

IChO 1987

Theory problems and solutions · Veszprém – Budapest, Hungary · 5 theory problems with complete solutions

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Problem 1: Carbohydrate oxidation and fermentation in a sewage plant

Treating waste water in a sewage plant, 45 % of its carbohydrate $(\text{CH}_2\text{O})_n$ is completely oxidized, 10 % undergoes anaerobic decomposition by fermentation (two components) and the rest remains in the sludge. The total gas formation is 16 m^3 per day (25°C , 100 kPa).

1.1 What is the amount of carbohydrate remaining in the sludge measured in kg per day?

1.2 Using the heat of combustion of methane (-882 kJ mol^{-1}), calculate the amount of energy that can be produced by combustion of the methane formed per day.

1.3 Knowing that the concentration of the carbohydrate in the waste water is 250 mg dm^{-3} , calculate the daily amount of waste water processed in the plant in m^3 of water per day.

Official English text of the problem.

Answers

To two significant figures:

- **1.1:** 16 kg day^{-1} of carbohydrate remains in the sludge.
- **1.2:** Methane combustion releases 52 MJ day^{-1} .
- **1.3:** The plant processes $1.4 \times 10^2 \text{ m}^3 \text{ day}^{-1}$ of waste water.

Solution

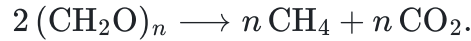
The molecular species involved are oxygen $\text{O}=\text{O}$, carbon dioxide $\text{O}=\text{C}=\text{O}$, water O , and methane C . The carbohydrate formula $(\text{CH}_2\text{O})_n$ specifies an empirical composition, so no unique molecular structure or SMILES can be assigned to it. Here, a "CH₂O unit" is a stoichiometric counting unit, not a separate molecule.

1.1 — Carbohydrate remaining in the sludge

Complete oxidation produces carbon dioxide and water:



Part 1.2 identifies methane as a fermentation product; the other gaseous product is carbon dioxide. The average oxidation state of carbon in the carbohydrate is zero. Formation of methane, with carbon at -4 , balances formation of an equal amount of carbon dioxide, with carbon at $+4$:



Thus, each mole of carbohydrate composition units produces:

- By complete oxidation: 1 mol of CO_2 .
- By fermentation: 0.5 mol of CH_4 and 0.5 mol of CO_2 .

Let F be the incoming amount of CH_2O units in mol day^{-1} . Counting the stated gas formation as the combined carbon dioxide and methane,

$$\dot{n}(\text{CO}_2) = (0.45 + 0.10/2)F = 0.50F,$$

$$\dot{n}(\text{CH}_4) = (0.10/2)F = 0.05F,$$

so

$$\dot{n}_{\text{gas}} = 0.55F.$$

Using the ideal-gas law with $T = 298.15\text{ K}$,

$$\dot{n}_{\text{gas}} = \frac{p\dot{V}}{RT} = \frac{(1.00 \times 10^5 \text{ Pa})(16 \text{ m}^3 \text{ day}^{-1})}{(8.314 \text{ Pa m}^3 \text{ mol}^{-1} \text{ K}^{-1})(298.15 \text{ K})} = 645.5 \text{ mol day}^{-1}.$$

Therefore,

$$F = \frac{645.5}{0.55} = 1.174 \times 10^3 \text{ mol day}^{-1}.$$

The fraction remaining in the sludge is

$$1 - 0.45 - 0.10 = 0.45.$$

Using $M(\text{CH}_2\text{O}) = 30.0 \text{ g mol}^{-1}$,

$$\dot{m}_{\text{sludge}} = 0.45F(30.0 \times 10^{-3} \text{ kg mol}^{-1}) = 15.84 \text{ kg day}^{-1}.$$

Hence,

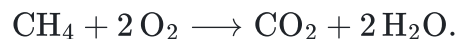
$$\boxed{\dot{m}_{\text{sludge}} \approx 16 \text{ kg day}^{-1}}.$$

1.2 — Energy from methane combustion

The methane production rate is

$$\dot{n}(\text{CH}_4) = 0.05F = 58.68 \text{ mol day}^{-1}.$$

Its combustion reaction is



Using the given combustion enthalpy, the positive amount of heat released per day is

$$\dot{E} = -\dot{n}(\text{CH}_4)\Delta_c H = (58.68 \text{ mol day}^{-1})(882 \text{ kJ mol}^{-1}) = 5.175 \times 10^4 \text{ kJ day}^{-1}.$$

Thus,

$$\boxed{\dot{E} \approx 52 \text{ MJ day}^{-1}}.$$

1.3 — Daily volume of waste water processed

The total incoming carbohydrate mass is

$$\dot{m}_0 = F(30.0 \times 10^{-3} \text{ kg mol}^{-1}) = 35.21 \text{ kg day}^{-1}.$$

Convert the given concentration:

$$250 \text{ mg dm}^{-3} = 250 \text{ g m}^{-3} = 0.250 \text{ kg m}^{-3}.$$

The required waste-water flow is therefore

$$\dot{V}_{\text{water}} = \frac{\dot{m}_0}{c} = \frac{35.21 \text{ kg day}^{-1}}{0.250 \text{ kg m}^{-3}} = 140.8 \text{ m}^3 \text{ day}^{-1}.$$

Hence,

$$\dot{V}_{\text{water}} \approx 1.4 \times 10^2 \text{ m}^3 \text{ day}^{-1}.$$

The solution was checked against the official solution.

Problem 2: Identification of a hydrated sodium phosphate by acid-base titration

500 mg of a hydrated sodium salt of phosphoric acid are dissolved in 50.0 cm³ of 0.1 molar sulphuric acid. This solution is diluted with distilled water to 100.0 cm³ and 20.0 cm³ of it are titrated with 0.100 molar NaOH solution using thymolphthalein as indicator. The average of the burette reading is 26.53 cm³. The pH at the end-point is 10.00.

Problems:

2.1 Calculate the percentage distribution by moles of all protonated $\text{H}_n\text{PO}_4^{n-3}$ species at the end-point.

2.2 What is the stoichiometric formula of the salt?

The cumulative protonation constants are given by

$$\beta_n = \frac{[\text{H}_n\text{PO}_4^{n-3}]}{[\text{PO}_4^{3-}][\text{H}^+]^n}$$

where $\log \beta_1 = 11.70$; $\log \beta_2 = 18.6$; $\log \beta_3 = 20.6$.

The relative atomic masses are: Na = 23.0; P = 31.0; H = 1.0; O = 16.0.

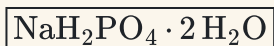
Official English text of the problem.

Answers

- 2.1:** The endpoint distribution, including unprotonated phosphate, is approximately:

Species	Name	SMILES	Mole percentage
PO_4^{3-}	Phosphate	<chem>O=P([O-])([O-])[O-]</chem>	1.95%
HPO_4^{2-}	Hydrogen phosphate	<chem>O=P(O)([O-])[O-]</chem>	97.97%
H_2PO_4^-	Dihydrogen phosphate	<chem>O=P(O)(O)[O-]</chem>	0.078%
H_3PO_4	Phosphoric acid	<chem>O=P(O)(O)O</chem>	$7.8 \times 10^{-10}\%$

- 2.2: Sodium dihydrogen phosphate dihydrate,

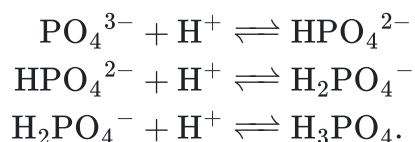


SMILES: [Na+].[O-]P(=O)(O)[O-].O.O. This represents the ionic composition and two waters of crystallization; crystal packing is unspecified.

Solution

2.1 — Phosphate distribution

The successive protonation equilibria are



Here the hydrogen ion, or proton, has SMILES [H+].

At pH 10.00,

$$h = [\text{H}^+] = 10^{-10.00} \text{ mol L}^{-1}.$$

Taking $\beta_0 = 1$, the mole fraction of the species containing n bound protons is

$$\alpha_n = \frac{\beta_n h^n}{D}, \quad D = 1 + \beta_1 h + \beta_2 h^2 + \beta_3 h^3.$$

The relative amounts are therefore

$$\begin{aligned}\text{PO}_4^{3-} &: 1, \\ \text{HPO}_4^{2-} &: 10^{11.70-10.00} = 50.1187, \\ \text{H}_2\text{PO}_4^- &: 10^{18.6-20.00} = 0.0398107, \\ \text{H}_3\text{PO}_4 &: 10^{20.6-30.00} = 3.98107 \times 10^{-10}.\end{aligned}$$

Thus $D = 51.1585$. Dividing each relative amount by D and multiplying by 100 gives the percentages listed above.

For the titration calculation, the mean number of bound protons per phosphate group is

$$\begin{aligned}\bar{n} &= \alpha_1 + 2\alpha_2 + 3\alpha_3 \\ &= 0.979674736 + 2(0.000778183) + 3(7.78183 \times 10^{-12}) \\ &= 0.981231.\end{aligned}$$

2.2 — Identification of the hydrated salt

Write the salt as



The 20.0 cm³ aliquot contains

$$m = 0.500 \text{ g} \times \frac{20.0}{100.0} = 0.100 \text{ g}$$

of the original salt, together with

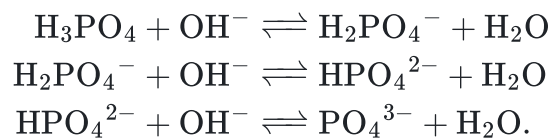
$$n_s = (0.1 \text{ mol L}^{-1})(0.0500 \text{ L}) \frac{20.0}{100.0} = 1.00 \times 10^{-3} \text{ mol}$$

of sulphuric acid.

At pH 10, sulphuric acid ($\text{O}=\text{S}(=\text{O})(\text{O})\text{O}$) has lost both acidic protons, forming sulfate ($\text{O}=\text{S}(=\text{O})([\text{O}-])$ $[\text{O}-]$):



Sodium hydroxide ($[\text{Na}+] \cdot [\text{OH}-]$) supplies hydroxide ions ($[\text{OH}-]$), which form water (O) on neutralization. The phosphate neutralization equilibria are



The amount of sodium hydroxide added is

$$n_{\text{B}} = (0.100 \text{ mol L}^{-1})(0.02653 \text{ L}) = 2.653 \times 10^{-3} \text{ mol}.$$

After accounting for the two acidic protons of sulphuric acid, the remaining base consumption is

$$n_{\text{B}} - 2n_{\text{S}} = 2.653 \times 10^{-3} - 2.000 \times 10^{-3} = 6.530 \times 10^{-4} \text{ mol}.$$

Each phosphate group initially carries $3 - x$ acidic protons and retains, on average, $\bar{n} = 0.981231$ at the endpoint. Neglecting free hydrogen and hydroxide ions in the endpoint balance, the net base consumption per mole of phosphate is consequently

$$(3 - x) - \bar{n} = 2.018769 - x.$$

If n_{P} is the amount of phosphate in the aliquot,

$$6.530 \times 10^{-4} = (2.018769 - x)n_{\text{P}}.$$

The hydrated salt's molar mass must therefore be

$$M = \frac{0.100 \text{ g}}{n_{\text{P}}} = \frac{(0.100 \text{ g})(2.018769 - x)}{6.530 \times 10^{-4} \text{ mol}}.$$

The three possible sodium contents give:

x	Inferred molar mass	Assessment
1	156.0 g mol^{-1}	Possible
2	2.874 g mol^{-1}	Impossible: the anhydrous salt alone has molar mass 142.0 g mol^{-1}
3	Would require a negative phosphate amount	Impossible

Hence $x = 1$. The anhydrous part has molar mass

$$M_{\text{anhydrous}} = 23.0 + 2(1.0) + 31.0 + 4(16.0) = 120.0 \text{ g mol}^{-1}.$$

The hydration number is

$$y = \frac{156.0 - 120.0}{18.0} = 2.00.$$

Therefore,

$$\text{sodium dihydrogen phosphate dihydrate, } \text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}.$$

As a check, this formula predicts

$$n_P = \frac{0.100}{156.0} = 6.41026 \times 10^{-4} \text{ mol},$$

and hence

$$V_B = \frac{2.000 \times 10^{-3} + (1.018769)(6.41026 \times 10^{-4})}{0.100} = 0.0265306 \text{ L} = 26.53 \text{ cm}^3,$$

in agreement with the reported titre.

The solution was checked against the official solution.

Problem 3: Potentiometric titration of a chloride-cyanide mixture with silver nitrate

25.00 cm³ of a neutral solution containing potassium chloride and potassium cyanide are potentiometrically titrated with a standard 0.1000 molar silver nitrate solution at 25 °C using a silver electrode and a normal calomel half-cell with KNO₃ - salt bridge. The protonation of cyanide ions is negligible. The potentiometric curve obtained (emf (V)) vs. burette readings (in cm³) is shown in Fig. 1.

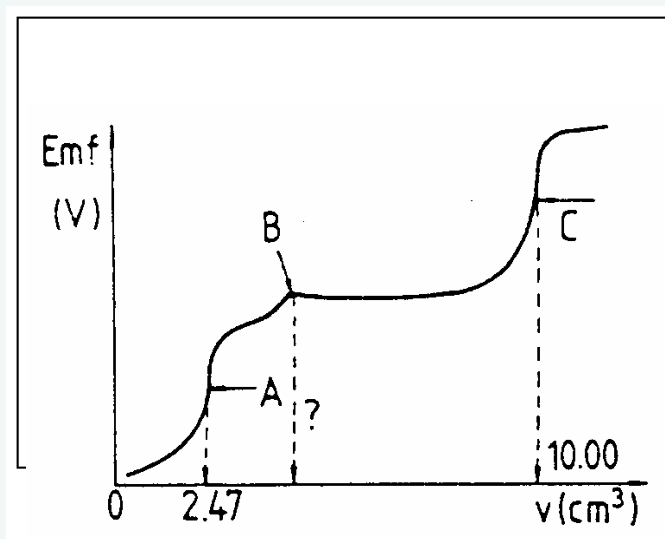


Fig. 1

3.1 The end points of the reactions taking place during the titration, are marked with A, B and C. Write the balanced ionic equation for each reaction.

3.2 What volume of the titrant is required to reach point B?

3.3 Calculate the concentrations of KCl and KCN (in mol dm⁻³) in the sample solution.

3.4 Calculate the emf readings at the points A and C in volts.

3.5 What is the molar ratio Cl⁻/CN⁻ in the solution and in the precipitate at point C?

Data:

$$E^\circ(\text{Ag}^+/\text{Ag}) = 0.800 \text{ V}$$

$$E^\circ(\text{Calomel}) = 0.285 \text{ V}$$

$$K_{\text{sp}}(\text{AgCN}) = 10^{-15.8}$$

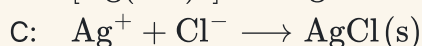
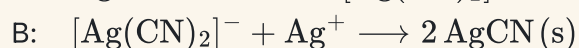
$$K_{\text{sp}}(\text{AgCl}) = 10^{-9.75}$$

$$\beta_2 = \frac{[\text{Ag}(\text{CN})_2]^-}{[\text{Ag}^+][\text{CN}^-]^2} = 10^{21.1}$$

Official English text of the problem.

Answers

• 3.1



• 3.2 $V_B = 4.94 \text{ cm}^3$.

• 3.3 The calculated concentrations are

$$c(\text{KCl}) = 0.02024 \text{ mol dm}^{-3} \approx 0.0202 \text{ mol dm}^{-3}$$

$$c(\text{KCN}) = 0.01976 \text{ mol dm}^{-3} \approx 0.0198 \text{ mol dm}^{-3}$$

• 3.4

$$E_A = 0.0467 \text{ V} \approx 0.047 \text{ V}, \quad E_C = 0.2287 \text{ V} \approx 0.229 \text{ V}.$$

• 3.5 At C:

• Free-ion ratio in solution: $[\text{Cl}^-]/[\text{CN}^-] = 1.12 \times 10^6$.

• Total dissolved chloride/cyanide ratio, including complexed cyanide: 2.81 .

• Chloride/cyanide ratio in the precipitate: $\approx 1.024 \approx 1.02$.

Solution

The chemical species used below have the following names and SMILES:

Species	Name	SMILES
Ag^+	Silver(I) ion	[Ag+]
Cl^-	Chloride ion	[Cl-]
CN^-	Cyanide ion	[C-]#N
$[\text{Ag}(\text{CN})_2]^-$	Dicyanoargentate(I) ion	N#[C-]->[Ag+]<-[C-]#N
AgCN	Silver cyanide	[Ag+] . [C-]#N
AgCl	Silver chloride	[Ag+] . [Cl-]
KCN	Potassium cyanide	[K+] . [C-]#N
KCl	Potassium chloride	[K+] . [Cl-]
AgNO_3	Silver nitrate	[Ag+] . [O-][N+](=O)[O-]

Species	Name	SMILES
KNO ₃	Potassium nitrate	[K+] . [O-] [N+] (=O) [O-]

The complex's SMILES uses arrows for coordination bonds; its two cyanide ligands bind through carbon, giving linear coordination at silver. The disconnected salt SMILES specify ionic formula units, not crystal lattices. The electrode materials are silver, [Ag], and calomel (mercury(I) chloride), [Cl-] . [Hg+] [Hg+] . [Cl-]; these representations likewise do not describe their extended solids.

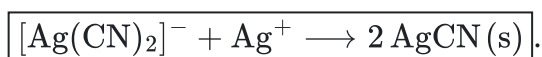
3.1 — Identification of the reactions

The large formation constant of dicyanoargentate(I) means that, while cyanide is available, added silver is strongly bound in the soluble complex:



In the intended stoichiometric interpretation, **A** marks conversion of the original cyanide into this complex. One mole of silver has then been added per two moles of original cyanide.

Further silver converts the complex into insoluble silver cyanide:

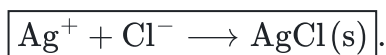


The equilibrium constant for this reaction is

$$K = \frac{1}{\beta_2 K_{\text{sp}}(\text{AgCN})^2} = \frac{1}{10^{21.1} (10^{-15.8})^2} = 10^{10.5},$$

so precipitation is strongly favoured. **B** is its stoichiometric endpoint: all original cyanide is counted as silver cyanide.

The remaining silver precipitates chloride:



C marks completion of this final precipitation.

3.2 — Volume at B

Let the original amount of cyanide be $n_{\text{CN},0}$, and let the titrant concentration be c_t . At A,

$$c_t V_A = \frac{n_{\text{CN},0}}{2}.$$

The second reaction requires another equal amount of silver. Therefore,

$$\boxed{V_B = 2V_A = 2(2.47) = 4.94 \text{ cm}^3}.$$

3.3 — Initial concentrations

From A,

$$n_{\text{CN},0} = 2c_t V_A = 2(0.1000)(2.47 \times 10^{-3}) = 4.94 \times 10^{-4} \text{ mol}.$$

At C, one mole of silver has been consumed per mole of original cyanide or chloride:

$$n_{\text{CN},0} + n_{\text{Cl},0} = c_t V_C = (0.1000)(10.00 \times 10^{-3}) = 1.000 \times 10^{-3} \text{ mol}.$$

Consequently,

$$n_{\text{Cl},0} = 1.000 \times 10^{-3} - 4.94 \times 10^{-4} = 5.06 \times 10^{-4} \text{ mol}.$$

Dividing by the original sample volume gives

$$c(\text{KCl}) = \frac{5.06 \times 10^{-4}}{25.00 \times 10^{-3}} = 0.02024 \text{ mol dm}^{-3} \approx 0.0202 \text{ mol dm}^{-3}$$

and

$$c(\text{KCN}) = \frac{4.94 \times 10^{-4}}{25.00 \times 10^{-3}} = 0.01976 \text{ mol dm}^{-3} \approx 0.0198 \text{ mol dm}^{-3}.$$

3.4 — Electromotive forces

At 25 °C, using concentrations as ideal activities,

$$E_{\text{cell}} = E^\circ(\text{Ag}^+/\text{Ag}) - E_{\text{calomel}} + (0.05916 \text{ V}) \log_{10} \left(\frac{[\text{Ag}^+]}{1 \text{ mol dm}^{-3}} \right).$$

Thus,

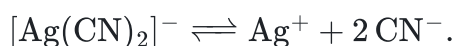
$$E_{\text{cell}} = 0.515 \text{ V} + (0.05916 \text{ V}) \log_{10} \left(\frac{[\text{Ag}^+]}{1 \text{ mol dm}^{-3}} \right).$$

At A.

In the idealised treatment of the titration curve, no precipitate is assumed at A. The complex concentration is taken as the amount of silver added divided by the total volume:

$$D_A = [[\text{Ag}(\text{CN})_2]^-]_A \approx \frac{(0.1000)(2.47 \times 10^{-3})}{(25.00 + 2.47) \times 10^{-3}} = 8.9916 \times 10^{-3} \text{ mol dm}^{-3}.$$

Dissociation occurs according to



Writing $s_A = [\text{Ag}^+]_A$, the stoichiometric balance gives

$$[\text{CN}^-]_A = 2s_A.$$

Therefore,

$$\beta_2 = \frac{D_A}{s_A(2s_A)^2} = \frac{D_A}{4s_A^3},$$

and hence

$$s_A = \left(\frac{8.9916 \times 10^{-3}}{4 \times 10^{21.1}} \right)^{1/3} = 1.2132 \times 10^{-8} \text{ mol dm}^{-3}.$$

Substitution into the Nernst equation gives

$$E_A = 0.515 + 0.05916 \log_{10}(1.2132 \times 10^{-8}) = 0.0467 \text{ V}.$$

At C.

Both precipitates are present, so both solubility-product relations apply. Define

$$s = [\text{Ag}^+], \quad \ell = [\text{Cl}^-], \quad c = [\text{CN}^-], \quad d = [[\text{Ag}(\text{CN})_2]^-].$$

Then

$$\ell = \frac{K_{\text{sp}}(\text{AgCl})}{s}, \quad c = \frac{K_{\text{sp}}(\text{AgCN})}{s},$$

and

$$d = \beta_2 s c^2 = \frac{\beta_2 K_{\text{sp}}(\text{AgCN})^2}{s}.$$

At the overall stoichiometric endpoint, the spectator-ion charges cancel. Electroneutrality therefore requires

$$s = \ell + c + d.$$

Notice that the complex contributes one negative charge, although it contains two cyanide ligands. Substitution gives

$$s^2 = K_{\text{sp}}(\text{AgCl}) + K_{\text{sp}}(\text{AgCN}) + \beta_2 K_{\text{sp}}(\text{AgCN})^2.$$

Numerically,

$$s = \sqrt{10^{-9.75} + 10^{-15.8} + 10^{21.1-31.6}} = 1.4472 \times 10^{-5} \text{ mol dm}^{-3}.$$

Thus,

$$E_C = 0.515 + 0.05916 \log_{10}(1.4472 \times 10^{-5}) = 0.2287 \text{ V}.$$

3.5 — Chloride/cyanide ratios at C

For the **free ions**, division of the two solubility-product equations eliminates the silver concentration:

$$\frac{[\text{Cl}^-]}{[\text{CN}^-]} = \frac{K_{\text{sp}}(\text{AgCl})}{K_{\text{sp}}(\text{AgCN})} = 10^{-9.75+15.8} = 10^{6.05} = 1.12 \times 10^6.$$

However, most dissolved cyanide is complexed. The concentrations calculated above give

$$\begin{aligned} &= 1.2287 \times 10^{-5} \text{ mol dm}^{-3}, \\ [\text{CN}^-] &= 1.0951 \times 10^{-11} \text{ mol dm}^{-3}, \\ [[\text{Ag}(\text{CN})_2]^-] &= 2.1850 \times 10^{-6} \text{ mol dm}^{-3}. \end{aligned}$$

If the requested solution ratio counts **all dissolved cyanide**, each complex must contribute two cyanide units:

$$\begin{aligned} R_{\text{dissolved}} &= \frac{[\text{Cl}^-]}{[\text{CN}^-] + 2[[\text{Ag}(\text{CN})_2]^-]} \\ &= \frac{K_{\text{sp}}(\text{AgCl})}{K_{\text{sp}}(\text{AgCN}) + 2\beta_2 K_{\text{sp}}(\text{AgCN})^2} \\ &= \boxed{2.81}. \end{aligned}$$

In the **precipitate**, each formula unit of silver chloride contains one chloride, and each formula unit of silver cyanide contains one cyanide. Neglecting the small dissolved fractions, as in the intended stoichiometric treatment,

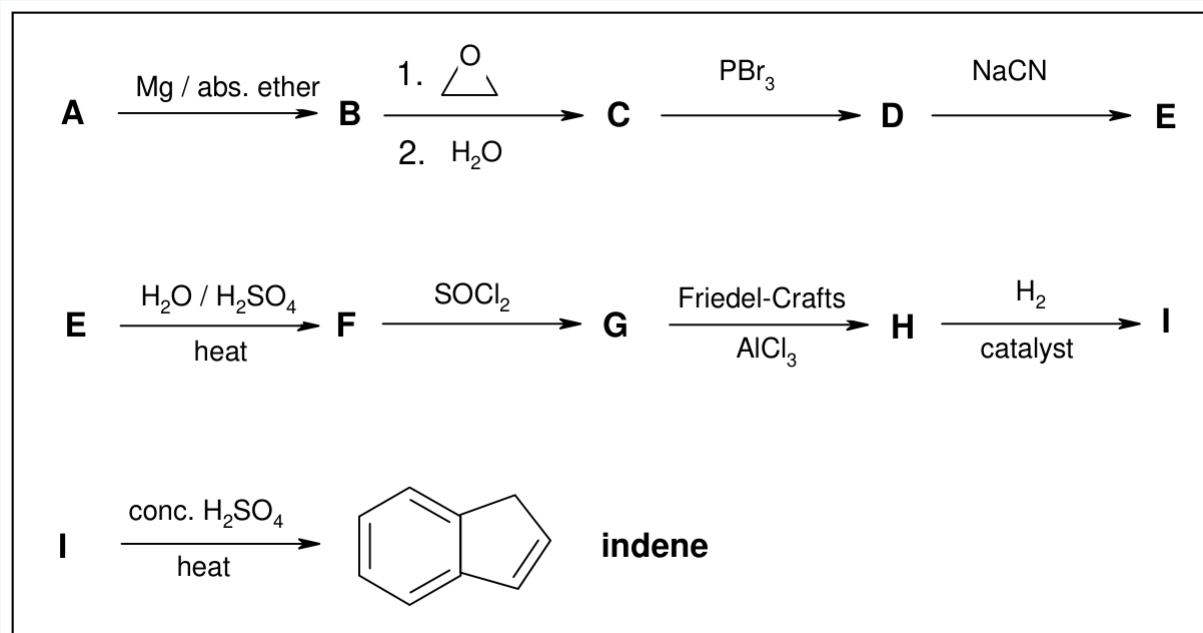
$$R_{\text{precipitate}} \approx \frac{n_{\text{Cl},0}}{n_{\text{CN},0}} = \frac{5.06 \times 10^{-4}}{4.94 \times 10^{-4}} = 1.0243 \approx 1.02.$$

Subtracting the calculated dissolved amounts would give 1.02374, which rounds to the same result.

The solution was checked against the official solution.

Problem 4: Reaction sequence leading to indene (compounds A-I)

Write the structural formulae of the compounds **A** to **I** in the following reaction sequence.



Official English text of the problem.

Answers

Problem 4 — compounds A–I. Taking bromobenzene as the starting halide:

- A:** Bromobenzene, $\text{C}_6\text{H}_5\text{Br}$. SMILES: BrC1=CC=CC=C1.
- B:** Phenylmagnesium bromide, $\text{C}_6\text{H}_5\text{MgBr}$. SMILES: Br[Mg]C1=CC=CC=C1.
- C:** 2-Phenylethan-1-ol, $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{OH}$. SMILES: OCCc1ccccc1.
- D:** (2-Bromoethyl)benzene, $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{Br}$. SMILES: BrCCc1ccccc1.
- E:** 3-Phenylpropanenitrile, $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CN}$. SMILES: N#CCCc1ccccc1.
- F:** 3-Phenylpropanoic acid, $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{COOH}$. SMILES: O=C(O)CCc1ccccc1.
- G:** 3-Phenylpropanoyl chloride, $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{COCl}$. SMILES: O=C(Cl)CCc1ccccc1.
- H:** Indan-1-one, $\text{C}_9\text{H}_8\text{O}$. SMILES: O=C1CCc2ccccc21.
- I:** Indan-1-ol, $\text{C}_9\text{H}_{10}\text{O}$. SMILES with stereochemistry unspecified: OC1CCc2ccccc21. With an achiral hydrogenation catalyst, it is a racemic mixture of O[C@H]1CCc2ccccc21 and O[C@@H]1CCc2ccccc21.

The starting halogen is not uniquely specified; the bromide choice gives a consistent complete sequence.

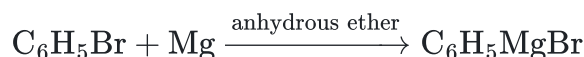
Solution

Problem 4

The final product is **indene**, SMILES C1C=Cc2ccccc21. Its five-membered ring contains three carbons in addition to the two shared with the aromatic ring. The indicated Friedel–Crafts cyclization therefore requires an aromatic ring bearing the chain $-\text{CH}_2\text{CH}_2\text{COCl}$. The ethylene oxide reaction supplies two side-chain carbons, and cyanide supplies the third.

A → B: Grignard reagent formation

Magnesium inserts into the carbon–bromine bond of bromobenzene in anhydrous ether:

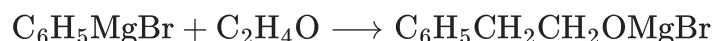


Thus **A** is bromobenzene and **B** is phenylmagnesium bromide.

The SMILES for **B** represents formal connectivity. In ether, the magnesium centre is coordinated by solvent, and the reagent can exist as associated species.

B → C: addition of two carbons using ethylene oxide

The three-membered oxygen-containing ring is **ethylene oxide (oxirane)**, SMILES C1CO1. The phenyl group attacks a ring carbon, opening the ring and forming a magnesium alkoxide:



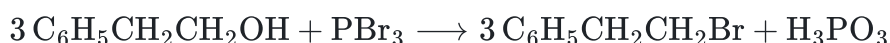
The intermediate is **magnesium bromide 2-phenylethanolate**, represented formally by SMILES Br[Mg]OCCc1ccccc1. Water protonates its oxygen:



Consequently, **C** is 2-phenylethan-1-ol. The two equivalent carbons of ethylene oxide become the two methylene groups between the phenyl group and the hydroxyl group.

C → D: replacement of hydroxyl by bromine

Phosphorus tribromide converts the primary alcohol into the corresponding bromide:



Thus **D** is (2-bromoethyl)benzene.

D → E: substitution by cyanide

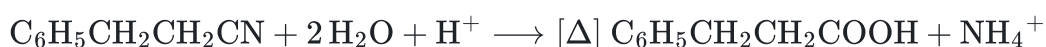
Cyanide attacks through carbon and displaces bromide by an S_N2 reaction:



This adds one carbon to the side chain. Therefore, **E** is 3-phenylpropanenitrile.

E → F: acidic hydrolysis of the nitrile

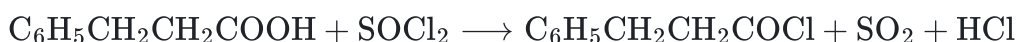
Heating with aqueous sulfuric acid hydrolyses the nitrile to a carboxylic acid. The balanced net ionic equation is:



The nitrile carbon becomes the carboxyl carbon, while nitrogen becomes **ammonium**, SMILES [NH4+], in the acidic solution. Hence **F** is 3-phenylpropanoic acid.

F → G: formation of the acyl chloride

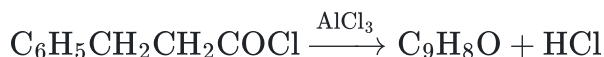
Thionyl chloride converts the carboxylic acid into its acyl chloride:



Thus **G** is 3-phenylpropanoyl chloride.

G → H: intramolecular Friedel–Crafts acylation

Aluminium chloride activates the acyl chloride. The aromatic ring forms a bond to the acyl carbon at a position ortho to the existing side chain, closing a five-membered ring:

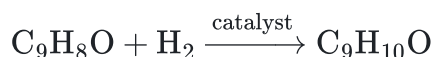


The new ring comprises the carbonyl carbon, the two methylene carbons, and two adjacent aromatic carbons. Its carbonyl carbon lies directly next to an aromatic fusion carbon, identifying **H** as **indan-1-one**.

The two available ortho positions are equivalent and give the same product.

H → I: reduction of the ketone

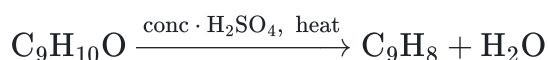
Catalytic hydrogenation reduces the carbonyl group to a secondary alcohol:



Therefore, **I** is **indan-1-ol**. The alcohol-bearing carbon is stereogenic. With an achiral catalyst, hydrogenation of either face of the carbonyl gives the two enantiomers in equal amounts.

I → indene: dehydration

Heating indan-1-ol with concentrated sulfuric acid eliminates water:



The hydroxyl group is removed from carbon 1 and a hydrogen from the neighbouring methylene carbon, forming the double bond between carbons 1 and 2. This produces the indene structure shown in the problem.

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

Problem 5: Organic chemistry questions: chlorination, alcohols, aldohexoses, C₄H₈ isomers, lecithin, citric acid cycle, NAD⁺

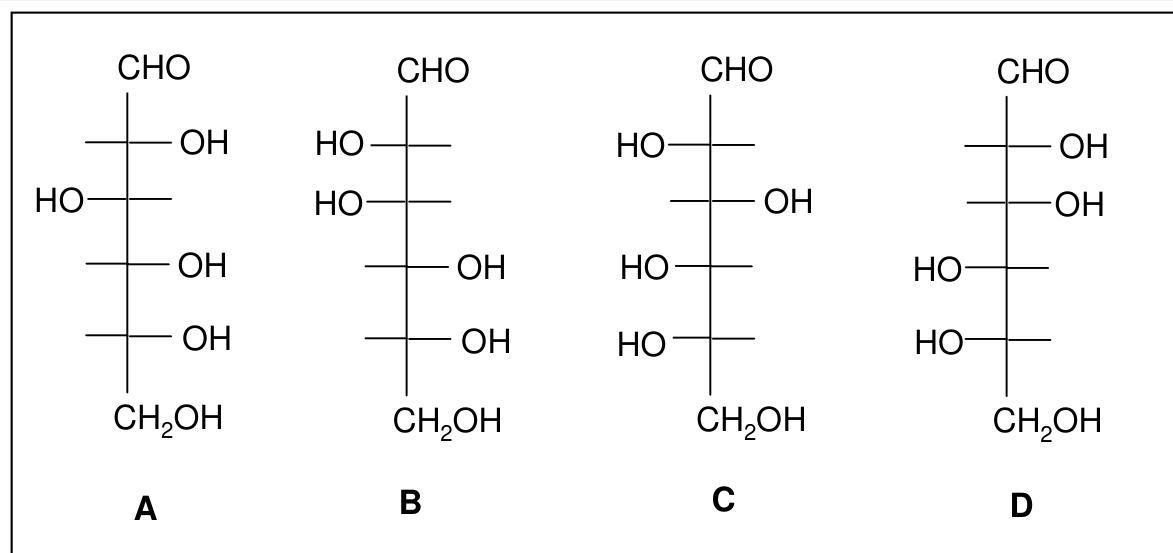
5.1 What ratio of primary / secondary / tertiary products can statistically be expected in the high temperature chlorination of methyl butane? Assume that the reaction rate of the substitution is equal for all C–H bonds.

5.2 Which of the following alcohols: pentan-1-ol, pentan-2-ol and 2-methyl-butan-2-ol react with the following reagents listed below?

1) cold, concentrated sulphuric acid; 2) CrO₃ / H₂SO₄; 3) ZnCl₂ / HCl; 4) I₂ / NaOH

5.3 Which of the following aldohexose structures are:

1) enantiomer pairs, 2) diastereomer pairs?



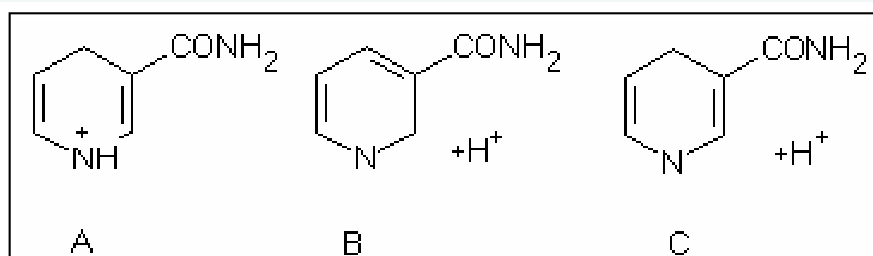
5.4 Two hydrocarbon compounds of the same molecular formula, C_4H_8 , easily react with hydrogen in the presence of a platinum catalyst. During ozonolysis only ethanal (acetaldehyde) is formed in both cases. The ^1H -NMR spectra of the two compounds show two types of protons in a ratio of 3 to 1. Draw the structures of the described compounds.

5.5 Select the components of the group listed below that can be obtained during complete hydrolysis of lecithin (a phospholipid): serine, phosphoric acid, sphingosine, choline, glycerol, myo-inositol, phosphatidic acid and fatty acids).

5.6 Which of the following carboxylic acid can be formed in the tricarboxylic acid cycle (Krebs' citric acid cycle):

maleic acid (cis-butenedioic acid), mandelic acid (α-hydroxy-phenylethanoic acid), malic acid (2-hydroxy-butanedioic acid), tricarballic acid (propane-1,2,3-tricarboxylic acid), oxalacetic acid (2-oxo-butanedioic acid), keto-glutaric acid (2-oxo-pentanedioic acid), fumaric acid (trans-butenedioic acid) and acetoacetic acid (3-oxo-butanoic acid).

5.7 To which structures is the nicotinamide moiety (part) of NAD^+ converted during the uptake of hydrogen to form NADH (A, B or C)?



Official English text of the problem.

Answers

- **5.1:** Primary : secondary : tertiary monochlorination products = $\boxed{9 : 2 : 1}$, corresponding to 75.0%, 16.7%, and 8.33%.
- **5.2:** The results are:

Alcohol	1) Cold, concentrated H_2SO_4	2) $\text{CrO}_3/\text{H}_2\text{SO}_4$	3) ZnCl_2/HCl , ordinary room-temperature Lucas test	4) I_2/NaOH
Pentan-1-ol <chem>CCCCCO</chem>	Reacts	Reacts	No observable reaction within the usual test time; reacts on heating	Negative
Pentan-2-ol <chem>CC(O)CCC</chem>	Reacts	Reacts	Reacts more slowly	Positive
2-Methylbutan-2-ol <chem>CC(O)(C)CC</chem>	Reacts	No normal oxidation	Reacts rapidly	Negative

- **5.3:** Enantiomer pairs: **A–C and B–D**. Diastereomer pairs: **A–B, A–D, B–C and C–D**.
- **5.4:** **cis-(Z)-But-2-ene** C/C=C\C and **trans-(E)-but-2-ene** C/C=C/C.
- **5.5:** **Phosphoric acid** OP(=O)(O)O, **choline** C[N+](C)(C)CCO, **glycerol** OCC(O)CO, and **fatty acids** [*]C(=O)O. Here [*] denotes an unspecified fatty-acid hydrocarbon residue.
- **5.6:** **L-(S)-Malic acid** O=C(O)[C@H](O)CC(=O)O, **oxaloacetic acid** O=C(O)C(=O)CC(=O)O, **2-oxoglutaric acid** O=C(O)C(=O)CCC(=O)O, and **fumaric acid** O=C(O)/C=C/C(=O)O.
- **5.7:** **C**, the **1,4-dihydronicotinamide moiety of NADH**, [*]N1C=C(C(=O)N)CC=C1. Here [*] represents the unchanged substituent connecting the ring nitrogen to the rest of the cofactor.

Solution

5.1 — Statistical chlorination

Methyl butane is **2-methylbutane**, CC(C)CC, with condensed structure $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_3$.

With equal substitution rates for every C–H bond, the probability of substitution at a particular kind of carbon is proportional to the number of hydrogens attached to that kind of carbon.

Carbon environment	Number of attached hydrogens	Product class
Three methyl groups	$3 \times 3 = 9$	Primary
One methylene group	2	Secondary
One methine group	1	Tertiary
Total	12	

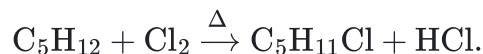
Therefore,

$$n(1^\circ) : n(2^\circ) : n(3^\circ) = 9 : 2 : 1.$$

The corresponding fractions are

$$\frac{9}{12} = 75.0\%, \quad \frac{2}{12} = 16.7\%, \quad \frac{1}{12} = 8.33\%.$$

The balanced monochlorination equation is



Chlorine has SMILES ClCl; hydrogen chloride has SMILES Cl.

There are four constitutional monochlorination products:

Product	SMILES	Statistical weight
Racemic 1-chloro-2-methylbutane	<chem>ClC[C@H](C)CC</chem> and <chem>ClC[C@@H](C)CC</chem>	6
1-Chloro-3-methylbutane	<chem>ClCCC(C)C</chem>	3
Racemic 2-chloro-3-methylbutane	<chem>C[C@H](Cl)C(C)C</chem> and <chem>C[C@@H](Cl)C(C)C</chem>	2
2-Chloro-2-methylbutane	<chem>CC(Cl)(C)CC</chem>	1

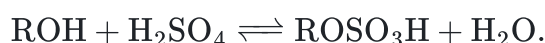
The two primary products together account for $6 + 3 = 9$ hydrogens. The enantiomers within each racemic product have equal statistical yields.

5.2 — Reactions of the alcohols

The three alcohols are respectively primary, secondary and tertiary. Their differing oxidation and substitution behaviour follows from the substitution of the carbon bearing the hydroxyl group.

1) Cold, concentrated sulphuric acid

All three alcohols react with sulphuric acid, OS(=O)(=O)O. Protonation and formation of alkyl hydrogen sulfates are possible:

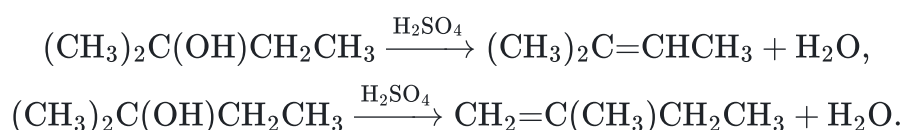


Water has SMILES O.

For the three alcohols, the corresponding sulfate ester structures are:

Alcohol-derived sulfate ester	SMILES
Pentyl hydrogen sulfate	<chem>CCCCCOS(=O)(=O)O</chem>
Pentan-2-yl hydrogen sulfate	<chem>CC(OS(=O)(=O)O)CCC</chem>
2-Methylbutan-2-yl hydrogen sulfate	<chem>CC(C)(OS(=O)(=O)O)CC</chem>

These structures do not imply that a single sulfate ester is the exclusive product under every acid concentration and temperature. In particular, the tertiary alcohol also undergoes facile acid-catalysed dehydration:

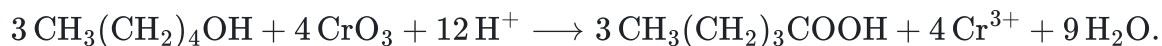


The alkenes are **2-methylbut-2-ene**, CC(C)=CC, and **2-methylbut-1-ene**, C=C(C)CC. Thus the qualitative answer is positive for all three alcohols.

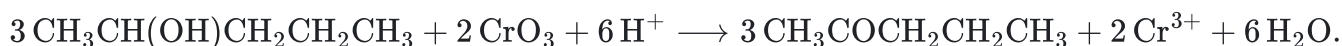
2) Chromium trioxide in sulphuric acid

Chromium trioxide, $O=[Cr](=O)=O$, oxidizes the primary and secondary alcohols under the usual aqueous acidic conditions.

Pentan-1-ol is oxidized through **pentanal**, $CCCC=O$, to **pentanoic acid**, $CCCC(=O)O$. The overall balanced ionic equation is



Pentan-2-ol is oxidized to **pentan-2-one**, $CC(=O)CCC$:

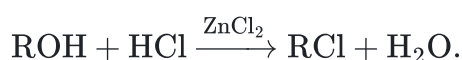


Here the hydrogen ion is $[H^+]$ and the chromium(III) ion is $[Cr^{3+}]$; sulfate spectator ions have been omitted.

The tertiary alcohol has no hydrogen on its hydroxyl-bearing carbon. It therefore does not undergo the normal alcohol-to-carbonyl oxidation without breaking carbon-carbon bonds.

3) Zinc chloride and hydrochloric acid: the Lucas reagent

Zinc chloride, $[Zn^{2+}] \cdot [Cl^-] \cdot [Cl^-]$, promotes replacement of the hydroxyl group by chloride:



The corresponding chlorides are:

Starting alcohol	Chloride product	SMILES
Pentan-1-ol	1-Chloropentane	<chem>CCCCC1</chem>
Pentan-2-ol	2-Chloropentane	<chem>CC(Cl)CCC</chem>
2-Methylbutan-2-ol	2-Chloro-2-methylbutane	<chem>CC(Cl)(C)CC</chem>

The tertiary alcohol reacts rapidly because formation of a tertiary carbocation is relatively favourable. The secondary alcohol reacts more slowly. The primary alcohol does not give the usual positive room-temperature Lucas test; its substitution is much slower and can be achieved on heating.

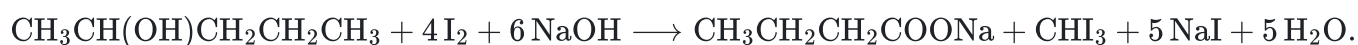
The problem specifies no configuration for pentan-2-ol, so the SMILES for its derivatives leave that stereochemistry unspecified.

4) Iodine and sodium hydroxide: the iodoform reaction

Iodine, I_2 , and sodium hydroxide, $[Na^+] \cdot [OH^-]$, give a positive iodoform reaction with a methyl ketone or an alcohol that can be oxidized to one.

Only pentan-2-ol has the required $CH_3CH(OH)^-$ group. It first forms pentan-2-one; iodination and cleavage then produce **iodoform**, $IC(I)I$, and **sodium butanoate**, $CCCC(=O)[O^-] \cdot [Na^+]$.

The balanced overall equation is



Sodium iodide has SMILES $[Na^+] \cdot [I^-]$.

The positive observation is a yellow iodoform precipitate. Pentan-1-ol does not have the required carbon skeleton, and the tertiary alcohol cannot undergo the necessary oxidation to a methyl ketone.

5.3 — Enantiomers and diastereomers

Read each Fischer projection from the aldehyde end, recording the hydroxyl positions at C2, C3, C4 and C5. Horizontal Fischer bonds point towards the viewer; vertical bonds point away.

Structure	Hydroxyl positions, C2 to C5	Identity	Open-chain stereochemical SMILES
A	Right, left, right, right	D-Glucose	<chem>O=C[C@H](O)[C@@H](O)[C@H](O)[C@H](O)CO</chem>
B	Left, left, right, right	D-Mannose	<chem>O=C[C@@H](O)[C@@H](O)[C@H](O)[C@H](O)CO</chem>
C	Left, right, left, left	L-Glucose	<chem>O=C[C@@H](O)[C@H](O)[C@@H](O)[C@@H](O)CO</chem>
D	Right, right, left, left	L-Mannose	<chem>O=C[C@H](O)[C@H](O)[C@@H](O)[C@@H](O)CO</chem>

Enantiomers have opposite configurations at **every** stereogenic centre. Accordingly,

Enantiomers: A–C and B–D.

Diastereomers differ at some, but not all, stereogenic centres:

Diastereomers: A–B, A–D, B–C, C–D.

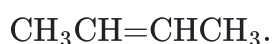
More specifically, A–B and C–D differ only at C2 and are **C2 epimers**. A–D and B–C differ at C3, C4 and C5.

5.4 — Identification of the two hydrocarbons

The molecular formula gives one degree of unsaturation:

$$\text{DBE} = \frac{2(4) + 2 - 8}{2} = 1.$$

Hydrogenation and ozonolysis identify this unsaturation as a carbon–carbon double bond. Since ozonolysis gives only **ethanal**, CC=O, each double-bond carbon must carry one methyl group and one hydrogen. The connectivity is therefore

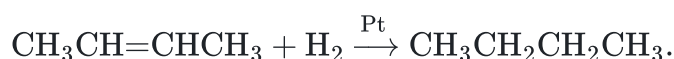


This connectivity has two geometrical isomers:

- **cis-(Z)-But-2-ene**, C/C=C\C: draw the two methyl groups on the **same side** of the double bond.
- **trans-(E)-But-2-ene**, C/C=C/C: draw the two methyl groups on **opposite sides** of the double bond.

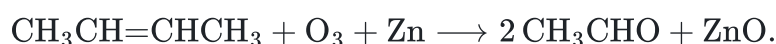
In each drawing, each alkene carbon also bears one hydrogen.

Both compounds hydrogenate to **butane**, CCCC:



Hydrogen has SMILES [H][H]; platinum is represented by [Pt].

For example, with a reductive zinc work-up, their ozonolysis can be written:



The additional species are ozone, [O-][O+]=O; zinc, [Zn]; and zinc oxide, [Zn+2].[O-2].

In either isomer, symmetry makes the two methyl groups equivalent and the two alkene hydrogens equivalent. The integrated proton counts are therefore

$$6 : 2 = \boxed{3 : 1},$$

as required.

5.5 — Complete hydrolysis of lecithin

Lecithin here means **phosphatidylcholine**. It contains a glycerol backbone, two fatty-acid ester groups, and a phosphate diester connecting glycerol to choline.

A generic connectivity SMILES is C[N+](C)(C)CCOP(=O)([O-])OCC(OC(=O)[* : 2])COC(=O)[* : 1].

The mapped wildcards represent the two unspecified hydrocarbon residues. Glycerol stereochemistry is immaterial to identifying the complete-hydrolysis products.

Complete hydrolysis breaks the two carboxylic ester bonds and both phosphate ester bonds. Consequently, one mole of lecithin yields:

Component	Amount per mole of lecithin
Glycerol	1 mol
Fatty acids	2 mol
Phosphoric acid	1 mol
Choline	1 mol

Writing the neutral zwitterionic phosphatidylcholine as PC, a balanced acid-hydrolysis equation is



The proton on the left accounts for the charge of the choline cation when the phosphorus-containing product is written as neutral phosphoric acid.

Phosphatidic acid, with generic neutral-acid SMILES O=P(O)(O)OCC(OC(=O)[* : 2])COC(=O)[* : 1], can arise during partial hydrolysis. It still contains ester bonds and is therefore not an end product of **complete** hydrolysis.

5.6 — Acids belonging to the citric acid cycle

Four of the listed acids correspond to cycle intermediates:

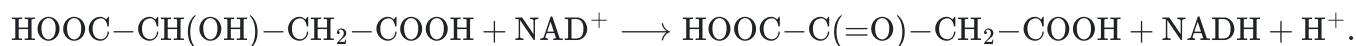
Selected acid	Reason
L-(S)-Malic acid	Its conjugate base, L-malate, is formed by stereospecific hydration of fumarate.
Oxaloacetic acid	Oxaloacetate is formed by oxidation of malate and regenerated at the end of the cycle.
2-Oxoglutaric acid	Also called α -ketoglutaric acid; it is the cycle's five-carbon 2-oxo dicarboxylic acid intermediate.
Fumaric acid	Its conjugate base, fumarate, is the cycle's trans-unsaturated dicarboxylate.

For example, using the acid forms to display their carbon skeletons, the hydration is



where the substrate is trans and the product has the L-(S) configuration.

The subsequent oxidation is



The other choices are excluded as follows:

Excluded acid	SMILES	Reason
Maleic acid	<chem>O=C(O)/C=C\C(=O)O</chem>	It has cis geometry; the cycle contains trans-fumarate.
Mandelic acid	<chem>O=C(O)C(O)c1ccccc1</chem>	This aromatic hydroxy acid is not a cycle intermediate.
Tricarballic acid	<chem>O=C(O)CC(CC(=O)O)C(=O)O</chem>	It is not a cycle intermediate; unlike citric acid, it lacks the hydroxyl group.
Acetoacetic acid	<chem>CC(=O)CC(=O)O</chem>	It belongs to ketone-body metabolism, rather than being an intermediate of the cycle itself.

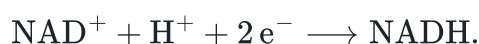
For comparison, **citric acid** has SMILES O=C(O)CC(O)(CC(=O)O)C(=O)O.

5.7 — Reduction of the nicotinamide ring

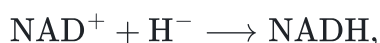
The correct structure is **C**.

Number the nicotinamide ring nitrogen as position 1. During reduction, a **hydride equivalent**—one hydrogen nucleus together with two electrons—is transferred to **C4**, the carbon opposite the nitrogen.

The balanced reduction half-equation is



Equivalently, the hydride-transfer bookkeeping is



where hydride has SMILES [H-]; this notation does not imply a free hydride ion in aqueous solution.

The relevant ring structures are:

State	Nicotinamide-moiety SMILES
Oxidized pyridinium moiety of NAD^+	<chem>[*][n+]1cc(C(=O)N)ccc1</chem>
Reduced 1,4-dihydronicotinamide moiety of NADH	<chem>[*]N1C=C(C(=O)N)CC=C1</chem>

Here [*] represents the unchanged ribosyl linkage to the remainder of the cofactor.

Hydride addition and rearrangement of the ring's π electrons neutralize the nitrogen. C4 becomes a methylene carbon, and the remaining double bonds are $\text{C2}=\text{C3}$ and $\text{C5}=\text{C6}$. These are precisely the features shown in **C**.

In a substrate dehydrogenation, such as malate oxidation above, the second hydrogen is released to the medium as H^+ , explaining the proton drawn alongside C. Structure A instead shows a protonated, positively charged nitrogen; B has the wrong double-bond arrangement.

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.