AgCl be too high or too low? Explain your answer showing by how many grams the two values will differ.

Data:

$$K_{\text{sp}}(\text{AgCl}) = 1.78 \times 10^{-10}$$

$$K_{\text{sp}}(\text{Ag}_2\text{CrO}_4) = 1.00 \times 10^{-12}$$

Official English text of the problem.

Answers

- **7.1** $[\text{Cl}^-] = 5.30 \times 10^{-4} \text{ mol dm}^{-3}$, using the usual stoichiometric endpoint approximation.
- **7.2 Yes.** The chloride concentration is 18.8 mg dm^{-3} , exceeding 8 mg dm^{-3} .
- **7.3** $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \longrightarrow \text{AgCl}(\text{s})$.
- **7.4** $2 \text{Ag}^+(\text{aq}) + \text{CrO}_4^{2-}(\text{aq}) \longrightarrow \text{Ag}_2\text{CrO}_4(\text{s})$. **Silver chromate** produces the brick-red colour.
- **7.5** $[\text{Cl}^-] \approx 2.5 \times 10^{-5} \text{ mol dm}^{-3}$.
- **7.6** $2 \text{CrO}_4^{2-}(\text{aq}) + 2 \text{H}^+(\text{aq}) \rightleftharpoons \text{Cr}_2\text{O}_7^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l})$.
- **7.7 Buffer 3**, the dihydrogen phosphate/hydrogen phosphate pair:

$$pK_{\text{a}} = 7.208, \quad \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = 0.983.$$

- **7.8** For anhydrous salts, fixing the acid component at 0.100 M, use approximately $6.00 \text{ g NaH}_2\text{PO}_4$ and $6.97 \text{ g Na}_2\text{HPO}_4$, diluted to 500 cm^3 . The nominal equal-0.10 M recipe uses 6.00 g and 7.10 g, respectively, and gives $\text{pH } 7.208 \approx 7.2$.
- **7.9** $[\text{Cl}^-] = 5.16 \times 10^{-4} \text{ mol dm}^{-3}$, equivalent to 18.3 mg dm^{-3} .
- **7.10** The apparent mass is **too high**, by 0.0059 g ; the measured solid has mass approximately 3.006 g .

Solution

Dot-disconnected SMILES below specify the ionic composition of salts. Their crystal lattices are not represented by these strings. Oxyanion SMILES give one formal bond and charge representation; the actual bonding includes resonance delocalization.

7.1

The chloride ion, $[\text{Cl}^-]$, reacts with the silver(I) ion, $[\text{Ag}^+]$, in a 1 : 1 molar ratio. Using the usual approximation that the observed endpoint represents stoichiometric equivalence,

$$\begin{aligned}
 n(\text{Cl}^-) &= n(\text{Ag}^+) \\
 &= (0.00164 \text{ mol dm}^{-3})(16.16 \times 10^{-3} \text{ dm}^3) \\
 &= 2.65024 \times 10^{-5} \text{ mol}.
 \end{aligned}$$

The original sample volume is $50.00 \times 10^{-3} \text{ dm}^3$, so

$$[\text{Cl}^-] = \frac{2.65024 \times 10^{-5}}{50.00 \times 10^{-3}} = \boxed{5.30 \times 10^{-4} \text{ mol dm}^{-3}}.$$

7.2

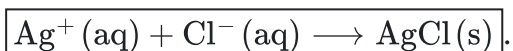
Using $M(\text{Cl}) = 35.45 \text{ g mol}^{-1}$,

$$\begin{aligned}
 \rho(\text{Cl}^-) &= (5.30048 \times 10^{-4} \text{ mol dm}^{-3})(35.45 \text{ g mol}^{-1}) \\
 &= 0.0187902 \text{ g dm}^{-3} \\
 &= \boxed{18.8 \text{ mg dm}^{-3}}.
 \end{aligned}$$

Since $18.8 > 8$, the sample contains sufficient chloride for normal oyster growth under the criterion stated in the problem.

7.3

The analyte is chloride, and the reacting titrant species is silver(I). They form insoluble silver chloride, $[\text{Ag}^+] \cdot [\text{Cl}^-]$:

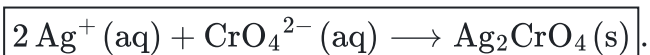


This net-ionic equation applies irrespective of the counterions originally accompanying chloride in the sample.

7.4

The indicator supplies chromate ions, $[\text{O}^-][\text{Cr}](=\text{O})(=\text{O})[\text{O}^-]$. Chromate has an approximately tetrahedral arrangement of oxygen atoms around chromium.

As the free silver(I) concentration rises, silver chromate precipitates:



The brick-red solid is **silver chromate**, $[\text{Ag}^+] \cdot [\text{Ag}^+] \cdot [\text{O}^-][\text{Cr}](=\text{O})(=\text{O})[\text{O}^-]$.

7.5

At the onset of silver chromate precipitation,

$$K_{\text{sp}}(\text{Ag}_2\text{CrO}_4) = [\text{Ag}^+]^2[\text{CrO}_4^{2-}].$$

Consequently,

$$[\text{Ag}^+] = \sqrt{\frac{1.00 \times 10^{-12}}{0.020}} = 7.071 \times 10^{-6} \text{ mol dm}^{-3}.$$

Solid silver chloride is also present, so its solubility equilibrium requires

$$K_{\text{sp}}(\text{AgCl}) = [\text{Ag}^+][\text{Cl}^-].$$

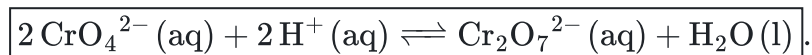
Thus,

$$\begin{aligned}
 &= \frac{1.78 \times 10^{-10}}{7.071 \times 10^{-6}} \\
 &= 2.517 \times 10^{-5} \text{ mol dm}^{-3} \\
 &\approx \boxed{2.5 \times 10^{-5} \text{ mol dm}^{-3}}.
 \end{aligned}$$

This is the dissolved chloride concentration in the titration mixture when the red precipitate first forms.

7.6

Acid converts chromate into dichromate:



The species introduced here are the hydrogen ion (proton), $[\text{H}^+]$; water, O ; and the dichromate ion, $[\text{O}-][\text{Cr}](=\text{O})(=\text{O})\text{O}[\text{Cr}](=\text{O})(=\text{O})[\text{O}-]$. Dichromate consists of two chromium–oxygen tetrahedra sharing one oxygen atom.

Increasing acidity shifts this equilibrium to the right, lowering the chromate concentration. Since precipitation requires

$$[\text{Ag}^+] = \sqrt{\frac{K_{\text{sp}}(\text{Ag}_2\text{CrO}_4)}{[\text{CrO}_4^{2-}]}} ,$$

less chromate means that a higher silver(I) concentration is needed to produce the indicator precipitate. The endpoint is therefore delayed.

7.7

A buffer works most effectively when its acid and conjugate-base concentrations are comparable, so its pK_{a} should be close to the desired pH.

From $pK_{\text{a}} = -\log_{10} K_{\text{a}}$:

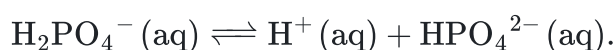
Buffer number	pK_{a}	Required base/acid ratio at pH 7.20
1	3.854	2.22×10^3
2	4.745	2.85×10^2
3	7.208	0.983
4	9.252	8.88×10^{-3}

The ratios follow from the Henderson–Hasselbalch equation,

$$\text{pH} = pK_{\text{a}} + \log_{10} \frac{[\text{conjugate base}]}{[\text{weak acid}]}.$$

Therefore, select **buffer 3**. Its weak acid is the dihydrogen phosphate ion, $\text{O}=\text{P}(\text{O})(\text{O})[\text{O}-]$, and its conjugate base is the hydrogen phosphate ion, $\text{O}=\text{P}(\text{O})([\text{O}-])[\text{O}-]$. Both have approximately tetrahedral coordination around phosphorus.

Their equilibrium is



At pH 7.20,

$$\begin{aligned}\frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} &= \frac{K_a}{[\text{H}^+]} \\ &= \frac{6.2 \times 10^{-8}}{10^{-7.20}} \\ &= \boxed{0.9826 \approx 0.983}.\end{aligned}$$

The nearly equal amounts provide effective buffering. The base component neutralizes added acid through



7.8

Assume anhydrous salts:

- Sodium dihydrogen phosphate, NaH_2PO_4 , $[\text{Na}^+] \cdot \text{O}=\text{P}(\text{O})(\text{O})[\text{O}^-]$, with $M = 119.98 \text{ g mol}^{-1}$.
- Disodium hydrogen phosphate, Na_2HPO_4 , $[\text{Na}^+] \cdot [\text{Na}^+] \cdot \text{O}=\text{P}(\text{O})([\text{O}^-])[\text{O}^-]$, with $M = 141.96 \text{ g mol}^{-1}$.

Take the acid concentration as $0.100 \text{ mol dm}^{-3}$, following the nominal concentration in the table. For $500 \text{ cm}^3 = 0.500 \text{ dm}^3$,

$$n(\text{NaH}_2\text{PO}_4) = (0.100)(0.500) = 0.0500 \text{ mol}.$$

The required base amount is

$$n(\text{Na}_2\text{HPO}_4) = 0.9826(0.0500) = 0.04913 \text{ mol}.$$

Therefore,

$$\begin{aligned}m(\text{NaH}_2\text{PO}_4) &= (0.0500)(119.98) \approx \boxed{6.00 \text{ g}}, \\ m(\text{Na}_2\text{HPO}_4) &= (0.04913)(141.96) \approx \boxed{6.97 \text{ g}}.\end{aligned}$$

Dissolve both salts in distilled water and dilute to a **final solution volume** of 500 cm^3 .

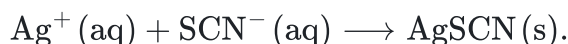
If the tabulated 0.10 M/0.10 M composition is used directly, each component requires 0.0500 mol. The corresponding masses are 6.00 g and 7.10 g, and

$$\text{pH} = \text{p}K_a + \log_{10} 1 = 7.208 \approx 7.2.$$

Thus this nominal recipe also meets the pH stated to one decimal place in 7.8.

7.9

Thiocyanate ion, $[\text{S}^-]\text{C}\equiv\text{N}$, precipitates excess silver(I) as silver thiocyanate, $[\text{Ag}^+] \cdot [\text{S}^-]\text{C}\equiv\text{N}$:



Both the chloride precipitation and this back-titration have 1 : 1 stoichiometry. Hence,

$$n(\text{Cl}^-) = n(\text{silver added}) - n(\text{silver remaining}).$$

The amount of silver added is

$$n_{\text{added}} = (50.00 \times 10^{-3})(0.00129) = 6.450 \times 10^{-5} \text{ mol}.$$

The thiocyanate titration measures

$$n_{\text{remaining}} = (27.46 \times 10^{-3})(1.41 \times 10^{-3}) = 3.87186 \times 10^{-5} \text{ mol}.$$

Therefore,

$$n(\text{Cl}^-) = 6.450 \times 10^{-5} - 3.87186 \times 10^{-5} = 2.57814 \times 10^{-5} \text{ mol.}$$

Using the original water-sample volume,

$$[\text{Cl}^-] = \frac{2.57814 \times 10^{-5}}{50.00 \times 10^{-3}} = \boxed{5.16 \times 10^{-4} \text{ mol dm}^{-3}}.$$

The corresponding mass concentration is

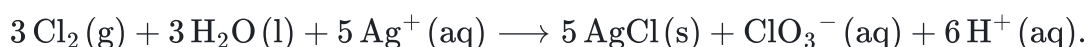
$$(5.15628 \times 10^{-4})(35.45)(10^3) = \boxed{18.3 \text{ mg dm}^{-3}}.$$

7.10

Photodecomposition produces metallic silver, represented atomically by [Ag], and chlorine, ClCl:



The chlorine then reacts with excess silver(I):



The soluble chlorine-containing product is chlorate ion, [O-][Cl](=O)=O.

For every six moles of silver chloride photodecomposed, three moles of chlorine form. These generate five moles of new silver chloride. The combined bookkeeping equation is



Both metallic silver and newly precipitated silver chloride remain in the weighed solid.

Using

$$M(\text{AgCl}) = 107.87 + 35.45 = 143.32 \text{ g mol}^{-1},$$

the amount initially photodecomposed is

$$n_{\text{decomp}} = \frac{0.010}{143.32} = 6.98 \times 10^{-5} \text{ mol.}$$

The retained metallic silver has mass

$$m(\text{Ag}) = \frac{0.010}{143.32}(107.87) = 0.00753 \text{ g.}$$

The newly formed silver chloride has mass

$$m(\text{AgCl})_{\text{new}} = \frac{5}{6} \left(\frac{0.010}{143.32} \right) (143.32) = 0.00833 \text{ g.}$$

Thus the mass change is

$$\begin{aligned} \Delta m &= m(\text{Ag}) + m(\text{AgCl})_{\text{new}} - m(\text{AgCl})_{\text{decomposed}} \\ &= 0.007526 + 0.008333 - 0.010 \\ &= +0.00586 \text{ g.} \end{aligned}$$

The apparent mass is therefore **too high by approximately 0.0059 g**:

$$m_{\text{apparent}} = 3.000 + 0.00586 = 3.00586 \text{ g} \approx \boxed{3.006 \text{ g}}.$$

The gain occurs because additional silver from solution becomes incorporated into the collected solid.

The solution was checked against the official solution.

Problem 8: Pourbaix diagrams of water, nitrogen and manganese

The Pourbaix diagrams for water, nitrogen and manganese are depicted in Fig. 1.

8.1 Write the formula of the species of nitrogen that is predominant

- i) in O_2 -rich lakes of $pH \approx 6$,
- ii) in highly O_2 -depleted lakes that are strongly contaminated with acid rain ($pH \approx 3$),

8.2 Which species of manganese is predominant

- i) in O_2 -rich lakes of $pH \approx 6$,
- ii) in highly O_2 -depleted lakes that are strongly contaminated with bases ($pH \approx 12$)?

8.3 People often find that clear, slightly acidic ($pH \approx 5$) water drawn from wells deposits a black manganese-containing solid on standing in toilet bowls.

- i) Write the chemical formula of the black solid?
- ii) Write the formula for the species of manganese found in well water while it is still underground?

8.4 According to Pourbaix diagrams two species of nitrogen should oxidize $Mn(s)$ to $Mn^{2+}(aq)$.

- i) Write the formulas of these two nitrogen species.
- ii) Which of the two species of nitrogen does not oxidize $Mn(s)$ (in practice) at room temperature?

8.5 According to the Pourbaix diagrams, some of the chemical forms of manganese should oxidize $NH_3(aq)$ or $NH_4^+(aq)$ to $N_2(g)$.

Choose in the following list the forms of Mn that should do it:



8.6 Ammonium permanganate, NH_4MnO_4 , is a well-known salt, but ammonium manganate, $(NH_4)_2MnO_4$, is a rarely known salt.

- i) Is NH_4MnO_4 expected to be thermodynamically stable? (YES or NO)
- ii) Is $(NH_4)_2MnO_4$ expected to be thermodynamically stable? (YES or NO)
- iii) Write and balance an equation for the decomposition of NH_4MnO_4 to give MnO_2 and N_2 .
- iv) Write and balance an equation for the decomposition of $(NH_4)_2MnO_4$ to give Mn and N_2 .

8.7 According to the Pourbaix diagrams, is it dangerous to grind together in a mortar and pestle

- i) potassium nitrate and manganese metal,
- ii) potassium nitrate and manganese dioxide?

8.8 The standard reduction potential, E^0 , for the reduction of MnO_4^- to MnO_2 is 1.692 V. Applying the Nernst equation calculate the reduction potential, E , for the reduction of 0.00100 M MnO_4^- solution at a $pH = 4.0$.

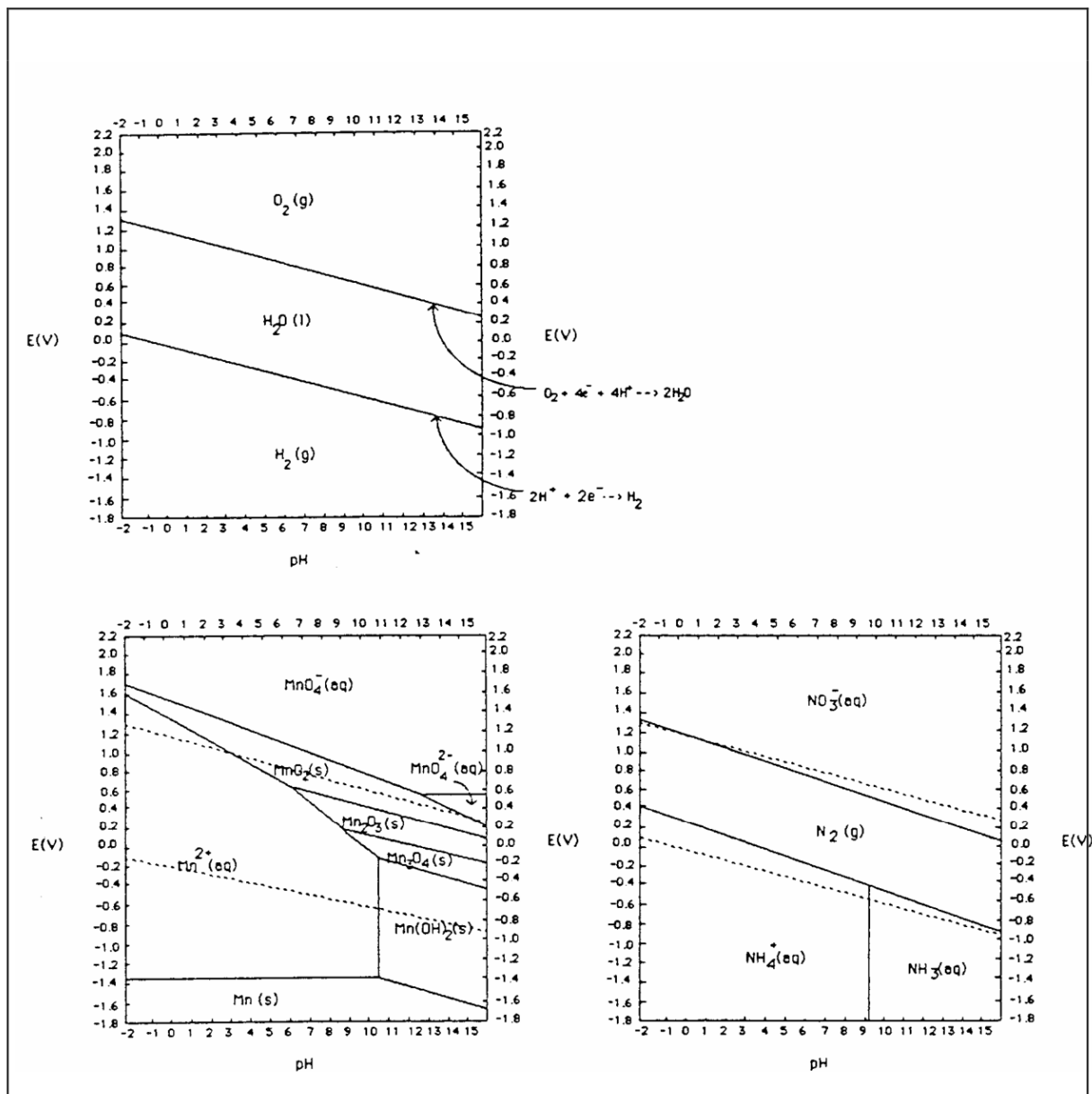


Figure 1

Official English text of the problem.

Answers

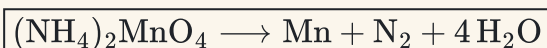
Names and SMILES are given at first identification. The manganese oxides, manganese hydroxide, and manganese metal are extended solids, so they have no discrete molecular SMILES representing their solid structures.

- **8.1(i):** Nitrate ion, NO_3^- , $\text{O}=[\text{N}+]([\text{O}-]) [\text{O}-]$.
- **8.1(ii):** Ammonium ion, NH_4^+ , $[\text{NH}_4+]$.
- **8.2(i):** Manganese(IV) oxide (manganese dioxide), $\text{MnO}_2(\text{s})$.
- **8.2(ii):** Manganese(II) hydroxide, $\text{Mn}(\text{OH})_2(\text{s})$.
- **8.3(i):** Manganese dioxide, $\text{MnO}_2(\text{s})$.
- **8.3(ii):** Manganese(II) ion, $\text{Mn}^{2+}(\text{aq})$, $[\text{Mn}+2]$.

- **8.4(i):** Nitrate ion, NO_3^- , and dinitrogen, N_2 , $\text{N}\equiv\text{N}$.
- **8.4(ii):** Dinitrogen, N_2 .
- **8.5:** Manganese(II,III) oxide, Mn_3O_4 ; manganese(III) oxide, Mn_2O_3 ; manganese dioxide, MnO_2 ; manganate(VI) ion, MnO_4^{2-} , $[\text{O}-][\text{Mn}](=\text{O})(=\text{O})[\text{O}-]$; and permanganate ion, MnO_4^- , $[\text{O}-][\text{Mn}](=\text{O})(=\text{O})=\text{O}$.
- **8.6(i):** **NO**.
- **8.6(ii):** **NO**.
- **8.6(iii):**



- **8.6(iv):**



- **8.7(i):** **Yes**.
- **8.7(ii):** **No**, according to the redox criterion of the diagrams.
- **8.8:** $E \approx 1.32 \text{ V}$ versus the standard hydrogen electrode, assuming 25°C .

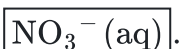
Solution

A Pourbaix diagram shows the thermodynamically predominant species as a function of pH and reduction potential. Higher potentials favor oxidized forms; lower potentials favor reduced forms. For the lake questions, oxygen-rich conditions are read near the upper water-stability boundary, while highly oxygen-depleted conditions are interpreted as strongly reducing, near the lower boundary.

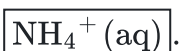
Water is H_2O , SMILES o , and dioxygen is O_2 , SMILES $\text{o}=\text{o}$. The manganese oxyanion SMILES above specify formal connectivity and charges; both oxyanions have tetrahedral arrangements of oxygen atoms, which these strings do not depict spatially.

8.1

i) At $\text{pH} \approx 6$, the oxygen/water boundary lies in the nitrate region of the nitrogen diagram. Thus the predominant nitrogen species under oxygen-rich conditions is

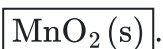


ii) At $\text{pH} \approx 3$, strongly reducing conditions lie below the boundary between nitrogen gas and ammonium. The acidic solution also favors ammonium over ammonia. Therefore,



8.2

i) At $\text{pH} \approx 6$, the potential associated with oxygen-rich water falls within the manganese dioxide stability region:



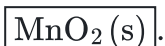
ii) At $\text{pH} \approx 12$, the strongly reducing part of the water-stability region falls within the manganese(II) hydroxide field:



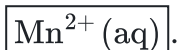
Although manganese metal is stable at still lower potentials, its region lies below the lower water-stability boundary.

8.3

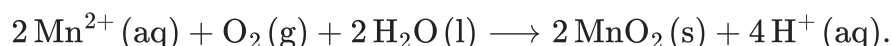
i) When the well water stands exposed to air, dissolved oxygen raises its redox potential. At $\text{pH} \approx 5$, this favors insoluble, black manganese dioxide:



ii) Underground, the water is oxygen-poor and has a lower redox potential. At this pH, dissolved manganese is predominantly



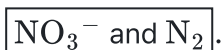
The precipitation upon aeration can be represented by



Here H^+ is the hydrogen ion, SMILES `[H+]`; in water it represents a solvated proton.

8.4

i) A species can thermodynamically oxidize manganese metal when its reduction potential is above the Mn^{2+}/Mn boundary at the same pH. Both nitrate and nitrogen gas satisfy this condition:



Nitrate can accept electrons by reduction to a lower nitrogen oxidation state. Nitrogen gas can accept electrons by reduction to ammonium; for example, the corresponding thermodynamic reaction with manganese is



ii) The species that does not appreciably oxidize manganese at room temperature is

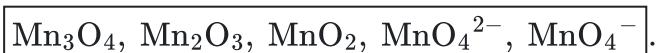


Reduction of nitrogen requires activation of its strong triple bond and has a large kinetic barrier. The Pourbaix diagram predicts thermodynamic favorability, not reaction rate.

8.5

Nitrogen has oxidation state -3 in both ammonia, NH_3 , SMILES `N`, and ammonium. Conversion to N_2 , where nitrogen has oxidation state 0 , releases three electrons per nitrogen atom.

The manganese species must therefore accept electrons at a potential above the nitrogen/ammonia or nitrogen/ammonium boundary. Comparison of the diagrams selects



These species contain manganese above oxidation state $+2$, at least in part:

Species	Manganese oxidation state
Mn_3O_4	One Mn(II) and two Mn(III) per formula unit
Mn_2O_3	$+3$
MnO_2	$+4$

Species	Manganese oxidation state
MnO_4^{2-}	+6
MnO_4^-	+7

Their relevant reduction boundaries lie above the nitrogen/ $\text{N}(-III)$ boundary.

The remaining candidates do not qualify. Manganese metal is the reduced form, while reduction of Mn^{2+} or $\text{Mn}(\text{OH})_2$ to metal requires potentials below the nitrogen/ammonia–ammonium boundary.

8.6

Ammonium permanganate has the constituent-ion SMILES $[\text{NH}_4+] \cdot [\text{O-}] [\text{Mn}] (=O) (=O) =O$.

Ammonium manganate has the constituent-ion SMILES $[\text{NH}_4+] \cdot [\text{NH}_4+] \cdot [\text{O-}] [\text{Mn}] (=O) (=O) [\text{O-}]$.

These disconnected SMILES describe ionic composition, not crystal packing.

i) NO. The ammonium and permanganate stability regions do not overlap. Ammonium can be oxidized while permanganate is reduced, so internal redox decomposition is thermodynamically favored.

ii) NO. Ammonium and manganate likewise do not have a common stability region and are thermodynamically incompatible.

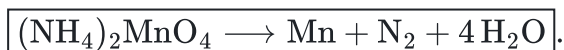
The existence of an isolable salt does not establish thermodynamic stability: an activation barrier can delay decomposition.

iii) In ammonium permanganate, nitrogen changes from -3 to 0 , losing three electrons per nitrogen atom. Manganese changes from $+7$ to $+4$, gaining three electrons per manganese atom. Two formula units supply the two nitrogen atoms needed for one nitrogen molecule:



Both sides contain two nitrogen atoms, eight hydrogen atoms, two manganese atoms, and eight oxygen atoms.

iv) In ammonium manganate, two nitrogen atoms each lose three electrons. The manganese atom gains all six electrons, changing from $+6$ to 0 . With the products specified in the question,



Both sides contain two nitrogen atoms, eight hydrogen atoms, one manganese atom, and four oxygen atoms.

8.7

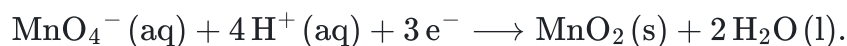
Potassium nitrate, KNO_3 , has the constituent-ion SMILES $[\text{K+}] \cdot [\text{O-}] [\text{N+}] (=O) [\text{O-}]$.

i) Yes. Nitrate is an oxidizing agent and manganese metal is a reducing agent. Their widely separated redox boundaries indicate a favorable redox reaction. Grinding brings them into intimate contact and can help initiate the reaction.

ii) No, according to the diagrams. Oxidizing manganese dioxide to manganate or permanganate requires a higher potential than nitrate reduction provides at the same pH. Thus the diagrams do not predict a favorable redox reaction between potassium nitrate and manganese dioxide.

8.8

First balance the reduction half-reaction:



Thus $n = 3$. Taking the activities of solid manganese dioxide and liquid water as unity,

$$Q = \frac{1}{a_{\text{MnO}_4^-} a_{\text{H}^+}^4}.$$

Using the concentration approximation for permanganate and the definition of pH,

$$a_{\text{MnO}_4^-} \approx 1.00 \times 10^{-3}, \quad a_{\text{H}^+} = 10^{-4.0}.$$

Therefore,

$$Q = \frac{1}{(10^{-3})(10^{-4})^4} = 10^{19}.$$

The Nernst equation at 25°C is

$$E = E^\circ - \frac{RT}{nF} \ln Q = E^\circ - \frac{0.05916 \text{ V}}{n} \log_{10} Q.$$

Substitution gives

$$\begin{aligned} E &= 1.692 \text{ V} - \frac{0.05916 \text{ V}}{3} (19) \\ &= 1.31732 \text{ V}. \end{aligned}$$

Allowing for the precision of the supplied pH,

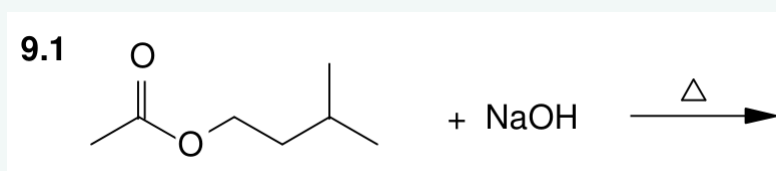
$$\boxed{E \approx 1.32 \text{ V}}.$$

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

Problem 9: Reactions of insect pheromones

Pheromones are chemicals or mixtures of certain chemicals secreted by insects and some animals for communication. They bring about certain responses in another individual of the same species. In the problem below you will find a number of pheromones undergoing reactions which were used in determining their structures. In each case give the structure or structures of the products produced. Show geometric (cis/trans) isomers where appropriate (in part (9.5)). You may ignore other forms of stereoisomerism.

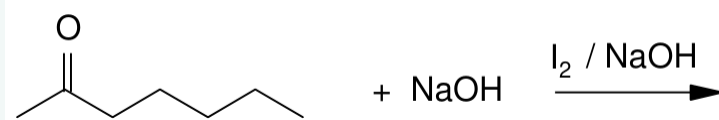
9.1



isoamyl acetate,
bee alarm pheromene

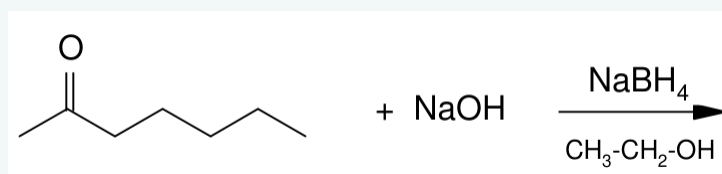
9.2

i)

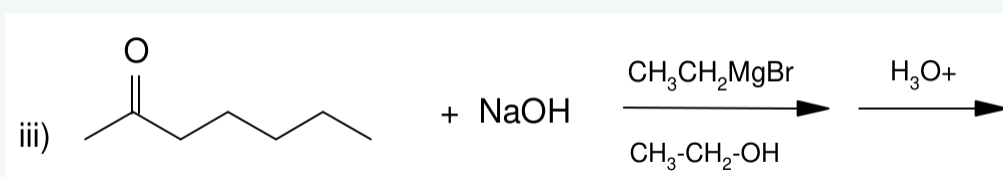


2-heptanone
ant alarm pheromone

ii)

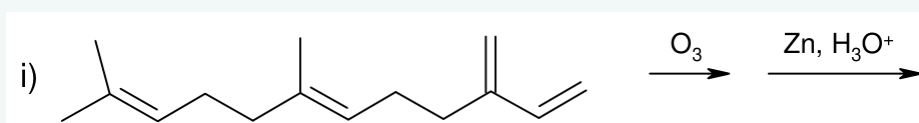


iii)



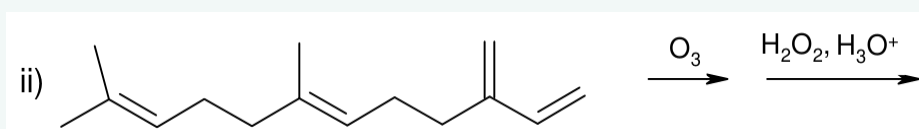
9.3

i)



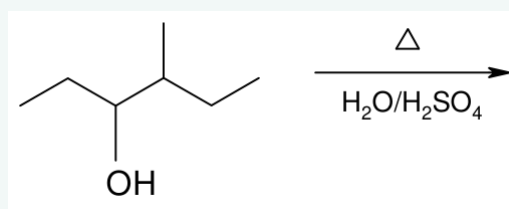
green peach -
aphid pheromone

ii)

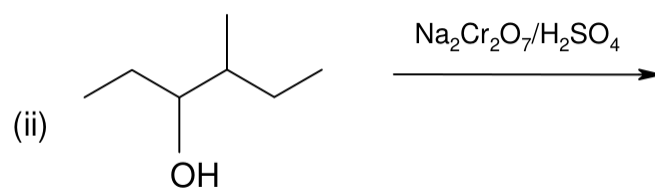


9.4

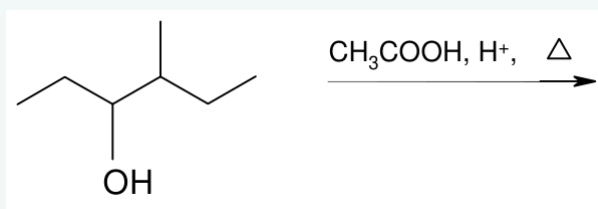
(i)



(ii)

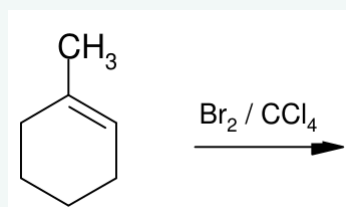


(iii)

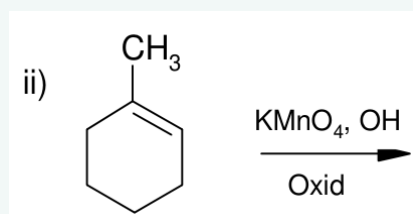


9.5

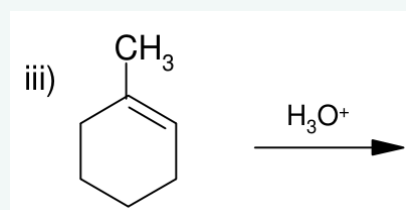
i)



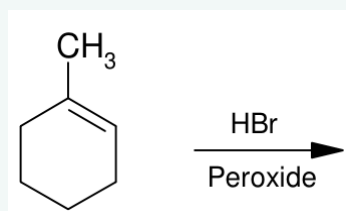
ii)



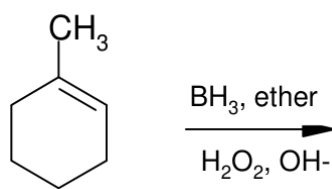
iii)



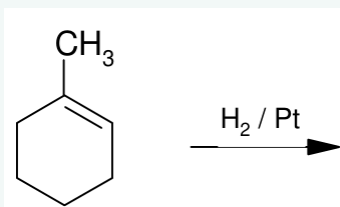
iv)



v)



vi)



Official English text of the problem.

Answers

Where stereochemical SMILES are given, one representative of each required relative configuration is shown; its mirror image need not be listed separately.

- **9.1:** Sodium ethanoate (sodium acetate), CC(=O)[O-].[Na+], and 3-methylbutan-1-ol (isoamyl alcohol), CC(C)CCO.
- **9.2(i):** Sodium hexanoate, CCCCC(=O)[O-].[Na+], and triiodomethane (iodoform), IC(I)I.
- **9.2(ii):** Heptan-2-ol, CC(O)CCCC.
- **9.2(iii):** **As printed**, ethanol quenches the Grignard reagent, producing ethane, CC, while heptan-2-one, CC(=O)CCCC, remains available. **If ordinary dry-ether Grignard conditions were intended**, followed by acidic work-up, the product is **3-methyloctan-3-ol**, CCC(C)(O)CCCC.
- **9.3(i):** Per molecule of pheromone:
 - one propan-2-one (acetone), CC(=O)C;
 - one 4-oxopentanal, CC(=O)CCC=O;
 - one 2-oxopentanedial, O=CC(=O)CCC=O;
 - two methanal (formaldehyde), C=O.
- **9.3(ii):** At the usual aldehyde-to-carboxylic-acid endpoint:
 - one propan-2-one, CC(=O)C;
 - one 4-oxopentanoic acid (levulinic acid), CC(=O)CCC(=O)O;
 - one 2-oxopentanedioic acid (α -ketoglutaric acid), O=C(O)C(=O)CCC(=O)O;
 - two methanoic acid (formic acid), O=CO.

Further oxidation can convert the one-carbon products into carbon dioxide, O=C=O; additional peroxide oxidation is discussed below.

- **9.4(i):** Direct dehydration gives:
- 3-methylhex-3-ene: E CC/C(C)=C/CC; Z CC/C(C)=C\CC;
- 4-methylhex-2-ene: E C/C=C/C(C)CC; Z C/C=C\C(C)CC.

A favorable hydride rearrangement also permits: - 3-methylhex-2-ene: E C/C=C(C)/CCC; Z C/C=C(C)\CCC; - 2-ethylpent-1-ene, C=C(CC)CCC.

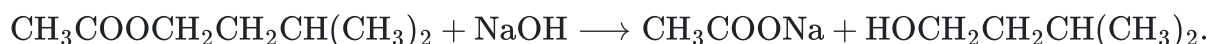
- **9.4(ii):** 4-Methylhexan-3-one, CCC(=O)C(C)CC.
- **9.4(iii):** 4-Methylhexan-3-yl ethanoate (acetate), CC(=O)OC(CC)C(C)CC.
- **9.5(i): trans-1,2-Dibromo-1-methylcyclohexane**, C[C@]1(Br)[C@H](Br)CCCC1. The bromine atoms occupy opposite ring faces.
- **9.5(ii): cis-1-Methylcyclohexane-1,2-diol**, C[C@]1(O)[C@@H](O)CCCC1. The hydroxyl groups occupy the same ring face.
- **9.5(iii): 1-Methylcyclohexan-1-ol**, CC1(O)CCCCC1.
- **9.5(iv):** Both **cis-1-bromo-2-methylcyclohexane**, C[C@H]1[C@@H](Br)CCCC1, and **trans-1-bromo-2-methylcyclohexane**, C[C@H]1[C@H](Br)CCCC1. Here cis/trans describes bromine relative to methyl.
- **9.5(v): trans-2-Methylcyclohexan-1-ol**, C[C@H]1[C@H](O)CCCC1. The hydroxyl and methyl groups occupy opposite ring faces.
- **9.5(vi): Methylcyclohexane**, CC1CCCCC1.

Solution

The equations below give balanced molecular or net ionic reactions. Common species are water, O ; hydrogen ion, $[H^+]$; hydroxide ion, $[OH^-]$; and hydronium ion, $[OH_3^+]$. Metals and solid metal oxides are represented by their chemical formulas.

9.1

The substrate is 3-methylbutyl ethanoate, commonly called isoamyl acetate, CC(=O)OCC(C)C. Heating with sodium hydroxide, $[Na^+] \cdot [OH^-]$, causes ester saponification:



Hydroxide attacks the ester carbonyl carbon. Collapse of the tetrahedral intermediate and proton transfer give the alcohol and the resonance-stabilized acetate ion. The basic medium leaves the carboxylic product as its sodium salt.

9.2(i)

Heptan-2-one, CC(=O)CCCCC, contains the methyl-ketone group CH_3CO^- , so it undergoes the iodoform reaction:



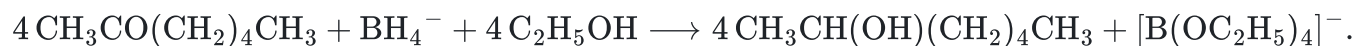
Iodine is I_2 , and the inorganic salt product is sodium iodide, $[Na^+] \cdot [I^-]$.

The three hydrogens of the carbonyl-adjacent methyl group are successively replaced by iodine. Hydroxide then induces cleavage between that carbon and the carbonyl carbon. The methyl carbon becomes iodoform; the remaining six-carbon fragment becomes hexanoate.

9.2(ii)

Sodium borohydride, $[\text{Na}^+] \cdot [\text{BH}_4^-]$, reduces the ketone carbonyl to a secondary alcohol. Ethanol, CCO , supplies a proton to the initially formed alkoxide.

An idealized balanced equation in ethanol is



Here the boron residue is represented as tetraethoxyborate, $[\text{B}^-](\text{OCC})(\text{OCC})(\text{OCC})\text{OCC}$; its actual speciation depends on water content.

Hydride adds to the carbonyl carbon, and protonation of oxygen produces heptan-2-ol. Its newly formed stereocentre need not be specified.

9.2(iii)

There is a material incompatibility in the printed scheme: ethylmagnesium bromide, $\text{CC}[\text{Mg}]\text{Br}$, is shown in ethanol.

A Grignard reagent undergoes rapid proton transfer with ethanol:



The products are ethane and ethoxymagnesium bromide, represented by $\text{CCO}[\text{Mg}]\text{Br}$. This organomagnesium SMILES specifies connectivity; it does not describe solvent coordination or aggregation.

The subsequent acidic work-up hydrolyses the magnesium ethoxide:

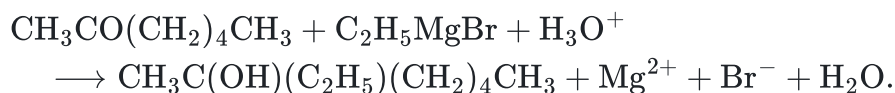


Magnesium(II) ion is $[\text{Mg}^{+2}]$, and bromide ion is $[\text{Br}^-]$. The printed hydroxide is also neutralized:



Thus the conditions as printed do not support the usual Grignard addition.

If dry ethereal conditions were intended—for example, diethyl ether, CCOCC , without the printed hydroxide—the ethyl group adds to the ketone carbonyl. Subsequent acidic work-up gives the tertiary alcohol. The combined balance for these **sequential** operations is

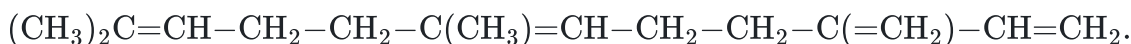


The longest chain containing the hydroxyl-bearing carbon has eight carbons. Both hydroxyl and methyl are at carbon 3, giving **3-methyloctan-3-ol**.

9.3(i)

The substrate is (*E*)-β-farnesene, systematically (6*E*)-7,11-dimethyl-3-methylidenedodeca-1,6,10-triene, $\text{CC}(\text{C})=\text{CCC}/\text{C}(\text{C})=\text{C}/\text{CCC}(=\text{C})\text{C}=\text{C}$.

Its connectivity can be written as

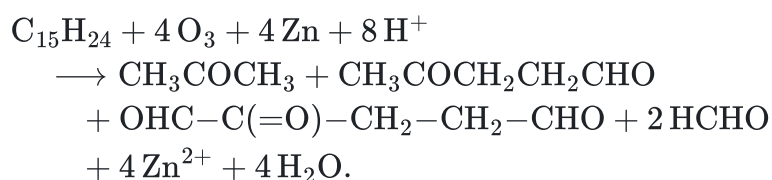


Ozone, $[O-][O+]=O$, cleaves all four double bonds. With reductive zinc work-up:

- an alkene carbon bearing no hydrogen becomes a ketone carbonyl;
- an alkene carbon bearing one hydrogen becomes an aldehyde carbonyl;
- a terminal $=CH_2$ carbon becomes formaldehyde.

Reading the fragments along the original skeleton gives acetone, 4-oxopentanal, 2-oxopentanedial, and two formaldehyde molecules.

A balanced equation is



Zinc(II) ion is $[Zn^{2+}]$.

The carbon check is

$$3 + 5 + 5 + 2(1) = 15.$$

There are eight carbonyl groups in total, as expected from cleavage of four double bonds.

9.3(ii)

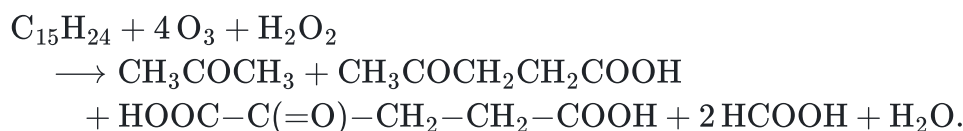
Hydrogen peroxide, OO , gives an oxidative work-up. At the standard carboxylic-acid endpoint, each aldehyde group is oxidized according to



The ketone carbonyl groups remain in the formal cleavage products. Consequently:

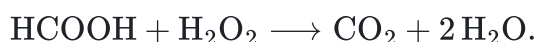
- acetone remains acetone;
- 4-oxopentanal becomes 4-oxopentanoic acid;
- both aldehyde groups of 2-oxopentanedial become carboxyl groups, giving 2-oxopentanedioic acid;
- each formaldehyde becomes formic acid.

A balanced overall equation for that endpoint is

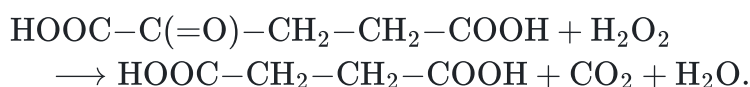


This is a net balance; it does not specify the laboratory excess of oxidant.

Further oxidation introduces an endpoint qualification. Formic acid can be oxidized to carbon dioxide:



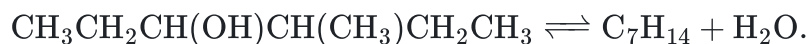
The α -keto acid can also undergo peroxide-mediated oxidative decarboxylation, producing butanedioic acid (succinic acid), $O=C(O)CCC(=O)O$:



The acid list in **Answers** is therefore the conventional functional-group cleavage answer; an exhaustive oxidation endpoint requires additional assumptions about the work-up.

9.4(i)

The starting alcohol is 4-methylhexan-3-ol, CCC(O)C(C)CC. Sulfuric acid, OS(=O)(=O)O, and heat promote dehydration. Each alkene-forming channel has the balance



Protonation of the hydroxyl group followed by loss of water gives the secondary 4-methylhexan-3-yl carbocation, CC[CH+](C)CC.

Removal of a β -hydrogen from either adjacent carbon gives the two direct elimination products:

- removal from carbon 2 gives **4-methylhex-2-ene**;
- removal from carbon 4 gives **3-methylhex-3-ene**, after renumbering.

Of these, 3-methylhex-3-ene is the more substituted, Zaitsev alkene.

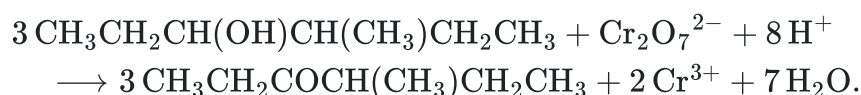
A 1,2-hydride shift from the adjacent methine carbon produces the more stable tertiary 3-methylhexan-3-yl carbocation, CC[C+](C)CCC. Elimination from its three adjacent carbon groups gives:

- 3-methylhex-3-ene again;
- **3-methylhex-2-ene**;
- **2-ethylpent-1-ene**.

All three internal alkene constitutions admit *E/Z* isomerism; their explicit SMILES appear in **Answers**. The terminal methylene product has no *E/Z* pair. The printed conditions do not determine product proportions or the extent of subsequent alkene equilibration.

9.4(ii)

Acidified dichromate oxidizes a secondary alcohol to a ketone. The carbon skeleton is retained:

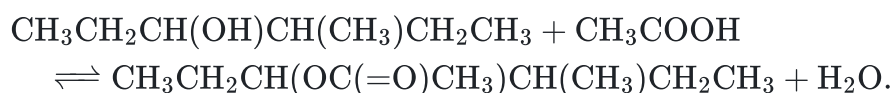


The reagent ion is dichromate, [O-][Cr](=O)(=O)O[Cr](=O)(=O)[O-]; the reduced chromium species is chromium(III), [Cr+3].

Each alcohol loses two hydrogen atoms, giving **4-methylhexan-3-one**.

9.4(iii)

Ethanoic acid (acetic acid), CC(=O)O, reacts with the alcohol by acid-catalysed Fischer esterification:



Carbonyl protonation facilitates attack by the alcohol oxygen; proton transfers and water elimination produce **4-methylhexan-3-yl acetate**. The reaction is reversible.

9.5

Every substrate in this part is **1-methylcyclohex-1-ene**, CC1=CCCCC1. For describing addition, call the methyl-bearing alkene carbon C1 and the adjacent alkene carbon C2.

9.5(i)

Bromine, Br_2 , in carbon tetrachloride, $\text{Cl}_2\text{C}(\text{Cl})_2$, adds across the double bond:

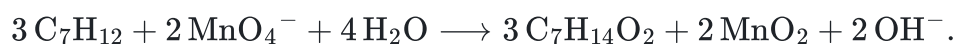


A bridged bromonium intermediate is opened by bromide from the opposite face, giving **anti addition**. The product is therefore **trans-1,2-dibromo-1-methylcyclohexane**.

To draw it, put one bromine on a solid wedge and the adjacent bromine on a hashed wedge.

9.5(ii)

Under the usual mild alkaline conditions, permanganate, $[\text{O}^-][\text{Mn}](=\text{O})_2$, gives **syn dihydroxylation**:



The inorganic precipitate is manganese(IV) oxide, MnO_2 .

Both oxygen atoms are delivered to the same alkene face through a cyclic intermediate. The product is **cis-1-methylcyclohexane-1,2-diol**.

Draw both hydroxyl groups as solid wedges, or both as hashed wedges.

9.5(iii)

Acid-catalysed hydration has the net balance

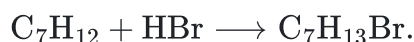


Protonation that places the carbocation at the methyl-bearing carbon gives the more stable tertiary carbocation. Water attacks that carbon, and deprotonation gives the Markovnikov product, **1-methylcyclohexanol**.

Draw the methyl and hydroxyl groups attached to the same ring carbon. There is no distinct cis/trans pair for this product.

9.5(iv)

Hydrogen bromide, HBr , adds by a radical chain mechanism in the presence of peroxide:



A bromine radical, $[\text{Br}\cdot]$, adds to C2, leaving the more substituted radical at C1. Hydrogen abstraction from another hydrogen bromide molecule then completes the anti-Markovnikov addition.

This radical sequence is not stereospecific. It produces both:

- **cis-1-bromo-2-methylcyclohexane**, with methyl and bromine on the same face;
- **trans-1-bromo-2-methylcyclohexane**, with methyl and bromine on opposite faces.

9.5(v)

Borane, $[\text{BH}_3]$, undergoes concerted **syn addition**: boron attaches to the less substituted carbon C2, while hydrogen attaches to C1. Oxidation replaces the carbon–boron bond with a carbon–oxygen bond with retention of configuration.

A balanced overall equation in basic solution is



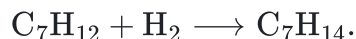
The boron-containing product is tetrahydroxyborate, $[B-](O)(O)(O)O$.

The newly added hydrogen at C1 and hydroxyl group at C2 are **syn**. Since the original methyl group at C1 lies opposite that newly added hydrogen, **methyl and hydroxyl are trans**.

The product is therefore **trans-2-methylcyclohexan-1-ol**. Draw methyl on a solid wedge and hydroxyl on a hashed wedge, or the mirror-image arrangement.

9.5(vi)

Hydrogen, $[H][H]$, adds over platinum:



Hydrogenation removes the double bond and gives **methylcyclohexane**. Although surface hydrogenation delivers hydrogen syn, the product has no distinct cis/trans isomers.

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.